In this doctoral thesis, the author, Vicum, Lars, investigates the influence of turbulent mixing on precipitation processes carried out in stirred tank reactors. The publication was released in 2005. The permanent link to the thesis is provided via DOI: https://doi.org/10.3929/ethz-a-005069682. The rights and license for this work are stated as In Copyright - Non-Commercial Use Permitted.
INVESTIGATION OF THE INFLUENCE OF TURBULENT MIXING ON PRECIPITATION PROCESSES CARRIED OUT IN STIRRED TANK REACTORS

A dissertation submitted to the

SWISS FEDERAL INSTITUTE OF TECHNOLOGY ZURICH

for the degree of

DOCTOR OF TECHNICAL SCIENCES

presented by

LARS VICUM
Dipl.-Ing. Universität Hannover
M. Sc. University of Wisconsin - Madison

born 31.05.1972
Citizen of Germany

Accepted on the recommendation of

Prof. Dr. M. Mazzotti (ETH Zurich), examiner
Prof. Dr. hab. J. Balistyga (Technical University of Warsaw), co-examiner
Prof. Dr. P. Rudolf von Rohr (ETH Zurich), co-examiner

ZURICH 2005
ACKNOWLEDGEMENTS

First and foremost, I would like to express my sincere gratitude to Prof. Marco Mazzotti for accepting me as a Ph.D. student in his group, for his continuous support, and for giving me the freedom to develop and pursue my own ideas. Our discussions were always stimulating helping me a lot to find my way.

I gratefully thank Prof. Jerzy Baldyga for his extraordinary support for my work and for accepting the task of co-examiner of this thesis. I thank him for the fruitful discussions we had during his stays at the Institute of Process Engineering and during my visits to his institute in Warsaw. I appreciate a lot that Prof. Jerzy Baldyga has patiently explained me almost everything I wanted to know about turbulent mixing and I want to thank him in particular for hosting me several times at Warsaw University of Technology.

I am also grateful to Prof. Philipp Rudolf von Rohr for accepting the task of being a co-examiner at a rather late stage of the project.

Many thanks to all colleagues and friends at IVUK/IPE who made my time at the institute a most valuable experience I would not want to miss.

Many thanks also to Patricia, my parents, my sisters and my grandfather for their continuous support, patience and encouragements.
ABSTRACT

Precipitation is a key step in the production of bulk and fine chemicals, pharmaceuticals and food products. Although precipitation can be considered as a well established unit operation, its design and in particular its scale-up can be difficult. When particle formation is fast, turbulent mixing can influence the course of a process. Under such conditions the precipitate properties depend not only on a multitude of simultaneously occurring and interlinked particle formation mechanisms, but also on the different mixing mechanisms from the micro- to the macro-scale.

The focus of this work was to investigate experimentally and through simulations the interaction between turbulent mixing and precipitation for processes in stirred tank reactors. Both semibatch and continuous processes were analyzed for a wide range of operating conditions using a newly designed and built up stirred tank reactor setup for precipitation of the model substance barium sulfate. Modeling tools of different complexity were developed, which differ mainly in their level of modeling detail for different categories of sub-process mechanisms. Overall model performance was assessed by comparing the simulation results obtained with different types of models with experimental data.

The classical E-model as well as a CFD based PDF-closure model were applied for the simulation of a reactive mixing process involving two parallel chemical reactions, accounting for all relevant mechanisms form the micro- to the macro-scale. Under the conditions analyzed, both types of models were found to predict experimental reaction yield data correctly. For the model substance barium sulfate the relevant particle formation mechanisms are analyzed in depth to formulate new kinetic relationships for nucleation and growth. For this purpose different activity based solution models for the aqueous \( \text{Ba}^{2+}/\text{SO}_4^{2-}/\text{Na}^+/\text{Cl}^- \) system were evaluated and the Pitzer model was found to be the best model to describe the solution composition and the particle formation driving force. The new kinetics relationships have been applied in several mixing-precipitation models. The E-model and a CFD based PDF-closure model were used for the simulation of a single feed semibatch process. In both cases accurate estimates of mean particle size could be produced. The CFD based mixing-precipitation model was also applied to a continuous stirred tank process and simulation results are compared with experimental data for a wide range of operating conditions. Thereby, the capability of the model is assessed in detail and the bottlenecks for accurate mixing-precipitation modeling are identified.
ZUSAMMENFASSUNG


Für die Simulation eines reaktiven Mischprozesses mit zwei parallelen chemischen Reaktionen wird sowohl das klassische E-Model als auch ein detailliertes CFD Model verwendet, wobei in beiden Fällen alle relevanten Mechanismen von der Mikro- bis zur Makroebene berücksichtigt werden. Es wird gezeigt, dass sich mit beiden Modellen experimentell bestimmte Reaktionsausbeuten für alle untersuchten Prozessbedingungen hervorsagen lassen.

Die Partikelbildungsmechanismen für die Fällung der Modellsubstanz Bariumsulfat werden im Detail diskutiert und neue Kinetikkorrelationen für Keimbildung und Wachstum werden präsentiert. Verschiedene auf Aktivitäten basierende Modelle für wässrige Ba²⁺/SO₄²⁻/Na⁺/Cl⁻ Lösungen werden getestet, wobei sich das Pitzer Model als am besten geeignet für die Beschreibung der Lösungszusammensetzung und der treibenden Kraft für die Partikelbildung erweist. Es wird gezeigt wie die auf diesem Modell basierenden
# Table of Contents

**Acknowledgements** ......................................................................................................................... I

**Abstract** ........................................................................................................................................ III

**Zusammenfassung** .......................................................................................................................... V

**Table of Contents** ............................................................................................................................... VII

1. **Introduction** ...................................................................................................................................... 1
   1.1 Background....................................................................................................................................... 2
   1.2 Motivation and Thesis Outline ....................................................................................................... 4
   1.3 References Chapter 1 ...................................................................................................................... 7

2. **Experimental Setup and Methods** .............................................................................................. 9
   2.1 Experimental setup ......................................................................................................................... 10
      2.1.1 Reactor design .......................................................................................................................... 10
      2.1.2 Experimental setup – Semibatch processes .......................................................................... 14
      2.1.3 Experimental setup – Continuous processes ........................................................................ 15
   2.2 Procedure for precipitation experiments ...................................................................................... 18
   2.3 Particle Characterization ............................................................................................................... 19
   2.4 References Chapter 2 ...................................................................................................................... 24

3. **Multi-scale Modeling of a Reactive Mixing Process in a Semibatch Stirred Tank** ..................... 25
   3.1 Introduction ..................................................................................................................................... 26
   3.2 Time-scale analysis ......................................................................................................................... 27
      3.2.1 Chemical reaction ..................................................................................................................... 28
3.2.2 Turbulent mixing

3.2.2.1 Macro-mixing

3.2.2.2 Meso-mixing

3.2.2.3 Micro-mixing

3.2.3 Time-scales for the double feed semibatch process

3.3. Challenges in multi-scale modeling of reactive mixing

3.4. Multi-scale models

3.4.1. Multiple-time-scale turbulent mixer model

3.4.1.1. Application of the turbulent-mixer model to the double feed semibatch process

3.4.2. E-model

3.5. Experimental Section

3.5.1. Experimental Setup

3.5.2 Materials

3.5.3 Experimental Procedure

3.6. Discussion of experimental and simulation results

3.6.1 Experimental results and application of the E-model

3.6.2 Experimental results and application of the multiple-time-scale turbulent mixer model

3.7. Conclusions

3.8. Nomenclature Chapter 3

3.9. References Chapter 3

4. APPLYING A THERMODYNAMIC MODEL TO THE NON-STOICHIOMETRIC PRECIPITATION OF BARIUM SULFATE

4.1 Introduction

4.2 Thermodynamics of aqueous Ba^{2+}/SO_4^{2-}/Na^+/Cl^- solutions

4.2.1 Solubility of barium sulfate in aqueous electrolyte solutions

4.2.2 Supersaturation ratio of barium sulfate in electrolyte solutions
4.3. Kinetics of barium sulfate nucleation and growth................................. 75
  4.3.1 Nucleation .......................................................................................... 76
  4.3.2 Growth ............................................................................................... 77
4.4. Mixing-precipitation model of barium sulfate formation...................... 80
  4.4.1 The mixing-precipitation model ....................................................... 82
  4.4.2 Results and discussion ...................................................................... 87
4.5 Conclusions ............................................................................................. 91
4.6 Nomenclature Chapter 4 .......................................................................... 92
4.7 References Chapter 4 .............................................................................. 94

5. INVESTIGATION OF A CONTINUOUS STIRRED TANK
   MIXING-PRECIPITATION PROCESS ............................................................ 97
  5.1 Introduction ............................................................................................. 98
  5.2 Mixing - precipitation modeling ............................................................. 100
    5.2.1 Mixing - precipitation model transport equations ....................... 101
    5.2.2 Aqueous solution and particle formation kinetics model.............. 106
  5.3 Application of the mixing-precipitation model to
      a continuous stirred tank process .......................................................... 108
    5.3.1. Implementation method for the model of the liquid phase
            and of the particle formation kinetics ............................................. 109
    5.3.2. Application of the composition PDF-closure
            to the continuous stirred tank process ........................................... 110
    5.3.3 Simulation strategy and convergence criteria ............................... 113
  5.4 Experimental Section ............................................................................. 117
    5.4.1. Experimental Setup ...................................................................... 117
    5.4.2 Materials ......................................................................................... 117
    5.4.3 Experimental Procedure .................................................................. 117
  5.5 Discussion of experimental and simulation results ................................. 118
    5.5.1 Discussion of experimental results ................................................. 118
      5.5.1.1 Experimental results for feed addition mode (1).............. 119
      5.5.1.2 Experimental results for feed addition mode (2)............ 122
5.5.1.3 Experimental results for feed addition mode (3)........ 124
5.5.1.4 Comparison of experimental results obtained for different feed points...................................................... 128
5.5.2 Discussion of simulation results................................................................. 130
5.5.3 Comparison of experimental and modeling results..................... 136
  5.5.3.1 Comparison of experimental and simulation results for addition mode (1)............................................. 136
  5.5.3.2 Comparison of experimental and simulation results for addition mode (2)............................................. 140
  5.5.3.3 Comparison of experimental and simulation results for addition mode (3)............................................. 142
  5.5.3.4 Comparison of experimental and simulation results for different feed addition modes....................... 150
5.6 Conclusions ....................................................................................................... 152
5.7 Nomenclature Chapter 5 ................................................................................ 154
5.8 References Chapter 5 ...................................................................................... 156

6. **SIMULATION OF A SEMIBATCH STIRRED TANK MIXING-PRECIPITATION PROCESS USING A CFD BASED MODEL** ........ 159
  6.1 Introduction ....................................................................................................... 160
  6.2 Application of the mixing-precipitation model to a semibatch stirred tank process................................................. 161
  6.3 Discussion of simulation results................................................................... 164
  6.4 Comparison of simulation results and experimental data...................... 170
  6.5 Conclusions ....................................................................................................... 176
  6.6 References Chapter 6 ...................................................................................... 177

7. **CONCLUDING REMARKS** ........................................................................... 179

**CURRICULUM VITAE** .............................................................................. 187
1. INTRODUCTION
1.1. BACKGROUND

Precipitation is a chemical process that has been applied for a long time in the production of bulk and fine chemicals including fertilisers, catalysts, food, pigments, and drugs. The Solvay process for the precipitation of sodium bicarbonate was invented already in 1861, as it is still used as a large scale industrial application nowadays with a production of several million tons per year.

Precipitation can be generally understood as the fast crystallization of sparingly soluble compounds. Supersaturation leading to particle formation is typically high and can be induced in two distinguished ways: either two miscible fluids are mixed to contact reactants that transform into a sparingly soluble substance or the solubility of a substance in solution is significantly reduced by addition of an antisolvent. Contrary to other crystallization techniques, the generated supersaturation in precipitation processes is typically high and particle formation occurs rapidly.

Commonly, industrial precipitation processes are carried out in rather simple reactors, such as continuously or semibatchwise operated stirred tank reactors. Although precipitation can be considered as a well established unit operation, its design and in particular its scale-up is difficult. This is due to the fact that processes have often to be designed to meet strict requirements for several product properties as average particle size, particle size distribution (PSD), morphology, purity and crystallinity at the same time. For example in the production of pigments, color strength and dispersability of the product particles can be significantly influenced by small changes in PSD or morphology.

Furthermore, all properties of a precipitate are influenced by a multitude of simultaneously occurring and interlinked particle formation mechanisms as nucleation, growth, aggregation, agglomeration, breakage, attrition and dissolution of particles. Since some of these mechanisms are still not fully understood or anyhow difficult to describe and predict, the design of precipitation processes has often to be based on empirical methods.
Additional complication can be added to the process design by the fact that product properties are not always controlled exclusively by the particle formation mechanisms. It is well known that the particle properties can strongly depend on mixing and hydrodynamic conditions during the process [1.1], [1.2], [1.3], [1.4], [1.5], [1.6], [1.7], [1.8]. Since chemical reaction and nucleation can be very fast in precipitation processes, even micromixing, the fastest stage of the turbulent mixing sequence, can influence the course of precipitation. Additionally, large scale mixing mechanisms may affect the process of crystal formation indirectly by influencing the rate of micromixing and directly by transporting reactants through the reactor leading to large scale inhomogeneities of the reactants distribution within the reactor. Since all the mixing mechanisms are dominated by different physical phenomena, especially the scale-up of mixing controlled processes can be challenging. Simple scale-up concepts based on keeping certain dimensionless numbers constant are often not applicable. Total similarity on different reactor scales cannot be established, as it is difficult or even impossible to maintain all the dimensionless numbers constant that characterize the process [1.1].

For these reasons a model based design approach seems to be most promising when aiming at a precipitation process, which reliably and precisely produces particles of desired properties. Three main goals must be met to be able to formulate an overall process model, which can serve as a feasible tool for process design. First, all particle formation and mixing mechanism relevant in a particular process must be identified. Second, each of the mechanisms has to be characterized separately by properly chosen models. Third, the interplay between the different mechanisms has to be elucidated and translated into an overall process model.

When trying to formulate adequate models for precipitation processes, the wide range of length and time scales for all phenomena involved can cause difficulties. The characteristic length scales for mixing mechanisms from the micro- to the macro-scale usually cover several orders of magnitude for typical stirred tank processes. The same applies to the corresponding time scales. On the contrary, chemical reaction, nucleation and crystal growth are essentially all
molecular level processes, but with widely differing time scales.

Due to large range of time and length scales for all the interlinked phenomena involved in a precipitation process, it is usually not feasible to fully resolve in space and time the process mechanisms in a model. Due to the limitations in computational power this is hardly possible, and process models have to compromise on the resolution. An important issue in modeling of such processes is to choose the right level of modeling detail, in particular for each of the mixing mechanisms, to be able to formulate an overall process model with good prediction capability.

Different kind of models for mixing influenced precipitation processes have been presented in recent years for applications of practical relevance, such as precipitation in a pipe [1.2], [1.3], in a Taylor-Couette reactor [1.4], and in a stirred tank reactor [1.5], [1.6], [1.7], [1.8], [1.9]. In most cases, processes were analyzed, where particle formation is controlled by nucleation and growth exclusively [1.2], [1.3], [1.4], [1.5], [1.6], [1.7], [1.8]. Mixing effects are described using different types of models characterizing in some cases large-scale mixing in detail while not accounting for small scale mixing effects [1.6], [1.7], in other cases focusing on a detailed small-scale mixing characterization but simplifying the large-scale mixing [1.5], [1.8], [1.9]. Mixing from the small to the large scales is accounted for in detail in [1.3], [1.4], however in these cases the precipitation reactor is described using only a two-dimensional model.

1.2. MOTIVATION AND THESIS OUTLINE

The work presented in this thesis aims at a better understanding of the interaction between mixing and precipitation for processes conducted in stirred tank reactors. In particular, the focus is on developing modeling tools, which allow to predict the influence of turbulent mixing on precipitate properties. Barium sulfate precipitation upon mixing of barium chloride and sodium sulfate solutions is chosen as a model system for this work, since this precipitation is widely studied in literature and experimental data for the kinetics of particle formation are available [1.10], [1.11]. An additional advantage of the model
system barium sulfate is that particle formation is known to be dominated only by nucleation and growth for a certain range of precipitation operating conditions [1.12].

For the modeling of mixing influenced precipitation processes, further on referred to as mixing-precipitation processes, different levels of detail can be adopted to describe each of the sub-process mechanisms. However, so far there is only limited experience in making the right choices for the level of detail of all the single mechanism models, which give in combination an overall process model of good prediction performance. This lack of knowledge is partly caused by the fact that only a small number of precipitation systems have been studied with respect to the influence of turbulent mixing on the process. Thus, the definition of general mixing precipitation modeling guidelines was so far impossible.

This thesis presents mixing-precipitation models of different complexity and their application to different kinds of stirred tank processes in comparison with experimental data. The different process models differ in their level of detail for different categories of sub-process mechanisms. Three main categories of mechanisms can be defined: First, all the mechanisms which contribute directly to the particle formation. Second, the small-scale mixing mechanisms which locally contact reactants and thereby generate supersaturation. Third, the large scale mixing mechanisms which convey reactants through the whole reactor.

In chapter 2 of this thesis the experimental setup, the general experimental procedure and the applied technique of particle characterization is described.

In chapter 3 it is shown how two different kinds of mixing models are applied to the simulation of a mixing sensitive process. In the first case a mechanistic mixing model is used, thus describing small-scale mixing in detail, but simplifying the large-scale mixing characterization. In the second case a detailed computational fluid dynamics based closure model is applied, thus characterizing both small-scale and large-scale mixing in detail. The analyzed process is a semibatch stirred tank process with two homogeneous parallel competitive chemical reactions. Contrary to the kinetics of precipitation those for homogeneous reactions are accurately known. Thus, the comparison of
experimental data with simulation results for such kind of a process can give a good indication of the mixing model quality. Results obtained with both types of mixing models are presented and compared with experimental findings.

In chapter 4 modeling results for a single feed semibatch barium sulfate precipitation process are presented. Mixing phenomena are modeled describing small-scale mixing in detail, but simplifying the large-scale mixing characterization. The particular focus is on the accurate characterization of particle formation kinetics based on a detailed liquid phase model. Using different activity models the driving force for particle formation is expressed and kinetics correlations for nucleation and growth are derived. Results obtained with the different models are assessed by comparison with experimental data.

In chapter 5 experimental and simulation results for a continuous stirred tank process are presented. Modeling results are obtained using a computational fluid dynamics based closure model characterizing mixing from the small to the large scales in detail and particle formation is described using the detailed model shown in chapter 4. The effect of changes in various operating parameters, e.g. feed point location, agitation rate and feed addition rate on particle properties is presented for experimental and simulation results, which are compared to access the model performance.

In chapter 6 simulation results for the semibatch precipitation process analyzed in chapter 4 are presented, which were obtained using the computation fluid dynamics based model presented in chapter 5. Simulation results are compared with experimental data and the simulation results presented in chapter 4, thereby highlighting the strength of the different mixing models.
1.3 REFERENCES CHAPTER 1


2. EXPERIMENTAL SETUP AND METHODS

In this chapter, the experimental setup and methods used in this work are described in detail. Design considerations for the main reactor unit and the overall setup are presented for the applications of semibatch and continuous processes. Features of the setup for liquid phase homogeneous chemical reaction experiments and continuous precipitation experiments are addressed. Special attention is given to the experimental methods used in the precipitation experiments. In particular, the techniques used for the particle characterization are described in depth.
2.1. EXPERIMENTAL SETUP

The stirred tank experimental setup employed in this work is designed for the use in both semibatch and continuous operation of a process. The same reactor unit is used for both types of processes. In the following sections design considerations for the reactor unit are presented and the experimental setups used for semibatch and continuous processes are described.

2.1.1. REACTOR DESIGN

The design concept for the reactor unit was developed based on three main criteria, which are summarized in the following. First, the reactor has to be suitable for performing precipitation experiments in a controlled and reproducible manner. Second, accurate process simulations should be possible for the chosen geometry. Third, the reactor design should allow performing optical measurements of flow field properties. Meeting all three requirements for the reactor design is somewhat difficult. Typically, reactors well suited for precipitation processes have a design, which is not favorable for performing process simulations, since the geometry is often rather complex.

In literature different kinds of reactor setups were proposed to study the impact of mixing on particle formation. In [2.1] a dished bottom reactor equipped with a Rushton turbine and four baffles is used, in [2.2] a vessel with three baffles and pitched paddle axial impeller is employed and in [2.3] precipitation in a flat bottom baffled reactor equipped with a turbine or propeller stirrer is studied. However, in none of these publications the reactor fluid dynamics are investigated in detail. Literature studies about stirred tank fluid dynamics often analyze flat bottom vessels equipped with four baffles and a Rushton turbine [2.4], [2.5], [2.6], [2.7].

That kind of reactor geometry was also chosen in this work. On one hand, the availability of an experimental database in literature for this reactor configuration is of advantage. Experimental flow field data published in [2.7] could be employed for modeling macro mixing as shown in chapter 3.4.2 and
chapter 4. An additional advantage of using a flat bottom reactor with a Rushton
turbine is, that the numerical grid necessary for a computational fluid dynamics
simulation can be developed easily to allow the precise computation of the flow
field.

The details of the reactor design used in this work are shown in Figs. 2.1 to 2.3.
In Fig. 2.1 and Fig. 2.2 technical drawings of the reactor and its components are
presented. In Fig. 2.3 a photo of the completely mounted reactor is shown.

The main reactor components are a glass cylinder used as reactor wall, the
bottom plate, the reactor lid, the bearing unit for the shaft, and the baffles and
Rushton turbine. The inner cylinder is made of Duran glass (Schott Medica,
Wertheim, Germany) and has an inner diameter of 0.2 m. The plate for the flat
bottom of the reactor is made of plexiglass. Both baffles and Rushton turbine
were produced using stainless steel. The baffles are produced as one connected
unit, which can be easily removed when cleaning the reactor. The bottom plate
has an opening at the center connected to a custom made plexiglass adapter.
Either a steel plug can be inserted into this adapter, when performing semibatch
experiments, or a connector to a hose can be installed, when operating the
reactor in continuous mode. The circular reactor lid and the bearing unit, which
is fixed at the lid center, are made of stainless steel. To allow for cooling or
heating of the reactor the vessel is jacketed. A double bottom plate is used and
the cylindrical reactor wall is surrounded by four perpendicular glass walls. This
kind of configuration is chosen to enable optical measurements of flow field
properties.

The reactor lid has several holes of different diameters at various positions,
where stainless steel feed pipes can be inserted. The feed pipes at the locations
used for the experiments presented in chapter 3 are schematically shown in
Fig. 2.1.

A close-up of the Rushton turbine is presented in Fig. 2.2. The turbine has six
blades and is fixed to the shaft using three screws to allow the modification of
the position on the shaft.
Fig. 2.1. Drawing of the reactor unit as used for semibatch mode experiments

1.) cylindrical glass wall of reactor
2.) plexiglass bottom plate
3.) bearing unit
4.) reactor lid
5.) steel plug (used only in semibatch mode)
6.) jacket of reactor made of four perpendicular glass plates.
Fig. 2.2. Drawing and photo of the Rushton turbine.

Fig. 2.3. Photo of the reactor.
2.1.2. EXPERIMENTAL SETUP – SEMIBATCH PROCESSES

The stirred reactor can be operated either with single feed or double feed addition in semibatch mode. For semibatch mode experiments the reactor is thermostated using a Compatible Control CC 230 (Huber, Offenburg, Germany) thermostat. Depending on the number of feed points either one or two gear pumps MCP-Z (Ismatec, Glattbrugg, Switzerland) are used to pump the reactant solutions through feed tubes into the reactor. As shown in Fig. 2.1, the feed tubes with an inner diameter $d_{in} = 0.2$ cm can be placed at three feed positions, namely $F_s$ below the surface, $F_d$ in the discharge and $F_I$ above the impeller. The impeller is powered by a stirrer Eurostar Power Control-Visc (IG Instrumenten-Gesellschaft, Zurich, Switzerland).

Fig. 2.4. Photo of setup as used for semibatch mode experiments.
2.1.3. EXPERIMENTAL SETUP – CONTINUOUS PROCESSES

The setup described in this section is used for conducting the continuous stirred tank precipitation experiments presented in chapter 5. For these experiments the reactor described in section 2.1.1 is used. However, in continuous mode experiments, the plug in the bottom outlet adapter, shown in Fig. 2.1, is replaced by a connector to a hose allowing the withdrawal of the suspension from the reactor bottom. A detailed schematic of the setup is presented in Fig. 2.5.

The two gear pumps MCP-Z (Ismatec, Glattbrugg, Switzerland) are used to continuously pump two solutions into the reactor through separate feed pipes. One feed pipe, which is typically used for feeding solution with high mass flow rate, has an inner diameter $d_{in,L} = 0.004$ m. The second feed pipe has an inner diameter of $d_{in,S} = 0.001$ m and is used to feed solution with low feed rate. The large feed tube is positioned in the discharge stream of the impeller with the feed point $F_L$ located at a height of 0.067 m from the bottom of the vessel and a radial distance of 0.060 m from the vessel axis. The small diameter feed tube can be placed at three different positions in the impeller discharge. All three feed positions are located at a height of 0.067 m from the bottom of the vessel, which is the same height as used for the large feed pipe. The first feed position $F_{1,S}$ for the small pipe is located at the same radial distance from the vessel axis as used for the large pipe $F_L$, but moved by 180 degrees around the vessel axis relative to the position of $F_L$. The second feed position $F_{2,S}$ for the small pipe is located at radial distance of 0.076 m from the vessel axis and at the same angular position as the feed point $F_L$. The third feed position $F_{3,S}$ for the small pipe is located at radial distance of 0.066 m from the vessel axis and the same angular position as the feed point $F_L$.

Typically, the small feed tube is used for feeding highly concentrated barium chloride into the reactor and the large tube is used for feeding dilute sodium sulfate solution into the system. Aqueous barium chloride solution is stored in a continuously stirred vessel of five liter volume, which is shown as T-3 in Fig. 2.5. Sodium sulfate aqueous solution is stored in a 120 liter supply tank, shown as T-1 in Fig. 2.5. To ensure good mixing in the large supply tank the
sodium sulfate solution is continuously circulated at a flow rate of approximately 5 liters/min through the vessel T-2, shown in Fig. 2.5, using the peristaltic pump P-1 (Watson-Marlow 704U/R, Watson-Marlow GmbH, Romerskirchen, Germany). The sodium sulfate solution, used for feeding into the main reactor, is withdrawn from vessel T-2, thereby keeping the backpressure for pump P-3 constant, since the liquid level in vessel T-2 is also constant.

The suspension is withdrawn from the reactor bottom through the outlet with an inner diameter \( d_{\text{outlet}} = 0.015 \) m. The reactor outlet is connected directly with vessel L-1, as shown in Fig. 2.5. Since vessel L-1 has an overflow outlet, the suspension flow rate through the reactor outlet automatically adjusts to keep the liquid level in the reactor constant. The height of the liquid level in the stirred tank can be modified by altering the relative height of vessel L-1.

The suspension leaving the vessel L-1 is either directed into a waste tank or into the one liter stirred tank reactor R-2, as shown in Fig. 2.5. In reactor R-2 the particle size can be monitored in-situ using a Focused Beam Reflectance Measurement (FBRM) device (Lasentec, Redmond WA, USA). To enable in-situ particle characterization the suspension entering the reactor R-2 has to be diluted, thus avoiding particle deposition on the measurement probe due to high supersaturation. The suspension is diluted by a factor of one hundred by pumping water into the vessel R-2 with the gear pump P-4 (V2E, Verder, Düsseldorf, Germany).
Fig. 2.5. Schematic of the setup used for continuous stirred tank precipitation experiments.

P-1: peristaltic pump
P-2: peristaltic pump
P-3: gear pump
P-4: gear pump
T-1: 120 liter storage tank for aqueous Na2So4 solution
T-2: 2 liter supply tank for aqueous Na2So4 solution
T-3: 2 liter storage tank for aqueous BaCl2 solution
T-4: 100 liter storage tank for quenching water
R-1: precipitation reaction
L-1: level controller
R-2: stirred tank
2.2 PROCEDURE FOR PRECIPITATION EXPERIMENTS

In precipitation processes the properties of product particles crucially depend on the applied experimental procedure. It is well known, that small changes in process operating conditions, e.g. changes in the impurity profile, can significantly influence the properties of particles obtained. Therefore, in this work special attention was given to establish an experimental procedure, which enables to perform precipitation experiments in a reproducible manner. The adopted procedure includes five main steps, namely preparation of reactant solutions, cleaning of the setup, reactant feeding and precipitation, sampling and particle characterization, which are briefly discussed in the following. The methods for particle characterization used in this work are explained in more detail in section 2.3.

Typically, reactant solutions were prepared using double distilled water. Several experiments were performed filtering the aqueous solutions with a nitrocellulose filter of 0.22 µm pore size, but this purification step was found to have no noticeable influence on particles properties. Thus, filtration of reactant solutions was usually omitted. However, proper cleaning of the stirred tank reactor was found to be a critical step of the experimental procedure. Even very small amount of particles present in the stirred tank prior to feed addition could influence the outcome of the experiment. Therefore, the reactor was always flushed with water for 30 min after mechanical cleaning.

The feed addition and the particle formation by precipitation can be assumed to be quite reproducible. The gear pumps allow feed addition with a flow rate deviation of about one percent. Since barium sulfate precipitation occurs at high supersaturation, the induction time for particle formation is very short and stochastic changes in the onset of particle formation are small in comparison with the feed addition time. Therefore, overall process dynamics are not influenced significantly by stochastic changes in the onset of particle formation.

Sampling of suspension was performed always at the same location in the impeller discharge using a pipette. Since barium sulfate particles were always in the size range from 1 µm to 30 µm, segregation in the reactor due to settling
could be neglected, especially because the reactor was intensely stirred in all experiments.

2.3 PARTICLE CHARACTERIZATION

In this work two different techniques were used for particle characterization. The particle size distribution was determined using the electrical sensing zone method employing a Multisizer 3 (Beckman Coulter, Nyon, Switzerland). Particle shape characterization was performed based on image analysis using scanning electron microscopy (SEM) with a Leo 1530 microscope (Zeiss/Leo, Oberkochen, Germany).

The particle size distribution was always measured directly after sampling. For that purpose 2 ml of suspension sample were diluted in 200 ml of 0.1 M aqueous sodium sulfate solution as electrolyte. Using this electrolyte the stability of barium sulfate particles over several hours could be confirmed. Different deagglomeration techniques were applied to ensure that the particle size distribution of primary particles could be determined. Modification of the suspension pH-value over a wide range, application of ultrasound and addition of several different surfactants did not lead to a noticeable difference in measured particle size distribution. Thus, it can be concluded that a barium sulfate suspension is stable and particle agglomeration is negligible for the process conditions analyzed in this work. This could be confirmed by image analysis of SEM pictures where no agglomerates could be observed.

For particle characterization using SEM several techniques of sample preparation were explored. In a first approach, a few drops of suspension were directly deposited onto a double coated conductive carbon tape, which was fixed on a copper grid. After water had evaporated, a 2 nm layer of platinum was sputtered onto the grid. A typical SEM picture taken after that sample preparation procedure is shown in Fig. 2.6. It can be noticed that particles tend to accumulate at one spot, which can be due to the deposition and evaporation of the suspension droplet.
In a second approach, the suspension is spread onto a nitrocellulose filtering membrane with 0.22 µm pore size, which in turn is fixed to a copper grid using double coated conductive carbon tape. After sputtering a 2 nm layer of platinum onto the sample, a SEM picture as shown in Fig. 2.7 can be obtained. It can be clearly noticed that primary particles are distributed well over the grid. However, the tradeoff is that the picture quality suffers from the clearly noticeable structure of the filter membrane.

In a third approach, the surface of a copper grid was activated by exposure to oxygen plasma for several minutes. Suspension droplets spread immediately over the copper grid after deposition. After evaporation and sputtering of a 2 nm layer of platinum a SEM image as shown in Fig. 2.8 could be obtained. Particles are distributed evenly over the grid and a good particle-background contrast could be obtained.

For particle shape characterization using SEM either the second or third sample preparation techniques were commonly applied. It could be noticed that for all precipitation experiments barium sulfate product particles have similar shapes as reported in [2.8]. Therefore, values for particle shape descriptors, e.g. the sphericity Φ, the volume shape factor $k_v$ and the surface shape factor $k_a$, are adopted from [2.8] for the three different particle shape categories reported. Following this approach, the particles shown in Fig. 2.6 to Fig. 2.8 can be described by a sphericity value of 0.405.
Figs. 2.6  SEM image of barium sulfate particles on double coated conductive carbon tape sputtered with 2 nm of platinum. Particles obtained in semibatch single feed precipitation feeding aqueous sodium sulfate solution into aqueous barium choride solution:

$c_{BaCl_2} = 0.0045 \text{ M}, c_{Na_2SO_4} = 0.225 \text{ M}, t_{\text{feed}} = 10 \text{ min}$  
$N_{\text{stirrer}} = 200 \text{ rpm}.$
Figs. 2.7  SEM image of barium sulfate particles on a nitrocellulose filtering membrane with 0.22 μm pore size sputtered with 2 nm of platinum.

Particles obtained in semibatch single feed precipitation feeding aqueous sodium sulfate solution into aqueous barium chloride solution:

\[ c_{\text{BaCl}_2} = 0.0045 \ M \ , \ c_{\text{Na}_2\text{SO}_4} = 0.225 \ M \ , \ t_{\text{feed}} = 10 \ min \]

\[ N_{\text{stirrer}} = 200 \ \text{rpm}. \]
Figs. 2.8 SEM image of barium sulfate particles on a copper grid treated with oxygen plasma, sputtered with 2 nm of platinum.

Particles obtained in semibatch single feed precipitation feeding aqueous sodium sulfate solution into aqueous barium chloride solution:

$c_{\text{BaCl}_2} = 0.0045 \, M$, $c_{\text{Na}_2\text{SO}_4} = 0.225 \, M$, $t_{\text{feed}} = 10 \, \text{min}$

$N_{\text{stirrer}} = 200 \, \text{rpm}$. 
2.4 REFERENCES CHAPTER 2


3. MULTI-SCALE MODELING OF A REACTIVE MIXING PROCESS IN A SEMIBATCH STIRRED TANK

In this chapter the influence of turbulent mixing on the course of two parallel chemical reactions (neutralization of sodium hydroxide and hydrolysis of ethyl chloroacetate) is investigated for a process carried out in a semibatch stirred tank reactor. The multi-scale nature of the process is highlighted by a time-scale analysis of controlling process mechanisms. Two reactive mixing models of different complexity, both accounting for all relevant phenomena from the micro- to the macroscale, are applied for the simulation of the process. Computational results of both models for various operating conditions are compared with experimental data, thus highlighting the strengths of the two models.
3.1. INTRODUCTION

A well-known issue in chemical reaction engineering is that side reactions produce undesired by-products, which reduce the reaction yield of the main product and later on complicate its downstream purification. In many practical applications it is possible to enhance selectivity by simple low cost means, e.g. by modifying the mixing conditions of reactants in the reactor. This is due to the fact that turbulent mixing in industrial vessels is often slower than some of the reactions involved. Therefore the course of reactions, and thereby their selectivity, is depending on mixing conditions. Although this has been generally known for a long time, there is still a need for a deeper understanding of reactive mixing. Moreover, in order to be able to manipulate the selectivity of specific reactions by changing mixing conditions, a detailed knowledge about the interplay of the mechanisms involved is essential.

To gain more insight about the nature of mixing-reaction interactions, competitive reactions processes of well-known kinetics have been studied extensively in the past through experiments [3.1], [3.2], [3.3], [3.4] and modeling [3.5], [3.6], [3.7]. It has been shown that a macroscopic description of a mixing-sensitive process yields only poor results. This is clearly due to the complexity of the interactions in such systems. Multiple chemical reactions with nonlinear reaction rates compete for reactants, turbulent mixing influences the progress of reactions on the small scale, and the process mechanisms have widely different time scales. Length and time scales that have to be resolved for an accurate characterization of such processes comprise the wide range from the reactor size and the overall process time to the length and time scales of molecular diffusion, which is locally responsible for contacting the reactants. Detailed models of such complex systems have been presented in recent years for processes of practical relevance, such as reactive mixing in a pipe [3.6], [3.8] and in a continuous stirred tank reactor [3.7], where the number of modeled scales was reduced to those corresponding to the most relevant mechanisms involved.
In this thesis chapter reactive mixing in the complex geometry of a stirred tank is analyzed in detail, where the double feed process is operated in semibatch mode, thus increasing the complexity of the process because of its time dependence. The comparison of all relevant time and length scales in the system highlights the need for a multi-scale modeling approach. Two different multi-scale models of the system are presented and applied to predict, how a change in process operating conditions affects reaction yields of parallel reactions. The application of a computational fluid dynamics (CFD) based closure model for a double feed semibatch process is presented. Furthermore a classical mixing model is used for the characterization of this process. Simulation results of both models are compared with experimental data, thus highlighting the strengths of the different models.

3.2. TIME-SCALE ANALYSIS

In this chapter the influence of turbulent mixing on the course of homogeneous chemical reactions is studied for the double feed semibatch process shown in Fig. 3.1. A well-known parallel reaction system, which has been frequently used to investigate reactive mixing [3.6], [3.7], [3.9], is employed:

\[
NaOH + HCl \xrightarrow{k_1} NaCl + H_2O \quad (A) \quad (B) \quad (P) \tag{3.1}
\]

\[
NaOH + CH_2ClCOOC_2H_5 \xrightarrow{k_2} CH_2ClCOONa + C_2H_5OH \quad (A) \quad (C) \quad (Q) \tag{3.2}
\]

Sodium hydroxide (A) and hydrochloric acid (B) are fed in semibatch mode through separate feed pipes into the tank reactor where ethyl chloroacetate (C) is initially present. Upon mixing the base reacts either in the neutralization reaction with the acid or it is consumed by the alkaline hydrolysis of the ester. The second order reaction rate constants of the first and the second reaction are \( k_1 = 1.3 \times 10^8 \ \text{m}^3 \ \text{mol}^{-1} \ \text{s}^{-1} \) and \( k_2 = 0.023 \ \text{m}^3 \ \text{mol}^{-1} \ \text{s}^{-1} \), respectively. Due to the huge difference, i.e. ten orders of magnitude in the reaction rate constants,
turbulent mixing strongly affects the reaction yields by masking one of the reactions. In fact, if mixing is fast, only the first, fast reaction occurs, whereas the second takes place only under slow mixing conditions. To characterize how mixing affects the reactions and thereby to identify the relevant mechanisms to be considered in the model of the process, time-scales of the reactions and of the mixing mechanisms are compared in the following.

Fig. 3.1. Schematic of the semibatch stirred-tank reactor setup.

### 3.2.1 CHEMICAL REACTION

The characteristic time $\tau_{Ri}$ of any of the two bimolecular reactions above can be defined as follows [3.5]:

$$\tau_{Ri} = \frac{1}{k_i \left( \overline{c}_1 + \overline{c}_2 \right)}$$  \hspace{1cm} (3.3)
where \( k_i \) is the kinetic constant of the \( i \)-th reaction, and \( \bar{c}_j \) is the local, average concentration of the \( j \)-th reactant.

### 3.2.2 TURBULENT MIXING

Chemical reactions are essentially molecular-level processes, so only mixing on that level can directly influence their course, whereas mixing mechanisms on larger scales have an indirect influence by changing the environment for local mixing. Mixing mechanisms can be grouped into three main categories depending on their characteristic length scale. Small scale mixing close to the molecular level is referred to as micromixing; macromixing is mixing on a large scale, and intermediate scale mixing is called mesomixing.

#### 3.2.2.1 MACRO-MIXING

For a process carried out in a stirred tank the largest scale of mixing is the scale of the whole reactor. Macromixing refers to flow processes controlling the mean concentration and the residence time distribution, i.e. the mean convective flow in the vessel. Macromixing can be characterized by the circulation time \( \tau_C \), which can be estimated as

\[
\tau_C = \frac{V}{Q_C} \tag{3.4}
\]

where \( Q_C = C_1 N d_{imp}^3 \), \( V \) is the liquid volume in the reactor, \( N \) the stirring rate, \( d_{imp} \) the impeller diameter, \( Q_C \) the circulation capacity, and \( C_1 = 1.5 \) is a constant depending on the pumping capacity of the impeller, which in this case is a Rushton turbine.

#### 3.2.2.2 MESO-MIXING

Mesomixing refers to the coarse scale turbulent exchange between the fresh feed and its surroundings. A fast chemical reaction is usually localized near the feed
point, where a plume of fresh feed is formed. This plume is of a coarse scale relative to the micromixing scales, but of a fine scale relative to the scale of the system. Spatial evolution of the plume can be identified with the mechanism of turbulent diffusion. A characteristic time for turbulent diffusion, \( \tau_D \), can be defined through the feed addition rate \( Q_{\text{feed}} \), the velocity magnitude \( \bar{u} \) close to the feed point, and the turbulent diffusivity, \( D_T \) [3.10]:

\[
\tau_D = \frac{Q_{\text{feed}}}{\bar{u} D_T}
\]  

Another aspect of mesomixing is related to the inertial-convective process of disintegration of large eddies, with a size \( r \) larger than the Kolmogorov microscale \( \eta \), but smaller than the large energy-containing eddies of size \( L \). Inertial-convective disintegration proceeds without being influenced by molecular mixing, but it influences itself the micromixing since the structure of the large eddies determines the environment for small scale mixing. When assuming equal integral scales for velocity and concentration, a characteristic time constant \( \tau_s \) for the inertial-convective mixing can be estimated as [3.11]:

\[
\tau_s = \frac{k}{2\varepsilon} = \frac{3 L^{2/3}}{4 \varepsilon^{1/3}}
\]  

where \( k \) is the turbulent kinetic energy and \( \varepsilon \) is the energy dissipation rate.

3.2.2.3 MICRO-MIXING

Small scale mixing in liquids is driven by the mechanism of the viscous-convective deformation of fluid elements, followed by molecular diffusion. An important feature of micromixing is the accelerating effect of viscous-convective deformation on molecular diffusion. A characteristic time constant for viscous-convective mixing (for \( r < \eta \)), \( \tau_E \), is known as the engulfment time constant [3.12]:
\[ \tau_E = \frac{1}{E} = 17.24 \left( \frac{\nu}{\epsilon} \right)^{1/2} \quad (3.7) \]

where \( E \) is the engulfment parameter, and \( \nu \) is the kinematic viscosity. A time-scale for molecular diffusion \( \tau_G \) can be estimated as

\[ \tau_G = \tau_E \left( 0.030 + \frac{17050}{Sc} \right)^{-1} \quad (3.8) \]

where \( Sc \) is the Schmidt number of the fluid [3.13].

### 3.2.3 TIME-SCALES FOR THE DOUBLE FEED SEMIBATCH PROCESS

To estimate the relative importance of the different mechanisms, the time-scales of the double feed semibatch process are to be analyzed. All information about operating conditions and reactor geometry is summarized in Fig. 3.1 and Tab. 3.1. Local flow field properties required for the time-scale estimations are calculated with a three-dimensional computational fluid dynamics (CFD) model of the process using the \( k-\epsilon \) model in FLUENT 6.1 (Fluent Inc., Lebanon, USA). Using the CFD results, average values of the flow properties are calculated for the volume close to the feed pipes where the reactions take place. Mixing time-scales are calculated based on these average values.

A comparison of the mixing related time-scales in Tab. 3.1 shows that a wide range, i.e. from a few milliseconds for molecular diffusion to 1020 s for feed addition, is covered. With a time-scale between 0.075 to 0.75 nanoseconds the neutralization reaction is much faster than any of the mixing mechanisms. Thus mixing is controlling the reaction, since the speed of reactant contacting determines how fast the neutralization reaction proceeds. Due to the competition of the parallel reactions for sodium hydroxide, the yield of the hydrolysis depends also on the mixing conditions. Locally reactants are contacted by micromixing. Thus mixing on the small scale is the mechanism that directly
influences the chemical reactions. For a stirring rate of 100 rpm the engulfment micromixing time $\tau_E$ is 0.136 s, and the diffusion time $\tau_G$ is 0.008 s. At a stirring rate of 200 rpm the corresponding values are 0.049 s and 0.003 s. Hence, micro-scale mixing by diffusion is faster than engulfment, since $\tau_E / \tau_G >> 1$. This confirms that effects of molecular diffusion are negligible for Schmidt numbers smaller than 4000, as it is in this case where $Sc \approx 1000$ [3.12].

<table>
<thead>
<tr>
<th>Chemical reaction time-scales</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Neutralization reaction</strong></td>
</tr>
<tr>
<td>for ($c_1 = c_2 = 5 - 50$ mol/m$^3$)</td>
</tr>
<tr>
<td><strong>Alkaline hydrolysis reaction</strong></td>
</tr>
<tr>
<td>for ($c_1 = c_2 = 5 - 50$ mol/m$^3$)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mixing related time-scales</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Process</strong></td>
</tr>
<tr>
<td><strong>Stirring rate</strong></td>
</tr>
<tr>
<td>$N$</td>
</tr>
<tr>
<td>100 rpm</td>
</tr>
<tr>
<td>200 rpm</td>
</tr>
</tbody>
</table>

**Table 3.1: Time-scales the double feed semibatch process mechanisms for a feed addition rate 3.5 ml/min and feed position $F_d$ in Fig. 3.1.**

For a stirring rate of 100 rpm: $\varepsilon(\text{feed plume}) = 0.0161$ m$^2$/s$^3$, $k(\text{feed plume}) = 0.0025$ m$^2$/s$^2$ and $\bar{v} = 0.17$ m/s.

For a stirring rate of 200 rpm: $\varepsilon(\text{feed plume}) = 0.125$ m$^2$/s$^3$, $k(\text{feed plume}) = 0.0095$ m$^2$/s$^2$ and $\bar{v} = 0.40$ m/s.

For all operating conditions applied in this work $\tau_E > \tau_S > \tau_D$. As listed in Tab. 3.1, $\tau_D$ is 0.009 s for a stirring rate of 100 rpm, and $\tau_D$ is 0.002 s for 200 rpm. Because the ratio $\tau_D / \tau_E$ is much smaller than one, mesomixing by turbulent diffusion plays no significant role in the process. However, mesomixing due to inertial-convective disintegration of large eddies can have some impact on the course of the reactions, since the ratio $\tau_S / \tau_E$ is with 0.56 for 100 rpm and 0.77
for 200 rpm stirring rate only slightly smaller than one. It is worth noting that mixing conditions with $\tau_E > \tau_S$ occur often in industrial applications of moderate Reynolds numbers. Accounting for viscous-convective mixing phenomena is essential under such conditions.

A comparison of feed addition time $\tau_{feed}$ and macromixing time $\tau_C$ shows that macromixing is much faster than reactant feeding. Since the feed volumes of reactant are small, it can be concluded that the bulk of the fluid is homogeneously mixed. Macromixing mainly influences the course of the process indirectly by transporting fluid elements through environments of different turbulence characteristics and chemical composition.

The comparison of the semibatch process time-scales leads to the general conclusion that it is essential to account for all scales of mixing in the process modeling, in order to capture the system dynamics correctly.

### 3.3. CHALLENGES IN MULTI-SCALE MODELING OF REACTIVE MIXING

A difficulty in modeling reactive mixing is due to the fact that not only time-scales of all process mechanisms, but also their corresponding length scales vary within a wide range. Therefore a very high time and spatial resolution would be required to resolve the characteristics of a process in all the details. Due to the limitations in computational power this is hardly possible, and mixing models have to compromise on the resolution.

Classical mixing models, such as the engulfment (E) model [3.12] or the interaction by exchange with the mean (IEM) model [3.14], compromise on spatial resolution as well as on the characterization of the system dynamics. Especially spatial reactant distribution by macromixing is simplified in these models by assuming a homogeneously mixed bulk. Other models like the engulfment-deformation-diffusion (EDD) model [3.5] characterize small scale mixing in all details and account for all mixing mechanisms, but compromise on the macro flow characterization.
Modern reactive mixing models follow the approach of transport equation modeling using a rather fine spatial discretization of the mixing device to capture the details of the macro-flow [3.7]. In principle, a process could be fully described by solving the Navier-Stokes, the continuity and the species mass balance equations. Thus the yield distribution of parallel reactions could be determined directly and no mixing model would be required. Since the smallest relevant length scale, i.e. the smallest scale of concentration fluctuations described by the Batchelor microscale, is very small especially in the case of liquid mixing, direct numerical simulation (DNS) is still limited to flows in simple geometries. In some cases large eddy simulations (LES) were performed for flows in complex geometries [3.15], but due to the large computational effort this compromise between DNS and Reynolds averaged transport equation modeling is not established as a standard tool yet. When using equations based on Reynolds averaging the well-known closure problem arises. To briefly highlight this problem, the result of Reynolds decomposition and averaging for the species mass balance equation of the ester, i.e. reactant C, is shown as an example:

\[
\frac{\partial \bar{c}_C}{\partial t} + \bar{u}_j \frac{\partial \bar{c}_C}{\partial x_j} = D_m \frac{\partial^2 \bar{c}_C}{\partial x_j^2} - \frac{\partial}{\partial x_j} \left( u'_j \bar{c}_C \right) - k_2 \left( \bar{c}_A \bar{c}_C + c_A' c_C' \right) \tag{3.9}
\]

Here \( \bar{c}_A \) and \( \bar{c}_C \) are the average, and \( c_A' \) and \( c_C' \) the local fluctuating components of the concentrations of reactants \( A \) and \( C \) respectively, and \( u'_j \) is the \( j \)-th component of velocity fluctuations. All equation terms containing products of fluctuating components have to be modeled to be able to solve the equation. An important issue in reactive mixing modeling is how to describe correctly the nonlinear term constituted of the averaged product of the concentration fluctuations. Since this average value crucially depends on the local distribution of reactants \( A \) and \( C \), information about the mixture structure is required to predict the reaction rate. Thus, reactant transport equations have to be solved in conjunction with mixing models for the local fluid structure and the dynamics of its evolution. Mixing models of such kind are the turbulent-mixer-model [3.13] and the spectral relaxation model [3.16]. These models describe
mixing dynamics on the meso- and microscale using a slightly simpler micromixing scheme than the EDD-model. In the following section two examples of mixing models and their application to the double feed semibatch process in Fig. 3.1 are presented. The first model is a closure model and the second one is the E-model. In section 3.6 results obtained with both models are compared with experimental data thus highlighting the strengths of the different modeling approaches.

3.4. MULTI-SCALE MODELS

3.4.1. MULTIPLE-TIME-SCALE TURBULENT MIXER MODEL

The reactive mixing model presented in this section follows a closure modeling approach of transport equations, to overcome the problem related to the reaction term in Eq. 3.9. The average reaction rate is calculated based on a model of the local mixture structure accounting for concentration fluctuations on different scales. By employing a multi-scale model the interactions between fluctuations on different scales are characterized, thus making it possible to capture in detail the dynamics of mixture structure changes. A common approach for the characterization of the local mixture structure everywhere in the contacting device is to describe in detail, how a passive non-reacting tracer $T$ undergoes mixing after its injection into the reactor [3.6]. The normalized concentration can be defined as

$$f = \frac{c_T}{c_{T0}}$$  \hspace{1cm} (3.10)

where $c_T$ is the concentration of the tracer, and $c_{T0}$ is its initial or feed concentration. By macromixing the injected fluid is diluted on the coarse scale without, however, mixing on the molecular scale. The decrease of average scalar concentration $\bar{f}$, which is equivalent to a mixture fraction, can be described by the following equation
\[
\frac{\partial \bar{f}}{\partial t} + \bar{u}_j \frac{\partial \bar{f}}{\partial x_j} = \frac{\partial}{\partial x_j} \left[ (D_m + D_T) \frac{\partial \bar{f}}{\partial x_j} \right]
\]

(3.11)

where \(D_m\) is the molecular diffusivity and \(D_T\) the turbulent diffusivity. A simple way of characterizing the mixture structure on the small scale is to express the variance \(\sigma_s^2\) of the local concentration distribution of \(f\) around its average value \(\bar{f}\) [3.7]:

\[
\sigma_s^2 = (f - \bar{f})^2
\]

(3.12)

Fig. 3.2. Schematic of a local distribution of the mixture fraction \(f\).

The variance is a measure for the segregation of the fluid on the small scale. This is visualized in Fig. 3.2 where a distribution of \(f\) along a spatial coordinate \(z\) is shown schematically. If the fluid were perfectly mixed, the concentration \(f\) would be equal to the average value \(\bar{f}\) everywhere, and the variance \(\sigma_s^2\) would
be equal to zero. The higher the fluid segregation, i.e. the fluctuations of $f$, the higher the variance $\sigma_S^2$. Fig. 3.2 also shows that the distribution of $f$ can be characterized in more detail, when concentration fluctuations around the average value $\bar{f}$ are decomposed into fluctuations on different scales around local average values $f_S$ and $f_E$. As shown elsewhere [3.13], this can be described by decomposing the variance $\sigma_S^2$ into different components

$$\sigma_S^2 = (f - \bar{f})^2 = (f - f_S)^2 + (f_S - f_E)^2 + (f_E - \bar{f})^2 = \sigma_1^2 + \sigma_2^2 + \sigma_3^2 \quad (3.13)$$

where the components $\sigma_1^2$, $\sigma_2^2$ and $\sigma_3^2$ characterize concentration fluctuations on different scales. Each of the three components of the variance corresponds to the scale where the specific mixing mechanisms act. The first component $\sigma_1^2$ is related to the inertial-convective mixing range, whereas $\sigma_2^2$ and $\sigma_3^2$ correspond to viscous-convective and viscous-diffusive mechanisms, respectively. The evolution of the variance components and thereby the change of the local mixture structure can be modeled by the transport equation

$$\frac{\partial \sigma_i^2}{\partial t} + \bar{u}_j \frac{\partial \sigma_i^2}{\partial x_j} = \frac{\partial}{\partial x_j} \left[ (D_m + D_T) \frac{\partial \sigma_i^2}{\partial x_j} \right] + R_{pi} - R_{Di}, \quad (i = 1, 2, 3) \quad (3.14)$$

where $R_{pi}$ and $R_{Di}$ represent the production and dissipation terms of the single variance components, respectively [3.13]. As shown elsewhere [3.7], the inertial-convective variance component $\sigma_1^2$ is produced by gradients of the mean scalar $\bar{f}$ according to

$$R_{pi} = -2u'_j f'_r \frac{df}{dx_j} = 2D_T \left( \frac{df}{dx_j} \right)^2 \quad (3.15)$$

when using a gradient diffusion approximation for the scalar flux. The variance $\sigma_1^2$ is dissipated due to the inertial-convective disintegration of eddies, which generates scalar fluctuations on the smaller scale represented by the variance $\sigma_2^2$. The changes in variance due to the inertial-convective mechanism can be
modeled with a first order decay equation [3.5], where the characteristic time-scale $\tau_s$ of this mechanism is defined by Eq. 3.6:

$$R_{D1} = R_{P2} = \frac{\sigma_1^2}{\tau_s}$$  \hfill (3.16)

Dissipation of $\sigma_2^2$ and production of $\sigma_3^2$ occur at the same time due to viscous-convective mechanisms, with rates $R_{P3}$ and $R_{D2}$ [3.13]:

$$R_{D2} = R_{P3} = \frac{1}{\tau_E} \sigma_2^2$$  \hfill (3.17)

where the characteristic time $\tau_E$ of this mechanism is defined by Eq. 3.7. Finally, the component $\sigma_3^2$ of the variance decays due to molecular diffusion at a rate given by

$$R_{D3} = \frac{1}{\tau_G} \sigma_3^2$$  \hfill (3.18)

with the characteristic diffusion time $\tau_G$ defined by Eq. 3.8 [3.13]. The mixing model, constituted of the system of eqs. 3.12 to 3.18, is known as the multiple-time-scale turbulent mixer model [3.13]. This set of equations can fully characterize the local mixture structure and its evolution by turbulent mixing.

When modeling mixing processes involving chemical reactions, it is helpful to describe the mixture structure with a probability density function (PDF) for $f$. For the process analyzed in this chapter the real shape of the PDF can be approximated with a Beta-function that is defined by [3.6]:

$$\Phi(f) = \frac{f^{\nu-1} (1-f)^{\nu-1}}{\int_{0}^{1} y^{\nu-1} (1-y)^{\nu-1} \, dy}$$

with $\nu = \bar{f} \left( \bar{f} (1-\bar{f}) / \sigma_3^2 - 1 \right)$, and $w = \left[ (1-\bar{f}) / \bar{f} \right] \nu$  \hfill (3.19)
It is worth noting that $\Phi(f)$ depends on time and position through $\sigma^2$ and $\overline{f}$. Using the Beta-function $\Phi(f)$, the nonlinear reaction rate term in Eq. 3.9 can be recast as:

$$\overline{r}_2 = -k_2 c_A c_C = -k_2 \int_0^1 c_A(f) c_C(f) \Phi(f) df$$

(3.20)

where $c_A(f)$ and $c_C(f)$ are the local reactant concentration of the ester and the base, respectively. As shown elsewhere [3.5], the concentration $c_C(f)$ can be determined by an interpolation between the concentrations $c_C^\infty(f)$ and $c_C^0(f)$ corresponding to the limiting cases where two instantaneous reactions occur and where an instantaneous reaction together with an infinitely slow one occurs [3.6]:

$$c_C(f) = c_C^\infty(f) + \frac{\overline{c}_C^\infty - c_C^\infty}{c_C^0 - \overline{c}_C^\infty} \left[ c_C^0(f) - c_C^\infty(f) \right]$$

(3.21)

Here $\overline{c}_C$ is the average reactant concentration, whose evolution is described by the following mass balance equation:

$$\frac{\partial \overline{c}_C}{\partial t} + \overline{u}_j \frac{\partial \overline{c}_C}{\partial x_j} = \frac{\partial}{\partial x_j} \left[ (D_m + D_T) \frac{\partial \overline{c}_C}{\partial x_j} \right] - \overline{r}_2$$

(3.22)

In principle the concentration $c_A(f)$ in Eq. 3.20 could be calculated using the interpolation of Eq. 3.21 written in the proper form for reactant $A$ [3.6]. However, in this case it would be required to determine the concentration $\overline{c}_A$ by solving an additional transport equation similar to Eq. 3.22. A more convenient approach is to make use of an equation for a pseudo species, whose concentration is defined by the following linear combination of the concentrations of reactants $A$, $B$ and $C$:

$$g = \frac{c_A - c_B - c_C + c_{B,\text{bulk}} + c_{C,\text{bulk}}}{c_{A,0} + c_{B,\text{bulk}} + c_{C,\text{bulk}}} = f$$

(3.23)
where \( c_{A,0}, c_{B,\text{bulk}} \) and \( c_{C,\text{bulk}} \) are the feed or bulk concentrations of reactants \( A, B \) and \( C \), respectively. The composition variable \( g \) behaves like the mixture fraction \( f \), i.e. \( g(\bar{x},t) \) is equal to \( f(\bar{x},t) \). Thus, Eq. 3.23 can be used to determine the concentration \( c_A(f) \) from \( c_C(f) \) and \( f \) together with

\[
c_U = c_A - c_B \\
c_A = \frac{|c_U| + c_U}{2}
\]

When following this approach only one reactant transport equation, namely Eq. 3.22, has to be solved to describe the progress of the neutralization and hydrolysis reaction.

### 3.4.1.1. APPLICATION OF THE TURBULENT-MIXER MODEL TO THE DOUBLE FEED SEMIBATCH PROCESS

In the following it is described how the reactive mixing model of the previous section is applied to the stirred tank process shown in Fig. 3.1. The finite volume based CFD software FLUENT 6.1 is employed to solve the model equations by discretizing the reactor domain into 300,264 cells. The flow-field was calculated using a standard \( k-\varepsilon \) model since a previous work [3.7] has shown for a similar stirred tank geometry that predictions of good accuracy can be obtained.

In principle the semibatch process could be simulated directly by calculating the time dependent solution of the partial differential equations describing the flow-field and mixing model. However, since the feed addition time \( \tau_{\text{feed}} \) is very large in comparison with the circulation time \( \tau_c \), this approach would require a very large computational time. Therefore a different simulation procedure is chosen, by approximating the course of the reactive mixing process through a time series of quasi-steady-state processes, and thereby decoupling the calculation of spatial distributions and their time evolution. This simplification is possible for two reasons. The first one is that the flow-field does not change significantly with time for the process conditions analyzed in this chapter, since the volume of added feed is small in comparison with the initial reactor content. Secondly, the
feed addition time $\tau_{\text{feed}}$ is much larger than the time-scales of all other sub-processes. Thus, changes in time are just controlled by the feed addition, whereas the action of all mixing mechanisms and chemical reactions is reflected in the spatial distributions of reactants and mixture structure properties.

The quasi-steady-state reactant and mixture structure distributions at a specific time can be calculated based on some further assumptions for the spatial distributions. For the sake of simplicity the process modeling with the turbulent mixer model is limited to feed addition at the points $F_d$ marked in Fig. 3.1. In this case the base and acid reactants do not get into contact immediately after entering the reactor. First the acid is diluted in the bulk fluid, which is mixed homogeneously, before contacting the base reactant plume. Thus, the reactor can be divided into two interacting sub-systems of different characteristic dynamics, i.e. the bulk fluid and the reaction plume close to the base feed point. The bulk fluid behaves like a system with slow dynamics, whereas the sub-system constituted of the base feed plume has very fast dynamics. Concentration changes in the bulk are slow, since they are caused by feed addition of the acid and reactant transfer to the base reactant plume. Both mechanisms modify the conditions in the bulk with the time-scale of the feed addition, i.e. $\tau_{\text{feed}}$. Since mixing in the bulk is much faster than feed addition, reactants can be assumed to be homogeneously distributed. Hence, the bulk can be fully characterized by its average composition. Changes in the sub-system consisting of the base feed plume during time occur mainly due to concentration changes in the surrounding bulk fluid. Feed addition of the base has a negligible influence on changes in the base feed plume, since the addition rate is very small. Because mixing and chemical reactions in the base plume have comparably small time-scales, distributions within the plume adapt very fast to changes in bulk concentrations, i.e. at a time-scale that is negligibly small with respect to $\tau_{\text{feed}}$. Therefore the spatial distributions in the reacting plume are those attained at steady-state conditions, i.e assuming constant bulk composition, and the time dependence of the overall process is characterized just by accounting for the changes of average bulk concentrations.
Based on these assumptions and considerations the semibatch process can be modeled as follows. The first step is to calculate the flow-field in the reactor. Since changes in the flow-field during the process are neglected, this is only calculated once, in order to characterize the distributions of the average velocity, \( \bar{u}_j \), the average kinetic energy, \( k \), and the average rate of the energy dissipation, \( \varepsilon \). A quasi-steady-state solution of the flow-field is obtained by creating a virtual outlet in the CFD reactor model, with a flow rate equal to the sum of the two feed streams, i.e. very small compared to the flow circulation, and thereby approximating the real situation by a continuous process. In the next step, it is computed how the flow distributes an inert tracer injected through the feed pipe of reactant \( A \) (see Fig. 3.1). The distribution of \( \bar{f} \) is calculated by solving Eq. 3.11 with \( \bar{f}(A \text{ feed}) = 1 \) and \( \bar{f}(B \text{ feed}) = 0 \) as boundary conditions. The solution is renormalized by defining

\[
f^* = \frac{f - \bar{f}_b}{1 - \bar{f}_b}
\]

where \( \bar{f}_b \) is the average mixture fraction of the bulk. The renormalized mixture fraction \( f^* \) should be understood as the mass fraction of fresh feed that is diluted by the older bulk fluid in the reactor. This definition of the mixture fraction is different from the one of Eq. 3.10, where \( f \) represents the local mass fraction of the fluid introduced into the system through the considered feed pipe. For the semibatch process the definition of \( f^* \) has the advantage, that its distribution stays constant throughout the whole feeding process, since the flow-field does not change significantly with time for the process conditions analyzed in this chapter, where the volume of added feed is small in comparison with the initial reactor content. Based on the distribution of the renormalized average mixture fraction \( \bar{f}^* \) the variance components \( \sigma_1^2 \), \( \sigma_2^2 \) and \( \sigma_3^2 \) are calculated by solving eqs. 3.14 to 3.18 with \( \sigma_1^2(A \text{ feed}) = 0 \) and \( \sigma_i^2(bulk) = 0 \) as boundary conditions. With the distributions of variance components and average mixture fraction the mixture structure is fully characterized everywhere in the reactor.

To determine the reactant distributions in the vessel the feed addition process is discretized into \( n \) time increments of length \( \Delta t \). Based on several tests the
number of 10 increments has been identified to obtain results of good accuracy within a reasonable computational time. The average bulk concentration during a specific time interval \(i\) beginning at time \(t_i\) and ending at \(t_{i+1}\) is determined by the following balance:

\[
\overline{C}_{C,\text{bulk}}(t_i) = \frac{1}{V(t_i + 0.5\Delta t)} \left[ V(t_{i-1}) \overline{C}_{C,\text{bulk}}(t_{i-1}) - \int_{t_{i-1}}^{t_i} \int_{0}^{V(t)} \overline{r}_2 dV d\tau \right]
\]

where \(\overline{C}_{C,\text{bulk}}(t)\) is the bulk concentration of ester, \(V(t)\) is the reactor fluid volume at time \(t\) and \(\overline{r}_2\) is the hydrolysis reaction rate within the time interval \(i\). The concentration of reactant \(B\) in the bulk is updated using a mass balance equation for the bulk. By applying the bulk concentrations as boundary conditions, the concentration distributions within the region around the feed plume of reactant \(A\) can be calculated by solving eqs. 3.20 to 3.25, where the mixture fraction is replaced by \(f^*\). For the semibatch process the bulk concentrations \(c_{B0}\) and \(c_{C0}\) in Eq. 3.23 attain the values of the updated bulk concentration \(\overline{C}_{B,\text{bulk}}\) and \(\overline{C}_{C,\text{bulk}}\).

The complete semibatch process is modeled by simulating the time sequence of \(n\) steps, and by updating at each time step the boundary conditions, i.e. the values of \(\overline{C}_{B,\text{bulk}}\) and \(\overline{C}_{C,\text{bulk}}\). After characterizing the complete process the overall yields of both parallel reactions can be calculated from the final average reactant concentrations.

### 3.4.2. E-MODEL

In this section the application of the classical E-model [3.12] to the semibatch process, illustrated in Fig. 3.1, is presented. As compared to the reactive mixing model described in the previous section, the E-model presented here is less detailed. Although the model does not characterize for example the distribution of the reactants by the macro-flow in all details, it can account for the most important mechanisms controlling the chemical reactions.

Another difference in comparison with the Eulerian model presented in the previous section is that the E-model describes the process in a Lagrangian
framework, i.e. by following the fluid elements along their circulation path through the reactor [3.5]. In order to simulate the effect of macromixing in the model, the reactor is divided into six different regions. In each of these regions, the velocity and the energy dissipation are described by given mathematical functions [3.9]. It is worth noting that the fluid elements are transported through the regions of different energy dissipation due to the velocity field. Mesomixing is neglected in this application of the E-model because of its small influence under the conditions analyzed in this chapter, as is explained in further detail elsewhere [3.17]. Micromixing could be fully described by the engulfment-deformation-diffusion model (EDD), but as shown in the time-scale analysis in section 3.2.3 only mixing by engulfment is the controlling mechanism on the microscale and thus the classical E-model is used. The local dynamics of the engulfment, defined by the engulfment parameter $E$ in Eq. 3.7, are mainly controlled by the local energy dissipation rate $\varepsilon$. This in turn depends on the local position in the reactor and is defined by the already mentioned mathematical functions in the six regions. The average energy dissipation rate $\bar{\varepsilon}$ in the reactor can be obtained as:

$$\bar{\varepsilon} = \frac{N_p d_{imp}^5 N^3}{V} \quad (3.28)$$

where $N_p$ is the power number of the stirrer and $V$ the volume of the fluid in the reactor [3.9]. The micromixed zone grows due to the engulfment of the surrounding fluid. However, self-engulfment, which is the engulfment of a fluid of the same composition, has no effect on the volume of the micromixed zone. The degree of mixedness is quantified by the volume fraction of the micromixed zone $Y_j$. Therefore the following relationship is valid for $Y_j$ [3.18]:

$$\frac{dY_j}{dt} = EY_j(1-Y_j) \quad (3.29)$$

In the following the double feed process in Fig. 3.1 is considered, where the two reactants $A$ and $B$ are independently fed to the reactor. The reactant $A$ fed to the
reactor builds up an $A$-rich zone which starts to engulf the bulk. The reactant $B$ fed to the reactor builds up a similar $B$-rich zone. In order to be able to describe the process, the circulation path of the micromixed $j$-rich zone is divided into two regions $I$ and $II$ separated by a contact point $K$ [3.17]. Before the contact point is reached, only engulfment of the bulk takes place. The two feed plumes $A$ and $B$ cannot get into contact with each other, therefore the two feed plumes can be considered independently in region $I$. For the volume fraction of the $j$-rich reaction zone $Y_j^I$, ($j = A, B$), the same relationship as in Eq. 3.29 is valid in region $I$ for $t < t_K$:

\[
\frac{dY_j^I(t';t')}{dt} = E(t;t') \left[ 1 - Y_j^I(t;t') \right] Y_j^I(t;t')
\] (3.30)

where the time $t$ is the fluid age with respect to the beginning of the circulation, and $t_K$ the fluid age at the contact point with respect to the beginning of the circulation. The symbol $t'$ indicates the time of semibatch operation during which the reactants have already been fed to the reactor. The initial values for the volume fraction at the beginning of each circulation can be obtained from the feed addition rate, $Q_{\text{feed},j}$, and the circulation capacity $Q_c$:

\[
Y_j^I(t = 0) = \frac{Q_{\text{feed},j}}{Q_{\text{feed},j} + \frac{Q_c}{2}}
\] (3.31)

The circulation capacity $Q_c$ results from Eq. 3.4. It is worth noting that the initial values of $Y_j^I$ for reactants $A$ and $B$ are equal because the feed addition rates $Q_{\text{feed},A}$ and $Q_{\text{feed},B}$ are equal. The number of circulations $n_{\text{circulation}}$ is equal to the ratio between the feed addition time $\tau_{\text{feed}}$ and the circulation time $\tau_C$:

\[
n_{\text{circulation}} = \frac{\tau_{\text{feed}}}{\tau_C}
\] (3.32)

The circulation time $\tau_C$ depends on the velocity field in the reactor and is the time it takes for the micromixed zone to undergo a full circulation in the reactor.
as seen in Fig. 3.1. The value for $\tau_C$ in Eq. 3.32 is calculated based on the mathematical functions that characterize the velocity field. The concentrations of all reactants $A$, $B$ and $C$ in the $j$-rich zone change along the circulation trajectory. The change in concentration is calculated using the following equation, which can be derived from material balances for reactant $i$ in the $j$-rich zone [3.17]:

$$
\frac{dc_{ij}(t;t')}{dt} = E(t;t')\left[1 - Y_j^l(t;t')\right]\left(\bar{c}_i(t') - c_{ij}(t;t')\right) + r_{ij}
$$

(3.33)

where $i = A, B, C$, and $j = A, B$. The symbols $c_{ij}$ and $\bar{c}_i$ indicate the concentrations of reactant $i$ in the $j$-rich zone and in the bulk, respectively. The concentration of reactant $i$ in the $j$-rich zone changes due to chemical reactions with the rate $r_{ij}$:

$$
r_{ij} = \begin{cases} 
-k_1c_{Aj}c_{Bj} - k_2c_{Aj}c_{Cj} & \text{for } i = A \\
-k_1c_{Aj}c_{Bj} & \text{for } i = B \\
-k_2c_{Aj}c_{Cj} & \text{for } i = C
\end{cases}
$$

(3.34)

where $k_1$ and $k_2$ are the rate constants of the fast neutralization reaction and of the slow alkaline hydrolysis, respectively. Because the first reaction is very fast, the reactant concentrations of $A$ and $B$ can be expressed as in Eq. 3.22 by the concentration differences $c_{Uj}$ in the $j$-rich zone and $\bar{c}_U$ in the bulk. This leads to the following four differential equations for both $j$-rich zones ($j = A, B$):

$$
\frac{dc_{Uj}}{dt} = E \left(1 - Y_j^l\right)\left(\bar{c}_U - c_{Uj}\right) - k_2\frac{c_{Uj} + c_{Uj}}{2}c_{Cj}
$$

(3.35)

$$
\frac{dc_{Cj}}{dt} = E \left(1 - Y_j^l\right)\left(\bar{c}_C - c_{Cj}\right) - k_2\frac{c_{Uj} + c_{Uj}}{2}c_{Cj}
$$

(3.36)

The system of two parallel chemical reactions is now described by the eqs. 3.30, 3.35 and 3.36 for $j = A, B$. This system can be solved subject to the following
initial conditions for the concentrations: there is only reactant $A$ in the $A$-rich zone and only reactant $B$ in the $B$-rich zone at the beginning of every circulation; the bulk contains only reactant $C$ at the beginning of the semibatch operation:

$$
c_{UA} (t = 0; t') = c_{A0} \quad c_{UB} (t = 0; t') = -c_{B0} \quad \overline{c}_U (t' = 0) = 0
$$

$$
c_{CA} (t = 0; t') = 0 \quad c_{CB} (t = 0; t') = 0 \quad \overline{c}_C (t' = 0) = c_{C0}
$$

(3.37)

(3.38)

In the following the region $II$ after the contact point $K (t > t_K)$ is considered. Here the two feed plumes are in contact with each other and therefore it is not possible to consider them separately anymore. The volume fraction of the $j$-rich zone changes by engulfment of the bulk and the fluid originating from the other feed plume. However, for equal feed addition rates engulfment of fluid originating from the other feed plume is not influencing $Y_{j}^{II}$, since fluid originating from the $j$-rich zone is engulfed by the other plume with the same rate [3.17]:

$$
\frac{dY_{j}^{II} (t; t')}{dt} = EY_{j}^{II} (t; t') Y_{b} (t; t')
$$

(3.39)

On the other hand, the volume fraction of the bulk is decreasing because the bulk is engulfed by the $A$ and $B$-rich zones:

$$
\frac{dY_{b} (t; t')}{dt} = -EY_{b} (t; t') \left[ Y_{A}^{II} (t; t') + Y_{B}^{II} (t; t') \right]
$$

(3.40)

The values for the volume fractions $Y_j$ at the contact point $K$ are not the same in the two regions $I$ and $II$. In the first region, the $A$ and $B$-rich zones are considered separately whereas they are considered together in the second region. The new initial values for $Y_{j}^{II}$ and $Y_{b}$ in region $II$ are determined by

$$
Y_{j}^{II} (t = t_K; t') = \frac{Y_{j}^{I} (t = t_K; t')}{2}
$$

$$
Y_{b} (t = t_K; t') = 1 - Y_{A}^{II} (t = t_K; t') - Y_{B}^{II} (t = t_K; t')
$$

(3.41)
The concentrations $c_{Uj}$ and $c_{Cj}$ in the $j$-rich zone change according to differential equations obtainable from material balances analogous to those in region $I$, $(i = A, B; j = A, B)$:

$$\frac{dc_{Uj}}{dt} = E \left[ Y_b \left( \bar{c}_{U} - c_{Uj} \right) + Y_i^{II} \left( c_{Ui} - c_{Uj} \right) \right] - k_2 \frac{c_{Uj} + c_{Uj}}{2} c_{Cj}$$  \hspace{1cm} (3.42)

$$\frac{dc_{Cj}}{dt} = E \left[ Y_b \left( \bar{c}_{C} - c_{Cj} \right) + Y_i^{II} \left( c_{Ci} - c_{Cj} \right) \right] - k_2 \frac{c_{Uj} + c_{Uj}}{2} c_{Cj}$$  \hspace{1cm} (3.43)

The eqs. 3.39, 3.40, 3.42 and 3.43 fully characterize the concentrations and mixture structure in region $II$. After a circulation is completed, the volume fractions of the $j$-rich zone are reset to the initial values $Y_j^I(t = 0)$ and the next circulation is simulated until the end of the feed addition time is reached.

**3.5. EXPERIMENTAL SECTION**

**3.5.1. EXPERIMENTAL SETUP**

The reactor used for the experiments presented in this chapter is described in detail in chapter 2.1.1 and the experimental setup is explained in chapter 2.1.2. The reactor is operated in a double feed mode such that two solutions of NaOH and HCl are pumped separately into the reactor initially containing a CH$_2$CICOOC$_2$H$_5$ solution. The feed tubes with an inner diameter $d_{in} = 0.2$ cm can be placed at two feed positions, namely $F_s$ below the surface and $F_d$ in the discharge. The feed position $F_s$ is located at a height of 0.18 m above the bottom of the vessel and a radial distance of 0.017 m from the vessel axis. On the other hand, the feed position $F_d$ is located at a height of 0.067 m and a radial distance of 0.060 m from the vessel axis.

For analysis a Novapak C-18 reversed phase chromatography column (Waters, Rupperswil, Switzerland) was used. The HPLC column has a length of 15 cm, a column diameter of 3.9 mm and a particle diameter of 4 $\mu$m. The eluent in the HPLC analysis was a binary water acetonitrile mixture at a volumetric ratio of
60:40 and a flow rate of 0.37 ml/min. The composition of the solution was analyzed at a wavelength of 220 nm with a UV detector at the end of the column. The concentration in CH₂ClCOOC₂H₅ could be determined using a calibration curve.

3.5.2 MATERIALS

Sodium hydroxide pellets were purchased from Schweizerhall (Basel, Switzerland). Hydrochloric acid fuming 37 %, p.a. and acetonitrile, puriss, p.a., were purchased from Fluka (Buchs, Switzerland). Ethyl chloroacetate, 99 % was purchased from Aldrich (Steinheim, Germany).

3.5.3 EXPERIMENTAL PROCEDURE

The NaOH solution at a concentration \(c_{A0}\) was obtained by dissolving sodium hydroxide pellets in distilled water. The HCl solution at a concentration \(c_{B0}\) was obtained by diluting concentrated hydrochloric acid in distilled water. For each experiment, the reactor was filled with a volume \(V_0 = 6 \, \text{dm}^3\) of CH₂ClCOOC₂H₅ solution at an initial concentration \(c_{C0}\). The solution in the reactor was kept at a constant temperature of 20 °C with the help of the thermostat. A sample of the reactor content was taken to determine its exact concentration. The reaction was started by simultaneously feeding a fixed volume \(V_{A0}\) of NaOH solution and \(V_{B0}\) of HCl solution through the two feed tubes into the reactor. The volumes \(V_{A0} = V_{B0} = 60 \, \text{ml}\) were fed during a feed addition time \(t_{feed} = 17 \, \text{min}\) which corresponds to a feed rate of 3.5 ml/min for each pump.

At the end of the feed addition time, a second sample of the reactor content was taken. The concentrations \(c_{C0}\) before the reaction and \(c_C\) after the reaction were determined by analyzing both samples by HPLC. These concentrations were subsequently used to calculate the yield \(X_Q\) of the slower hydrolysis reaction using the following equation:

\[
X_Q = \frac{V_0 c_{C0} - (V_0 + V_{A0} + V_{B0}) c_C}{V_{A0} c_{A0}}
\]

(3.44)
3.6. DISCUSSION OF EXPERIMENTAL AND SIMULATION RESULTS

In the following the experimental results are discussed that were obtained using the procedure defined in section 3.5.3. The effect of changes in operating conditions, e.g. the feed position, stirring rate and reactant concentrations, on the reaction yield are presented and compared with simulation results. In section 3.6.1 the application of the E-model is presented, whereas the results obtained with the detailed CFD closure model are discussed in section 3.6.2.

3.6.1 EXPERIMENTAL RESULTS AND APPLICATION OF THE E-MODEL

The experimental results are presented in Fig. 3.3 to 3.6 in terms of yield of the alkaline hydrolysis as a function of different process parameters. Experiments illustrated in Fig. 3.3 were performed with feed addition at the point F_S as indicated in Fig. 3.1 and for the operating conditions summarized in the caption of the figure. Fig. 3.3 shows how the reaction yield changes with decreasing stirring rate, which is given in terms of the engulfment micromixing time $\tau_E$, as to Eq. 3.7. The experimental error in measuring the reaction yield is about 2%, i.e. rather small; therefore error-bars are omitted in the presentation of experimental data. The reproducibility of the experiments is in the same range as the experimental error as it can be seen in Fig. 3.3, in the cases where runs at the same conditions were repeated. Experimental data follow the trend of an increasing yield with increasing engulfment time-scale, e.g. decreasing stirring rate. For the analyzed situation, the time-scales of the chemical reactions are constant, since the concentrations remain unchanged. Since micromixing is masking the neutralization reaction, a decrease of the engulfment time relative to the characteristic reaction time enhances the fast reaction and the yield of the hydrolysis reaction decreases. A change in stirring rate also influences the macromixing time-scale $\tau_C$ given by Eq. 3.4. Macromixing conveys the fluid away from the point F_S into the zone of high energy dissipation rate close to the stirrer, thus conveying the fluid to a zone of intense micromixing. Therefore, a
decrease of the macromixing time $\tau_C$ has the same effect on the reaction yield $X_Q$ as the decrease of the engulfment time $\tau_E$. The yields calculated with the E-model are visualized as a solid line in Fig. 3.3. Simulation results follow the same trend as the experimental data. For the engulfment time $\tau_E$ of 2.6 s, e.g. a stirring rate of 75 rpm, the calculated yield of 0.34 matches perfectly the experimental results. With decreasing $\tau_E$ to 0.2 seconds, corresponding to a stirring rate of 400 rpm, the E-model reaction yield prediction decreases to 0.13 whereas the experimental value for this condition is 0.17. Thus, the E-model underpredicts the yield by more than 20%.

---

**Fig. 3.3.** Influence of the stirring rate, visualized as micromixing time-scale $\tau_E$, on $X_Q$; $c_{A0} = c_{B0} = 5000 \text{ mol/m}^3$, $c_{C0} = 50 \text{ mol/m}^3$, $t_{feed} = 17 \text{ min}$, feed point $F_S$, application of the E-model, $\tau_{R1} = 0.075 \times 10^{-9} \text{ s}$, $\tau_{R2} = 0.43 \text{ s}$. 
A prediction error of the same order can be observed for the feed addition at the point F_d marked in Fig. 3.1. Experimental and simulation results for this case are given in Fig. 3.4. Under these conditions deviations between experimental and model predictions are high at large values of the engulfment time $\tau_E$. For the maximum value of $\tau_E = 0.1$ s the experimentally determined yield $X_Q$ is 0.28 whereas the predicted value is 0.36. Experimental and simulation results for the reaction yield decrease with decreasing engulfment time to a minimum value $X_Q = 0.07$ at $\tau_E = 0.008$ s. The strong decrease of reaction yields from 0.28 to 0.07 with increasing stirring rate shows that the change in micromixing conditions is more dominating than the influence of changing macromixing. Fluid entering the reactor through the feed pipe at point F_d is transported by the macro-flow motion from a region of large energy dissipation close to the impeller into regions of smaller dissipation rate. In this way, macromixing changes the local environment for the micromixing and thereby an improvement in macromixing hinders the fast reaction, i.e. it causes an increase of the yield $X_Q$. Combining eqs. 3.7 and 3.28 yields the relationship $\tau_E \sim N^{-1.5}$, whereas
Eq. 3.4 gives \( \tau_C \sim N^{-1} \). Thus, the influence of a change in stirring rate is stronger for the micromixing by engulfment than for the macromixing. Another important fact is that the reaction zone is localized at the feed point and the chemical reaction in a fluid element of fresh base is finished quite fast after entering the reactor. These considerations explain the decrease of the yield with increasing stirring rate.

\[ \tau_E \] refers to the time-scale of the reaction process. Figure 3.5 illustrates the influence of the reactant concentrations, visualized as time-scale \( \tau_r \), on \( X_Q \); \( c_{A0} = c_{B0} = 100 \), \( c_{C0} \), \( t_{\text{feed}} = 17 \text{ min} \), \( \tau_E \) (100 rpm) = 1.69 s, \( \tau_E \) (200 rpm) = 0.59 s, feed point \( F_S \), application of the E-model.

A comparison of the reaction yields obtained for the different feed points \( F_S \) and \( F_d \) in the Fig. 3.3 and 3.4 shows, that yields are larger for feed addition at the point \( F_S \), when comparing results for the same stirring rate. One reason for that is the smaller local energy dissipation rate at the feed point \( F_S \). The difference in energy dissipation rates for the two feed points is reflected in the ranges of \( \tau_E \) in Fig. 3.3 and Fig. 3.4. In Fig. 3.3 \( \tau_E \) varies from 0.2 s to 2.6 s whereas in Fig. 3.4 \( \tau_E \) goes from 0.008 s to 0.1 s. Another important difference between feeding at the point \( F_d \) and at \( F_S \) is in the influence of the macro-flow. For feed addition at \( F_d \) and \( \tau_E = 0.1 \text{ s} \), the experimental reaction yield is \( X_Q = 0.28 \), whereas for
feeding at F$_{S}$ and $\tau_E = 0.2$ s, the experimental reaction yield is $X_Q = 0.17$. Based on the value for the engulfment time-scale the yield for feed addition at F$_S$ should be larger than for F$_d$. The opposite result is obtained because of the interaction between micro- and macromixing. By macromixing the fluid is transported in one case into regions of higher energy dissipation rate $\varepsilon$ and in the other case into regions of smaller dissipation. Thus, local micromixing conditions are either improved or worsened by action of macromixing.

In Fig. 3.5 the influence of mixing on the reaction yield $X_Q$ is shown by two series of experiments, each for constant mixing conditions but varying reactant concentrations. The change in reactant concentrations is shown in the figure in terms of the characteristic time of the hydrolysis reaction $\tau_{R2}$ defined by Eq. 3.3. The triangles in the figure indicate the experimental results for a stirring rate of 100 rpm, and the squares refer to the data for 200 rpm. The corresponding E-model simulation results are represented by the dashed line for 200 rpm, and by the solid line for 100 rpm. For the stirring rate of 100 rpm the experimental data drop from $X_Q = 0.31$ for $\tau_{R2} = 0.43$ s to the minimum $X_Q = 0.10$ at $\tau_{R2} = 4.3$ s. The simulation results match the experimental findings closely for high reactant concentrations, but underestimate the reaction yields with decreasing concentrations. The maximum prediction error is approximately 50%. For a stirring rate of 200 rpm the prediction has a slightly smaller error. Yields are smaller in comparison with the slow stirring rate, which can be explained by enhanced mixing. Experimental yield data range from $X_Q = 0.26$ for $\tau_{R2} = 0.43$ s, to $X_Q = 0.07$ at $\tau_{R2} = 4.3$ s. Simulations with the E-model underpredict the yield within the whole range of reaction time-scales. The trend of decreasing reaction yield $X_Q$ with increasing time-scale $\tau_{R2}$ can be explained by the shift of reaction time-scales relative to the mixing time-scales. The time-scale of the neutralization reaction $\tau_{R1}$ changes from 0.075 to 0.75 nanoseconds. Since $\tau_{R1}$ is much smaller than the engulfment time-scale $\tau_E$, the neutralization is always masked by micromixing. The yield mainly changes due to the time-scale change of $\tau_{R2}$. For a stirring rate of 200 rpm the micromixing time is $\tau_E = 0.59$ s. Since the minimum value of $\tau_{R2}$ is 0.43 s, mixing is almost always faster than the reaction. Therefore a decrease of the time-scale $\tau_{R2}$ increases the yield $X_Q$. For a stirring rate of 100 rpm the engulfment time is $\tau_E = 1.69$ s, so for high
concentrations even the hydrolysis reaction is masked to some extent by mixing, but the yield is still increased by a decrease of $\tau_{R2}$.

To summarize the comparison of experimental and E-model simulation results, it can be concluded that the E-model predicts all trends exhibited by the reaction yield correctly. For most operating conditions the prediction error is within a reasonable range. Only for small stirring rates and low reactant concentrations the relative error goes up to 50%. A positive feature of the E-model simulations is, that the required computational time for one specific operating condition is small, i.e. of the order of a few minutes. A drawback of the E-model simulations is that only limited information can be obtained about the details of mixture structure and reactant distributions. Thus, the interpretation of the local interplay between the different process mechanisms is rather difficult.

### 3.6.2 EXPERIMENTAL RESULTS AND APPLICATION OF THE MULTIPLE-TIME-SCALE TURBULENT MIXER MODEL

In Fig. 3.6 experimental reaction yield results are presented for the case of modified reactant concentrations and feed addition at the point $F_d$. Mixing conditions are kept constant for each of the data series. For a stirring rate of 100 rpm experimental values decrease from $X_Q = 0.26$ for $\tau_{R2} = 0.43$ s to $X_Q = 0.08$ for $\tau_{R2} = 4.3$ s. The simulation results, obtained with the CFD closure model described in section 3.4, match the experimental finding closely for high reactant concentrations, but tend to underestimate the reaction yield with decreasing concentrations. The maximum prediction error is around 50%. For a stirring rate of 200 rpm the prediction has a slightly smaller error. Yields are again smaller in comparison with the slow stirring rate. Experimental yield data range from $X_Q = 0.16$ for $\tau_{R2} = 0.43$ s to $X_Q = 0.04$ for $\tau_{R2} = 4.3$ s. The CFD closure modeling results for both data series predict experimental findings well, except for very low concentrations, where the E-model performs better. However, applying the multiple-time-scale turbulent mixer model enables to obtain good yield predictions at high feed concentrations and small stirring rates where the E-model fails, as shown in Fig. 3.4 and Fig. 3.6.
Fig. 3.6. Influence of the reactant concentrations, visualized as time-scale $\tau_{R2}$, on $X_Q; c_{A0} = c_{B0} = 100 c_{C0}, t_{feed} = 17 \text{ min}, \tau_E (100 \text{ rpm}) = 1.69 \text{ s}, \tau_E (200 \text{ rpm}) = 0.59 \text{ s},$ feed point $F_d$, application of the multiple-time-scale turbulent mixer model and the E-model.

Fig. 3.7. Distribution of the average mixture fraction at the NaOH feed inlet; $c_{A0} = c_{B0} = 100 c_{C0}, t_{feed} = 17 \text{ min},$ feed point $F_d$, application of the multiple-time-scale turbulent mixer model, stirring rate $N = 200 \text{ rpm}$. 
Fig. 3.8. Visualization of reaction zone: $c_{A0} = c_{B0} = 3000 \text{ mol/m}^3$, $c_{C0} = 30 \text{ mol/m}^3$, $N = 100 \text{ rpm}$, after a) 100 s, b) 500 s, c) 1000 s.
Fig. 3.9. Visualization of reaction zone: $c_{A0} = c_{B0} = 3000 \text{ mol/m}^3$, $c_{C0} = 30 \text{ mol/m}^3$, $N = 200 \text{ rpm}$, after a) 100 s, b) 500 s, c) 1000 s.
One major advantage of the CFD closure model over the E-model is that distributions of reactants and mixture structure properties are calculated in detail. In Fig. 3.7 the distribution of the average mixture fraction $\bar{f}$ close to the feed point of the base is visualized. It is shown that the mixture fraction has values smaller than one even inside the feed pipe close to its outlet. This is caused by backmixing of the fluid into the feed pipe. Backmixing can occur, because the flow rate of the feed is too small to avoid transport of fluid from the reactor into the feed pipe by turbulent diffusion, as can be explained through a time-scale analysis. Convection transporting the feed into the reactor can be characterized by

$$\tau_{\text{conv}} = \frac{d_{in}}{u_{\text{feed}}}$$

(3.45)

with the inner pipe diameter $d_{in}$ and the feed velocity $u_{\text{feed}}$ inside the pipe. For the feed addition rate of 3.5 ml/min and the inner diameter of 2 mm the convection time-scale is $\tau_{\text{conv}} = 0.108$ s. Turbulent diffusion outside the pipe can be characterized by the time-scale

$$\tau_{D} = \frac{d_{in}^2}{D_T}$$

(3.46)

where $D_T$ is the turbulent diffusivity, which is $7.31 \times 10^{-5}$ m$^2$ s$^{-1}$ close to the feed pipe, as estimated with the local turbulence properties listed in Tab. 3.1. Thus, the turbulent diffusion time-scale is 0.055 s, which is smaller than the convection time-scale. To avoid backmixing and thereby chemical reactions already within the pipe the convection time-scale should be decreased either by increasing the feed flow rate or decreasing the pipe diameter. In the application of the CFD based reactive mixing model backmixing effects can be accounted for by modeling the chemical reactions also within the feed pipe. This is not possible with the E-model.

In Fig. 3.8 the change of the reaction plume during the course of the semibatch process is visualized for a process at a stirring rate of 100 rpm. The grey shaded
volume represents the region where the base reactant is present. The time sequence presented by the three figures shows the reaction zone almost at the beginning, in the middle and at the end of the feed addition. Initially the reaction zone is large, but it shrinks during the feed addition. This can be explained by the increase of acid concentration in the bulk during the feed addition. Initially the bulk concentration of acid is zero, but it is increasing during the semibatch process. Since the time-scale of the neutralization reaction $\tau_{R1}$ has a very small value almost immediately after the start of the feed addition, the local availability of acid is exclusively controlling the consumption of the base reactant by the neutralization reaction. Thus, the increase of acid bulk concentration leads directly to a decrease of reaction plume size. The same effect can be seen in Fig. 3.9, where the evolution of the feed plume is shown for a higher stirring rate, but otherwise identical operating conditions as in Fig. 3.8. The feed plume size decreases during the feeding, but the change of the plume is less significant compared to the situation for a stirring rate of 100 rpm. Also the size of the plume is smaller for a high stirring rate. This is due to the fact that mixing time-scales are smaller for 200 rpm. As pointed out in section 3.6.1, the time-scale for viscous-convective mixing by engulfment $\tau_E$ is more sensitive to changes in stirring rate than the time-scale for the macromixing $\tau_C$. Therefore the improvement of reactant contacting on the small scale is dominating and the increase of the stirring rate decreases the size of the reactant plume.

3.7. CONCLUSIONS

A reactive mixing process involving two parallel chemical reactions with nonlinear reaction rates has been investigated experimentally and through simulations. By performing a time-scale analysis for the semibatch stirred tank process, it was shown to be essential for the modeling that mixing mechanisms in a wide range of time and length scales are accounted for. Two different reactive mixing models, both describing all relevant phenomena from the micro- to the macroscale, were applied to predict the yields of the parallel reaction for various process operating conditions. The classical E-model as well as the CFD
closure model were both found to predict experimental data with similar, rather satisfactory accuracy. This is contrary to other applications, where it was shown that the E-model failed to predict experimental reaction yield data while on the other hand the CFD closure model yielded accurate results [3.7]. This difference in prediction quality of the E-model can be explained by the impact of turbulent diffusion on the process. At high feed addition rates, effects of turbulent diffusion that are neglected in the E-model become influential and the CFD based model works better than the E-model. For a process with small feed addition rates, as analyzed in this chapter, the E-model and the CFD based model can give yield predictions of similar accuracy.

The simulations with the E-model have the obvious advantage of being computationally efficient, whereas the CFD closure model, based on the multiple-time-scale turbulent mixer model, has the drawback of a large computational time. Therefore in this case, the E-model can be a feasible tool to predict the trends of changes in reaction yield with varying operating conditions. On the other hand, the CFD closure model has the advantage of characterizing the process in greater detail. Especially the distribution of reactants by the action of the macro-flow is captured precisely, since the fluid in the reactor is characterized with a rather fine spatial discretization in all three dimensions. Thereby details of the mixing process, like the backmixing of the fluid into the feed pipes or the evolution of the reaction plumes during feeding, can be resolved accurately when using this model. Thus, simulations with the CFD closure model give detailed information, which is essential for the optimization of the reactor design and for the scale-up. Such results find a natural extension to mixing-precipitation processes where the chemical reaction triggers the formation of a new solid phase [3.8].
### 3.8 NOMENCLATURE CHAPTER 3

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Unit</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A, B, C$</td>
<td>[-]</td>
<td>reactant: NaOH, HCl, CH$_2$CICOOC$_2$H$_5$</td>
</tr>
<tr>
<td>$c_i$</td>
<td>[mol m$^{-3}$]</td>
<td>local concentration of $i$</td>
</tr>
<tr>
<td>$c_{A0}$</td>
<td>[mol m$^{-3}$]</td>
<td>initial or feed concentration of $A$</td>
</tr>
<tr>
<td>$c_{i,bulk}$</td>
<td>[mol m$^{-3}$]</td>
<td>bulk concentration of $i$, $i = B, C$</td>
</tr>
<tr>
<td>$c_{T0}$</td>
<td>[mol m$^{-3}$]</td>
<td>initial or feed concentration of a passive non-reacting tracer</td>
</tr>
<tr>
<td>$c_T$</td>
<td>[mol m$^{-3}$]</td>
<td>local concentration of a passive non-reacting tracer</td>
</tr>
<tr>
<td>$c_C^\infty$</td>
<td>[mol m$^{-3}$]</td>
<td>local concentration of reactant $C$ of instantaneous reaction</td>
</tr>
<tr>
<td>$\tau_C^\infty$</td>
<td>[mol m$^{-3}$]</td>
<td>average concentration of reactant $C$ for an instantaneous reaction</td>
</tr>
<tr>
<td>$c_{i0}$</td>
<td>[mol m$^{-3}$]</td>
<td>initial concentration of reactant $i$ in micromixed reaction zone</td>
</tr>
<tr>
<td>$c_{ij}$</td>
<td>[mol m$^{-3}$]</td>
<td>concentration of reactant $i$ in $j$-rich zone</td>
</tr>
<tr>
<td>$\tau_i$</td>
<td>[mol m$^{-3}$]</td>
<td>concentration of reactant $i$ in bulk; local average concentration of $i$</td>
</tr>
<tr>
<td>$c_i'$</td>
<td>[mol m$^{-3}$]</td>
<td>local concentration fluctuation of $i$</td>
</tr>
<tr>
<td>$c_0$</td>
<td>[mol m$^{-3}$]</td>
<td>initial concentration of reactants</td>
</tr>
<tr>
<td>$c_{Uj}$</td>
<td>[mol m$^{-3}$]</td>
<td>concentration difference in $j$-rich zone</td>
</tr>
<tr>
<td>$\tau_u$</td>
<td>[mol m$^{-3}$]</td>
<td>concentration difference in bulk</td>
</tr>
<tr>
<td>$\tau_{i,bulk}$</td>
<td>[mol m$^{-3}$]</td>
<td>concentration of $i$ in bulk</td>
</tr>
<tr>
<td>$D$</td>
<td>[m]</td>
<td>inner reactor diameter</td>
</tr>
<tr>
<td>$D_m$</td>
<td>[m$^2$ s$^{-1}$]</td>
<td>molecular diffusivity</td>
</tr>
<tr>
<td>$D_T$</td>
<td>[m$^2$ s$^{-1}$]</td>
<td>turbulent diffusivity</td>
</tr>
<tr>
<td>$d_{imp}$</td>
<td>[m]</td>
<td>impeller diameter</td>
</tr>
<tr>
<td>$d_{in}$</td>
<td>[m]</td>
<td>inner diameter of feed tube</td>
</tr>
<tr>
<td>$d_{sh}$</td>
<td>[m]</td>
<td>impeller shaft diameter</td>
</tr>
<tr>
<td>$E$</td>
<td>[s$^{-1}$]</td>
<td>local engulfment parameter</td>
</tr>
<tr>
<td>$f$</td>
<td>[-]</td>
<td>local dimensionless concentration of non-reacting tracer</td>
</tr>
<tr>
<td>$f^*$</td>
<td>[-]</td>
<td>local renormalized mixture fraction</td>
</tr>
<tr>
<td>Symbol</td>
<td>Units</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------</td>
<td>-------------</td>
</tr>
<tr>
<td>( \bar{f} )</td>
<td>[-]</td>
<td>average dimensionless concentration of non-reacting tracer</td>
</tr>
<tr>
<td>( \bar{f} )</td>
<td>[-]</td>
<td>renormalized average mixture fraction</td>
</tr>
<tr>
<td>( \bar{f}_b )</td>
<td>[-]</td>
<td>average bulk dimensionless concentration of non-reacting tracer</td>
</tr>
<tr>
<td>( H_{\text{liq}} )</td>
<td>[m]</td>
<td>height of water level above the bottom of the vessel</td>
</tr>
<tr>
<td>( H_{\text{imp}} )</td>
<td>[m]</td>
<td>height of impeller above the bottom of the vessel</td>
</tr>
<tr>
<td>( K )</td>
<td>[-]</td>
<td>contact point</td>
</tr>
<tr>
<td>( k )</td>
<td>([m^2 s^{-2}])</td>
<td>kinetic energy of turbulence</td>
</tr>
<tr>
<td>( k_1 )</td>
<td>([m^3 mol^{-1} s^{-1}])</td>
<td>rate constant of the neutralization reaction</td>
</tr>
<tr>
<td>( k_2 )</td>
<td>([m^3 mol^{-1} s^{-1}])</td>
<td>rate constant of the alkaline hydrolysis</td>
</tr>
<tr>
<td>( L )</td>
<td>[m]</td>
<td>size of the large energy containing eddies</td>
</tr>
<tr>
<td>( n_{\text{circulation}} )</td>
<td>[-]</td>
<td>number of circulations</td>
</tr>
<tr>
<td>( N )</td>
<td>([s^{-1}])</td>
<td>stirring rate</td>
</tr>
<tr>
<td>( N_P )</td>
<td>[-]</td>
<td>power number of stirrer</td>
</tr>
<tr>
<td>( Q_C )</td>
<td>([m^3 s^{-1}])</td>
<td>circulation capacity</td>
</tr>
<tr>
<td>( Q_{\text{feed}} )</td>
<td>([m^3 s^{-1}])</td>
<td>feed addition rate</td>
</tr>
<tr>
<td>( r_{ij} )</td>
<td>([mol l^{-1} s^{-1}])</td>
<td>rate of creation of substance ( i ) in ( j )-rich zone</td>
</tr>
<tr>
<td>( R_{Di} )</td>
<td>([s^{-1}])</td>
<td>dissipation rate of variance component ( i )</td>
</tr>
<tr>
<td>( R_{Pi} )</td>
<td>([s^{-1}])</td>
<td>production rate of variance component ( i )</td>
</tr>
<tr>
<td>( Sc )</td>
<td>[-]</td>
<td>Schmidt number</td>
</tr>
<tr>
<td>( t )</td>
<td>([s])</td>
<td>fluid age with respect to beginning of circulation</td>
</tr>
<tr>
<td>( t' )</td>
<td>([s])</td>
<td>time of semibatch operation</td>
</tr>
<tr>
<td>( t_K )</td>
<td>([s])</td>
<td>fluid age at the contact point ( K )</td>
</tr>
<tr>
<td>( \bar{u} )</td>
<td>([m s^{-1}])</td>
<td>local average velocity</td>
</tr>
<tr>
<td>( u_{\text{feed}} )</td>
<td>([m s^{-1}])</td>
<td>feed velocity</td>
</tr>
<tr>
<td>( u_i' )</td>
<td>([m s^{-1}])</td>
<td>local fluctuation of velocity component ( I )</td>
</tr>
<tr>
<td>( V_0 )</td>
<td>[m³]</td>
<td>initial liquid volume in reactor</td>
</tr>
<tr>
<td>( V )</td>
<td>[m³]</td>
<td>liquid volume in reactor at time ( t' )</td>
</tr>
<tr>
<td>( X_Q )</td>
<td>[-]</td>
<td>yield of product ( Q ) of the slower reaction</td>
</tr>
</tbody>
</table>
$Y^I_j$ [-] volume fraction of $j$-rich zone, in region $I$ before contact point

$Y^II_j$ [-] volume fraction of $j$-rich zone, in region $II$ after contact point

$Y_b$ [-] volume fraction of bulk, in region $II$ after contact point

**Greek letters**

$\varepsilon$ [m$^2$ s$^{-3}$] local energy dissipation rate

$\bar{\varepsilon}$ [m$^2$ s$^{-3}$] average energy dissipation rate in the tank

$\sigma^2_s, \sigma^2_i$ [-] dimensionless concentration variances

$\tau_C$ [s] circulation time

$\tau_D$ [s] time-scale of turbulent diffusion

$\tau_E$ [s] time-scale of micromixing by engulfment

$\tau_{feed}$ [s] feed addition time

$\tau_G$ [s] time-scale of micromixing by diffusion

$\tau_{Ri}$ [s] time-scale of reaction $i$

$\tau_S$ [s] time-scale of inertial-convective mixing

$\tau_{conv}$ [s] time-scale of convection

$\nu$ [m$^2$ s$^{-1}$] kinematic viscosity

### 3.9 REFERENCES CHAPTER 3


4. APPLYING A THERMODYNAMIC MODEL TO THE NON-STOICHIOMETRIC PRECIPITATION OF BARIUM SULFATE

Thermodynamic models for aqueous Ba\(^{2+}\)-SO\(_4^{2-}\)-Na\(^+\)-Cl\(^-\)-solutions are compared in their accuracy to predict ion activities in saturated and supersaturated solutions. The Pitzer and the Bromley model are employed, taking into account ion pair formation of barium sulfate. Such models are then used to describe particle nucleation and growth, and finally they are imbedded in a mechanistic mixing-precipitation model for a single feed semibatch process. The effect of the key operating parameters on the mean particle size is analyzed through simulations. The results are compared with experimental data, thus highlighting the significance of a proper choice of the thermodynamic model.
**4.1. INTRODUCTION**

Most sparingly soluble solid materials are produced through precipitation processes. The elementary steps in precipitation (chemical reaction, nucleation, crystal growth) are usually very fast, so that mixing can be the rate-determining step and affect significantly the final product quality, i.e. its crystal size distribution (CSD) and morphology. The identification and understanding of the interaction mechanisms among hydrodynamics, mixing and precipitation enable the formulation of adequate mixing-precipitation models.

Various mixing-precipitation models of different complexity have been proposed in the literature, whose validation calls for the use of well-defined experimental test systems. Several authors have used the precipitation of barium sulfate for this purpose. Some of the models have been proven to be suitable tools for predicting BaSO₄ precipitate properties [4.1], [4.2], [4.3]. However, model accuracy is satisfactory only under dilute conditions, and decreases with increasing local excess of one reactant during mixing. This is due to the fact that the description of the precipitation kinetics adopted is often either empirical or based on strongly simplified thermodynamic models.

The aim of the work presented in this chapter is to improve the accuracy of the model predictions by combining a precipitation model with a detailed description of the properties of the BaSO₄ electrolyte solution. These include the effect of various ions present in the solution and of the association of ions to form ion-pairs, and are determined using a thermodynamic model, whose accuracy is verified by comparison with solubility measurements. The new model is then used to calculate supersaturation and through this, nucleation and growth rates, which in turn are compared with the corresponding experimental results reported in the literature. The new correlations for precipitation kinetics are imbedded into a mixing-precipitation model describing a semibatch stirred tank reactor, where BaSO₄ precipitation occurs upon mixing of BaCl₂ and Na₂SO₄:

\[
\text{BaCl}_2(aq) + \text{Na}_2\text{SO}_4(aq) \rightarrow \text{BaSO}_4(s) + 2 \text{NaCl}(aq)
\]  

(4.1)
Simulation results obtained with the new model for the mean particle size of the particles formed under different operating conditions are compared with available experimental data. In particular the influence of different activity models on the overall model performance is analysed.

4.2. THERMODYNAMICS OF AQUEOUS BA$^{2+}$/SO$_4^{2-}$/NA$^+$/CL$^-$ SOLUTIONS

4.2.1 SOLUBILITY OF BARIUM SULFATE IN AQUEOUS ELECTROLYTE SOLUTIONS

There is a significant amount of literature about the thermodynamic characterization of electrolyte solutions containing barium sulfate, originated in different research fields. The solubility of BaSO$_4$ was studied to analyze scale formation in petroleum pipelines [4.4]. An ion-interaction model was developed to predict the scale formation on membranes used for seawater desalination [4.5]. A combined Pitzer ion-interaction and ion-association model was employed to describe the BaSO$_4$ saturation level in seawater [4.6], [4.7]. The thermodynamic models applied for these and other situations vary widely in their complexity. Comparison of the different applications highlights the fact that the appropriate model choice depends mainly on the ionic strength $I$ of the characterized solution, which is defined by

$$I = 0.5 \sum_i m_i z_i^2$$  \hspace{1cm} (4.2)

where $z_i$ and $m_i$ are the molal concentration and the number of charges of ion $i$, respectively.

The solubility of a salt such as barium sulfate can be calculated by enforcing the equilibrium condition through the relationship giving the solubility product $K_{sp}$, which for non-ideal electrolyte solutions is expressed in terms of the ion activities as follows:
\[ K_{SP} = a_{Ba^{2+}(aq)} a_{SO_4^{2-}(aq)} = m_{Ba^{2+}} m_{SO_4^{2-}} \gamma_{Ba^{2+}} \gamma_{SO_4^{2-}} = m_{Ba^{2+}} m_{SO_4^{2-}} \gamma_{\pm}^2 \] (4.3)

where \( \gamma_i \) is the activity coefficient of the ionic species \( i \), and \( \gamma_\pm \) is the mean ionic activity coefficient, which is the only one that can be measured. Most of the numerous electrolyte solution models developed to calculate the activity coefficient \( \gamma_i \) or \( \gamma_\pm \) have the general form:

\[
\log \gamma_\pm = A_{DH} a(I) + f(I, m_i) \] (4.4)

where \( A_{DH} \) is the Debye-Hückel constant. The first term \( a(I) \) accounts for long-range ion interactions due to Coulombic forces between unlike charged ions, whereas the second term \( f(I, m_i) \) for short-range ion interactions, which are of particular importance at high concentrations.

An equation accounting for Coulomb interactions between ions only is the Debye-Hückel limiting law

\[
\log \gamma_\pm = -A_{DH} \left| z_{Ba^{2+}} z_{SO_4^{2-}} \right| \sqrt{I} \] (4.5)

which was derived using concepts from classical electrostatics [4.8]. This equation is applicable to solutions of ionic strength up to 0.01 M only. For higher concentrations several semi-empirical corrections to the Debye-Hückel equation have been proposed. One of those was developed by Bromley for ionic strength values up to 6 M,

\[
\log \gamma_\pm = -A_{DH} \left| z_{Ba^{2+}} z_{SO_4^{2-}} \right| \sqrt{I} \frac{1}{1+\sqrt{I}} + \frac{1}{2} \left( F_{Ba^{2+}} + F_{SO_4^{2-}} \right) \] (4.6)

where the \( F_i \) terms account for interactions between unlike charged ions in solution [4.9]; ion-pair interactions between like charged ions and ion-triplets are not included in the Bromley equation. These contributions to short-range interionic forces are accounted for by the virial-type expansion of the Gibbs excess energy proposed by Pitzer [4.10]:
\begin{equation}
\log \gamma_i = \left[ \frac{\partial \left( \frac{g_{ex}}{RT} \right)}{\partial m_i} \right] \tag{4.7}
\end{equation}

\begin{equation}
\frac{g_{ex}}{RT} = f(I) + \sum_j \sum_k \lambda_{jk} (I) m_j m_k + \sum_j \sum_k \sum_l \mu_{jkl} m_j m_k m_l \tag{4.8}
\end{equation}

where \( f(I) \) accounts for long-range interactions and the other terms for ion specific short-range interactions between ions in solution. The \( \lambda_{jk}(I) \) terms describe ion-pair interactions, whereas the \( \mu_{jkl} \) coefficients are ion-triplet interaction constants. The parameters in the interaction functions \( \lambda_{jk}(I) \) and the constants \( \mu_{jkl} \) for each possible ion pair and ion triplet in solution have to be estimated from experimental data. Single ion activity coefficients \( \gamma_i \) for barium and sulfate ions as well as the corresponding \( \gamma_\pm \) can be determined from the Gibbs excess energy. The equation given above is applicable to solutions of concentration up to 6 M. When applied to higher concentrations fourth or even higher-order terms in the virial expansion may be required [4.10]. For practical use Pitzer rearranged Eq. 4.8 by combining several terms in order to reduce the number of pair and triplet interaction functions needed (see eq. 59, ch. 3 of [4.10]). Specific interaction functions, particularly suitable to represent properties of different electrolytes, are reported in the literature (see [4.11], and Eqs. 48 to 56, ch. 3 of [4.10]). These functions were parameterized for aqueous \( \text{Ba}^{2+}/\text{SO}_4^{2-}/\text{Na}^+/\text{Cl}^- \) solutions using experimental data obtained at a concentration as large as 6 M [4.6], [4.7].

In addition to the activity coefficient models above, it should also be considered that \( \text{BaSO}_4 \) does not behave like a strong electrolyte that dissociates completely in water, but rather forms un-dissociated ion-pairs (complexes) through the following reaction [4.6], [4.7]:

\begin{equation}
\text{Ba}^{2+} (\text{aq}) + \text{SO}_4^{2-} (\text{aq}) \rightleftharpoons \text{BaSO}_4(\text{aq}) \tag{4.9}
\end{equation}

The corresponding equilibrium is described by the following relationship:
where $K_{IP}$ is the equilibrium constant, $m_{BaSO_4(aq)}$ and $\gamma_{BaSO_4(aq)}$ the molality and the activity coefficient of BaSO$_4$ complexes, respectively. Assuming that the activity coefficient for the rather dilute complex is close to one and substituting Eq. 4.3 into Eq. 4.10 yields the concentration of complexes in a saturated solution, i.e. where solid BaSO$_4$ is present. The equilibrium constant $K_{IP}$ can be estimated experimentally, and the following two values at 25°C have been reported: log($K_{IP}$) = -2.72 [4.6], and log($K_{IP}$) = -2.26 [4.7].

Based on the considerations above, the equilibrium composition of BaSO$_4$ solutions can be calculated using two different approaches, namely by accounting either for the presence of ions only, i.e. through Eq. 4.1, or also for the formation of ion-pairs, i.e. including Eq. 4.9 as well. The comparison between the two approaches is illustrated in Fig. 4.1, where the saturation concentration of barium ions in water solutions containing also Na$_2$SO$_4$ is plotted as a function of the concentration of sulfate ions. Activity coefficients were calculated using the Bromley model, Eq. 4.6, and the Pitzer model, Eqs. 4.7 and 4.8, using log($K_{SP}$) = -10.05 for the solubility product [4.7]. It can be seen that accounting for complex formation, adopting as equilibrium constant in one case log($K_{IP}$) = -2.72 and log($K_{IP}$) = -2.26 in the other, improves the model accuracy in describing the corresponding experimental data, particularly at high concentration.

The fact that the rather simple Bromley activity coefficient model is suited to describe ion interactions well is due to the relatively low ionic strength of the aqueous Ba$^{2+}$/SO$_4^{2-}$/Na$^+$ solutions considered in Fig. 4.1. Under these conditions the Pitzer and the Bromley models virtually coincide. In BaSO$_4$ precipitation carried out by mixing aqueous BaCl$_2$ and Na$_2$SO$_4$ solutions for instance, the ionic strength can be two orders of magnitude higher than that achieved in the data reported in Fig. 4.1. Under such conditions the Pitzer model is expected to be more accurate than the Bromley model. Since thermodynamic equilibrium can be predicted better when explicitly taking ion-pair formation into account,
complex formation should also be considered in supersaturated solutions, as discussed next.

![Graph showing solubility of BaSO₄ in Na₂SO₄ water solution at 25°C, model predictions determined with Bromley & Pitzer model.]

**Fig. 4.1. Solubility of BaSO₄ in Na₂SO₄ water solution at 25°C, model predictions determined with Bromley & Pitzer model.**

### 4.2.2 SUPERSATURATION RATIO OF BARIUM SULFATE IN ELECTROLYTE SOLUTIONS

When analyzing the kinetics of precipitation, a proper definition of the driving force for the elementary processes involved is essential. The correlations characterizing particle formation kinetics are usually expressed in terms of a chemical potential difference between the supersaturated state and the equilibrium one. This driving force is commonly expressed in terms of the dimensionless supersaturation ratio, whose definition for BaSO₄ precipitation is:

$$S_A = \left( \frac{m_{\text{Ba}^{2+}} m_{\text{SO}_4^{2-}}}{K_{SP}} \right)^{0.5} \gamma_\pm$$  \hspace{1cm} (4.11)
When accounting for ion-pair formation along the lines of what discussed in the previous section, a lower concentration of free $\text{Ba}^{2+}$ and $\text{SO}_4^{2-}$ ions in solution and thereby a smaller supersaturation ratio than when ion-pairs are neglected are obtained under otherwise identical conditions. The quantitative impact of complex formation on supersaturation in an aqueous $\text{Ba}^{2+}/\text{SO}_4^{2-}/\text{Na}^+/\text{Cl}^-$ solution is illustrated in the precipitation diagram of Fig. 4.2. Iso-supersaturation contour lines, calculated with the Bromley model accounting in one case for complex formation and neglecting it in the other, are shown. The comparison of these two sets of curves demonstrates that close to stoichiometric conditions complex formation has a significant impact on the supersaturation ratio only at high concentrations. For non-stoichiometric conditions complex formation causes a major decrease in supersaturation, particularly with increasing solution concentration.

Fig. 4.2. Solubility and supersaturation diagram for $\text{BaCl}_2$ and $\text{Na}_2\text{SO}_4$ in water at 25°C.
Contrary to what presented for barium sulfate solubility calculations in the previous section, the choice of the activity coefficient model has a significant impact on the supersaturation ratio. The iso-supersaturation contour lines calculated with the Pitzer model taking complex formation into account are significantly different from those calculated using the corresponding Bromley model, especially for non-stoichiometric conditions and large supersaturation levels.

Since supersaturation predictions cannot be compared with experimental data, it is rather difficult to give an exact estimate of the relative accuracy of the two models. However, it can be expected that the Pitzer model estimates the activity coefficients better than the Bromley model. In fact, the Bromley model accounts for the interactions between unlike charged ions in solution only, and its parameters are estimated using single electrolyte data [4.9]. The Pitzer model has the advantage of accounting also for like charged ion interactions as well as for triplet interactions, and its parameters are obtained from mixed electrolyte experimental data for aqueous $\text{Ba}^{2+}/\text{SO}_4^{2-}/\text{Na}^+$ and $\text{Ba}^{2+}/\text{SO}_4^{2-}/\text{Na}^+\text{/Cl}^-$ solutions of concentrations up to 6 M.

4.3. KINETICS OF BARIUM SULFATE NUCLEATION AND GROWTH

Although the kinetics and mechanisms of barium sulfate nucleation and growth have been studied rather thoroughly by several researchers [4.12], [4.13], [4.14], [4.15], the reported experimental data and the proposed kinetic models are not always consistent. This is likely to be due to different experimental conditions and methods used for determining the kinetics. Experimental data and kinetic equations are almost exclusively reported for the case of precipitation under stoichiometric conditions. When using such equations to describe non-stoichiometric precipitation processes, experimental data are often predicted rather poorly [4.16]. This is due to the use of simplified thermodynamics models, which are not adequate to represent solution properties under non-stoichiometric conditions.
4.3.1 NUCLEATION

To obtain better predictions of the rates of nucleation and growth, new correlations based on the supersaturation ratio defined in the previous section have been developed. The following nucleation rate equation has been used:

\[ R_N = R_{\text{max}} \exp \left( \frac{-A}{\ln^2 S_A} \right) \]  \hspace{1cm} (4.12)

By fitting the experimental data by Nielsen [4.12] using Eqs. 4.11 and 4.12, the parameters of the nucleation rate correlation for heterogeneous and homogeneous nucleation have been estimated and reported in table 1. The Bromley model, Eq. 4.6, and the Pitzer model, Eqs. 4.7 and 4.8, were used to determine activity coefficients, and in both cases complex formation was considered.

A rather satisfactory agreement between experimental nucleation data and model results can be observed in Fig. 4.3, where the activity coefficients have been calculated using the Pitzer model. A similar comparison using the Bromley model is reported elsewhere [4.17]. It is worth noting that the transition between homogeneous (higher supersaturation, i.e. left hand side of the plot) and heterogeneous nucleation (lower supersaturation, right hand side of the plot) occurs at \( S_A \approx 280 \).
Tab 4.1. Parameter of the nucleation rate correlation Eq. 4.12 for heterogeneous and homogeneous nucleation.

<table>
<thead>
<tr>
<th></th>
<th>Bromley model w/ complex formation</th>
<th>Pitzer model w/ complex formation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{het}$ [-]</td>
<td>43.1</td>
<td>40.0</td>
</tr>
<tr>
<td>$R_{\text{max},het}$ [$m^{-3} s^{-1}$]</td>
<td>$5.36 \times 10^{11}$</td>
<td>$3.75 \times 10^{11}$</td>
</tr>
<tr>
<td>$A_{hom}$ [-]</td>
<td>3137.0</td>
<td>2254.0</td>
</tr>
<tr>
<td>$R_{\text{max},hom}$ [$m^{-3} s^{-1}$]</td>
<td>$1.24 \times 10^{49}$</td>
<td>$1.45 \times 10^{42}$</td>
</tr>
</tbody>
</table>

Fig. 4.3. Nucleation rate of BaSO$_4$ upon mixing of BaCl$_2$ and Na$_2$SO$_4$ under stoichiometric conditions. Model results, obtained by using Eqs. 4.3 and 4.7 to 4.12, i.e. Pitzer activity coefficients including complex formation.

4.3.2 GROWTH

Since growth of BaSO$_4$ particles can be either integration or diffusion limited, a two step model accounting for both effects has been chosen by different groups to describe experimental data [4.3], [4.13], [4.15]. The best description of the integration step has been proved to be the following parabolic rate law [4.13]: 
where the subscript \( \text{int} \) refers to interface solid/solution conditions. The model parameter \( k_r \) has been estimated by fitting growth rate experimental data in the literature [4.13]. At low supersaturation barium sulfate growth is purely integration limited [4.15], [4.13]; therefore the integration rate coefficient \( k_r \) can be estimated using data at low concentrations. The value \( k_r = 9.1 \times 10^{-12} \text{ m s}^{-1} \) was determined, which is four times smaller than previously published values [4.18]. For activity coefficients calculated with the Pitzer model a comparison between experimental growth rate data and model results is illustrated in Fig. 4.4, showing a rather satisfactory agreement. Since the integration rate coefficient is determined using experimental data for low concentrations where the Pitzer and the Bromley model behave similarly, an identical value for \( k_r \) is obtained with both activity models.

The diffusion limitation of barium sulfate particles can be accounted for using the following equation:

\[
G = k_D \left( m_{i,\text{bulk}} - m_{i,\text{int}} \right) \left( i = \text{Ba}^{2+}_{(aq)}, \text{SO}_4^{2-}_{(aq)}, \text{BaSO}_4^0_{(aq)} \right)
\]  

(4.14)

The mass transfer coefficient has been assumed to be the same for barium ions, sulfate ions and barium sulfate ion-pairs, namely \( k_D = 4.0 \times 10^{-5} \text{ (m s}^{-1})(\text{kg mol}^{-1}) \) [4.3]. Although there is no direct integration of barium sulfate ion-pairs at the crystal surface, accounting for their mass transfer towards the particle surface has an impact on the growth rate. In fact within the mass transfer layer ion-pairs are converted into ions and vice versa, due to the concentration gradients with respect to the bulk of the liquid phase. Such phenomenon and its effect on the growth rate can be accounted for by enforcing equilibrium conditions for Eq. 4.9 at every point within the mass transfer layer.
A comparison between experimental data by Nielsen [4.13] and results obtained with the two-step growth model given by Eqs. 4.13 and 4.14 is illustrated in Fig. 4.5. Iso-growth rate lines within the range from 0.64 nm/sec to 640 nm/sec are plotted. Nielsen determined particle growth rates based on changes of the average size $d_{43}$ of the particles; Eqs. 4.13 and 4.14 refer to the change of a certain characteristic particle dimension. Therefore, for comparison, information about the particle shape are required. Particle shapes of barium sulfate crystals precipitated under different conditions were determined in [4.20], where their dependence on supersaturation was analyzed only for some of the conditions considered in Fig. 4.5. Shapes were assumed to be constant along the iso-growth lines drawn in Fig. 4.5. Although this introduces some error in the calculation of growth rates, it can be readily observed that the growth model of Eqs. 4.13 and 4.14 estimates growth rates rather satisfactorily.

![Experimental data vs model results](image)

Fig. 4.4. Growth rate of BaSO$_4$ upon mixing of BaCl$_2$ and Na$_2$SO$_4$ under stoichiometric conditions. Model results, obtained by using Eqs 4.3, 4.7 to 4.11 and 4.13, i.e. Pitzer activity coefficients including complex formation.
Fig. 4.5. Growth rate of BaSO₄ upon mixing of BaCl₂ and Na₂SO₄. Model results, obtained by using Eqs 4.3, 4.7 to 4.11 and 4.13 to 4.14, i.e. Pitzer activity coefficients including complex formation; experimental data from [4.13].

4.4. MIXING-PRECIPITATION MODEL OF BARIUM SULFATE FORMATION

Barium sulfate has been frequently used as a test system to validate mixing-precipitation models, namely mechanistic mixing models [4.3], [4.16], [4.20], as well as closure models [4.1].

Since the aim of the work presented in this chapter is to evaluate the role of thermodynamics and kinetics models on precipitation, a rather simple mixing-precipitation application has been selected, namely the semibatch single feed process schematized in Fig. 4.6, which is described using a mechanistic model. In this process a concentrated aqueous Na₂SO₄ solution is fed into a stirred tank,
where initially a diluted aqueous BaCl₂ solution is present. Upon mixing barium sulfate is precipitated. The concentrations of Na₂SO₄ and BaCl₂ are so small that particle formation is controlled by nucleation and growth exclusively, whereas secondary phenomena such as agglomeration play no role. The reactor studied in this chapter is a flat-bottom cylindrical vessel, equipped with four baffles and a Rushton type flat blade turbine (see Fig. 4.6 for dimensions and other details).

![Fig 4.6. Process schematic: precipitation of BaSO₄ upon mixing of BaCl₂ and Na₂SO₄.](image)

### 4.4.1 THE MIXING-PRECIPITATION MODEL

The mixing-precipitation model presented in this chapter accounts for all mixing phenomena described in the following, which influence the chemical reaction, the nucleation and the growth of the particles [4.2].

With reference to the process in Fig. 4.6, first macromixing, i.e. the mixing at the scale of the vessel, is considered. Under the action of macromixing, fluid elements are conveyed through local environments of varying turbulence
characteristics and chemical composition. Next, the inertial-convective mixing, i.e. mesomixing, describes mixing of segregated reactants on a scale larger than the Kolmogorov microscale, but smaller than the integral scale of turbulence. Since mesomixing was found to be of small importance under the conditions analyzed in this chapter, a description of mesomixing models is omitted here, and more details can be found elsewhere [4.3]. For the sake of simplicity the mixing model equations given in the following sections are written without the mesomixing terms. Finally, under the conditions examined here micromixing is controlled by viscous-convective engulfment. The micromixing intensity is characterized by the engulfment parameter $E$, which is defined in terms of the local energy dissipation rate $\varepsilon$ and viscosity $\nu$ as [4.2]:

$$E = 0.058 \left( \frac{\varepsilon}{\nu} \right)^{1/2}$$

(4.15)

Macromixing is simulated using the loop plug flow model schematized in Fig. 4.7, which has been proven to provide a satisfactory approximation of the main circulation flow in a stirred tank equipped with a Rushton turbine [4.3], [4.2]. The circulation capacity $Q_{circulation}$ can be approximated using the pumping capacity of the Rushton turbine as presented in [4.20]. The course of the mixing of the feed stream with the bulk fluid is described in a Lagrangian framework, i.e. by following the fluid elements circulating. The circulation can be characterized by the mean circulation time

$$t_{circ} = \frac{V_{tank}}{Q_{Circulation}}$$

(4.16)

which is assumed to be constant for the process under observation, since the total fluid volume in the tank, $V_{tank}$, is large when compared to the volume of the feed added during precipitation, $V_{feed}$. Since additionally the feeding time $t_{feed}$ is much longer than the circulation time $t_{circ}$ the influence of the feed stream on the flow pattern can be neglected.
Spatial inhomogeneity of the system is accounted for by updating the local mixing intensity by plugging into Eq. 4.15 the energy dissipation rate $\varepsilon$ corresponding to the fluid age $t$ along the Lagrangian trajectory. The distribution of the energy dissipation, $\varepsilon$, in the reactor is discretized in space, by dividing the reactor loop into two regions having significantly different energy dissipation levels, i.e. the impeller and the bulk region [4.19]. The total energy dissipation can be quantified by the mean dissipation rate $\bar{\varepsilon}$ given by

$$\bar{\varepsilon} = \frac{4N_p N_{stirrer}^3 d_{imp}^5}{V_{tank}}$$  \hspace{1cm} (4.17)

in terms of the power number $N_p$, of the Rushton turbine, of the tank geometry and of the stirring rate, $N_{stirrer}$. Details about calculating how the dissipation is distributed between the zones are provided elsewhere [4.2], [4.3].
The degree of fluid mixedness in the loop is quantified by the volumetric fraction \( X(t) \) of mixture, that contains fluid of the injected feed stream, in this case the \( \text{Na}_2\text{SO}_4 \) solution. The initial value \( X(0) \) is defined as the ratio of the feed flow rate \( Q_{\text{feed}} \) to the flow rate of the circulating stream:

\[
X(0) = \frac{Q_{\text{feed}}}{Q_{\text{Circulation}} + Q_{\text{feed}}} \tag{4.18}
\]

Upon mixing along the Lagrangian trajectory, the mixture fraction \( X(t) \) increases according to the following equation

\[
\frac{dX(t)}{dt} = E X(t) \left[1 - X(t)\right] \tag{4.19}
\]

until \( X(t) \) approaches one [4.2]. After completing a circulation at \( t_{\text{circ}} \), the feed point, indicated at the top of the loop in Fig. 4.7, is reached again; then the mixture fraction is reset to the initial value \( X(0) \), and the simulation of a new circulation loop is carried out.

Within the fluid fraction \( X(t) \), \( \text{Na}_2\text{SO}_4 \) originating from the feed and \( \text{BaCl}_2 \) from the bulk coexist and barium sulfate particles can be formed via precipitation. In the following, the fluid fraction \( X(t) \), where reactants are well mixed on the microscale, is called mixing-precipitation zone and indicated as MP. Upon mixing of the fluid in the MP-zone with the bulk fluid, concentrations of all species in the MP-zone change according to the following equations [4.2]:

\[
\frac{dc_{i,\text{MP}}}{dt} = E \left[1 - X(t)\right] \left[\langle c_i \rangle - c_{i,\text{MP}}\right] + V_i \frac{\rho_{\text{BaSO}_4}}{M_{\text{BaSO}_4}} \frac{G_{\text{MP}}}{2} A_{g,\text{MP}}
\]

\[
\left(i = \text{Ba}^{2+}_{(aq)}, \text{SO}_4^{2-}_{(aq)}, \text{Na}^+_{(aq)}, \text{Cl}^-_{(aq)}, \text{BaSO}_4^0_{(aq)}\right) \tag{4.20}
\]

where \( c_{i,\text{MP}} \) and \( \langle c_i \rangle \) are the concentrations of species \( i \) in the MP-zone and in the bulk, respectively, \( G_{\text{MP}} \) is the particle growth rate in the MP-zone, and \( A_{g,\text{MP}} \) is the specific surface area of all particles in the MP-zone:
\[ A_{g,MP} = \int_{0}^{\infty} k_a n_{MP}(L)L^2 dL \] (4.21)

where \( n_{MP} \) is the population density function of particles in the MP-zone and \( k_a \) the particles surface shape factor. The stoichiometric coefficients \( \nu_i \) in Eq. 4.20 refer to \( \text{BaSO}_4 \) precipitation, hence they are \(-1\) for \( \text{Ba}^{2+} \) and \( \text{SO}_4^{2-} \), and \(0\) for \( \text{Na}^+ \), \( \text{Cl}^- \), and \( \text{BaSO}_4 \) complexes. The initial conditions in the MP-zone, defining the conditions at the beginning of a new circulation starting from the feed point, are characterized by the feed concentration of \( \text{Na}_2\text{SO}_4 \) with no species other than \( \text{Na}^+ \) or \( \text{SO}_4^{2-} \) ions being present.

Assuming that the volume of newly formed nuclei is zero, the population balance equation for the density function in the MP-zone \( n_{MP} \) can be cast as:

\[ \frac{\partial n_{MP}}{\partial t} + G_{MP} \frac{\partial n_{MP}}{\partial L} = E \left[ 1 - X(t) \right] \left[ \langle n \rangle - n_{MP} \right] \] (4.22)

where \( \langle n \rangle \) represents the population density function for particles in the bulk, and \( R_{N,MP} \) the nucleation rate in the MP-zone. This equation is solved together with the following initial and boundary conditions:

\[ n_{MP}(L,t = 0) = 0 \] (4.23)
\[ n_{MP}(L = 0,t) = \frac{R_{N,MP}}{G_{MP}} \] (4.24)

When integrating Eqs. 4.19 to 4.22 along the Lagrangian trajectory using the precipitation kinetics functions Eqs. 4.12 to 4.14 and a thermodynamic model to calculate the supersaturation ratio \( S_A \), the course of mixing can be fully described for one circulation. For the next circulation the values of bulk concentrations \( \langle c_i \rangle \) and population density function \( \langle n \rangle \) must be updated to the conditions in the MP-zone.

For the integration of Eq. 4.22 the method of moments has been used representing the population density function by six moments. The detailed equations describing the evolution of moments during mixing are given...
elsewhere (see Eq. 26 of [4.16]). Changes in the bulk population density function $\langle n \rangle$ and bulk concentrations $\langle c_i \rangle$ along the Lagrangian trajectory are accounted for by integrating proper equations; in particular the following material balances apply to $\langle c_i \rangle$:

$$\frac{d\langle c_i \rangle}{dt} = +\nu_i \frac{\rho_{\text{BaSO}_4}}{M_{\text{BaSO}_4}} \frac{G_{\text{bulk}}}{2} A_{g,\text{bulk}}$$

$$\left(i = \text{Ba}^{2+}_{(aq)}, \text{SO}_4^{2-}_{(aq)}, \text{Na}^+_{(aq)}, \text{Cl}^-_{(aq)}, \text{BaSO}_4^0_{(aq)}\right)$$

(4.25)

where $G_{\text{bulk}}$ is the particle growth rate in the bulk, and $A_{g,\text{bulk}}$ is the specific surface area of all particles in the bulk. The initial conditions for the first circulation correspond to the initial $\text{BaCl}_2$ concentrations in the vessel with only $\text{Ba}^{2+}$ and $\text{Cl}^-$ ions being present. After the first circulation, at the beginning of a new circulation the initial bulk concentrations are equal to the MP-zone concentrations at the end of the previous circulation. The population balance equation describing changes of the density function in the bulk $\langle n \rangle$ is

$$\frac{\partial \langle n \rangle}{\partial t} + G_{\text{bulk}} \frac{\partial \langle n \rangle}{\partial L} = 0$$

(4.26)

This equation is solved together with the following initial and boundary conditions:

$$\langle n \rangle(L, t = 0) = 0 \quad \text{for first circulation}$$

(4.27)

$$\langle n \rangle(L, t = 0) = n_{\text{MP, prev. circ.}}(t = t_{\text{circ}}) \quad \text{after first circulation}$$

(4.28)

$$n_{\text{MP}}(L = 0, t) = \frac{R_{N,\text{bulk}}}{G_{\text{bulk}}}$$

(4.29)
4.4.2 RESULTS AND DISCUSSION

The mixing-precipitation model above has been applied to describe BaSO$_4$ precipitation in the reactor shown in Fig. 4.6. Model results obtained by changing the key operating conditions of the process are compared in the following with experimental data reported previously [4.20]. In both experiments and simulations, at the end of each operation the reactor contains the same volume, i.e.:

$$V_{BaCl_2,0} + V_{feed} = const.$$  \hspace{1cm} (4.30)

with $V_{BaCl_2,0}$ being the initial volume of the BaCl$_2$ solution in the reactor. The two volume values in the last equation are selected by choosing a value of the volume ratio $\alpha$ that is defined as:

$$\alpha = \frac{V_{BaCl_2,0}}{V_{feed}}$$  \hspace{1cm} (4.31)

Under all conditions analyzed in this chapter the amounts of BaCl$_2$ and Na$_2$SO$_4$ fed into the reactor are identical, i.e. the following relationship applies:

$$c_{BaCl_2,0}V_{BaCl_2,0} = c_{Na_2SO_4,feed}V_{feed}$$  \hspace{1cm} (4.32)

It follows that only one concentration can be chosen independently whereas the other is calculated from the last equation. When changing the volume ratio $\alpha$ while keeping the total amount of BaCl$_2$ and Na$_2$SO$_4$ in the reactor constant, the actual initial concentrations of BaCl$_2$ and Na$_2$SO$_4$ change. Therefore it is convenient to express the concentration level in the tank in terms of mean initial concentration, which stays constant when $\alpha$ changes:

$$\bar{c}_{BaCl_2,0} = c_{BaCl_2,0} \frac{V_{BaCl_2,0}}{V_{BaCl_2,0} + V_{feed}}$$  \hspace{1cm} (4.33)
In all cases the Na$_2$SO$_4$ is fed at a flow rate $Q_{\text{feed}} = 9.85$ ml/min, which is slow enough to avoid a significant effect of mesomixing. The reference operating conditions of the reactor for the three operating parameters that have been analyzed in the following are $\overline{c}_{\text{BaCl}_2,0} = 0.0045$ mol/l, $N_{\text{Stirrer}} = 5$ s$^{-1}$ and $\alpha = 50$. Information about particle shapes, which is required in the simulation, is taken from [4.20] with $k_a = 6$, $k_v = 8.17$. In all simulations the Bromley and the Pitzer model, both including complex formation, will be used; in the figures the results obtained with the former will be plotted using dashed lines, and those obtained with the latter using solid lines.

In Fig. 4.8 mean particle sizes $d_{43}$ for different stirring rates are illustrated. Feed is added close to the impeller, indicated as position 2 in Fig. 4.6. Experimentally determined mean particle sizes, represented in the figure by boxes, have similar values for all stirring rates. Deviations from the average value 4.1 µm do not show any clear dependence on the stirring rate, but are most likely due to experimental inaccuracy of particle size measurement. Particle sizes calculated with both thermodynamic models are able to predict the influence of stirring rate with satisfactory accuracy, but with the Pitzer model giving slightly better approximations. The difference between Pitzer and Bromley model particle size predictions is about 5 percent.
Fig. 4.8. Effect of stirring rate on mean size $d_{43}$ of BaSO$_4$ particles: comparison between experimental and mixing-precipitation model results, $\overline{c}_{BaCl_2,0} = 0.0045$ mol/l, $\alpha = 50$.

Fig. 4.9. Effect of volume ratios $\alpha$ on mean size $d_{43}$ of BaSO$_4$ particles: comparison between experimental and mixing-precipitation model results, $\overline{c}_{BaCl_2,0} = 0.0045$ mol/l, $N_{\text{Stirrer}} = 5$ s$^{-1}$.
In Fig. 4.9 changes of mean particle size $d_{43}$ with varying volume ratio $\alpha$ as defined by Eq. 4.31 are presented. Feed is added close to the surface, indicated as position 1 in Fig. 4.6. Experimental data show the trend of decreasing particle size with increasing values of $\alpha$, starting at the size of 4.1 $\mu$m for $\alpha = 20$ and decreasing to 2.5 $\mu$m for $\alpha = 200$. At low volume ratios the mean particle size can be predicted with good accuracy using either the Bromley or Pitzer model, but for increasing values of $\alpha$ both models fail to predict experimental data. The difference between predictions employing either the Pitzer or Bromley model is comparable to Fig. 4.8.

In Fig. 4.10 the dependence of mean particle size $d_{43}$ on the reactant concentration level is shown. Data presented in this figure have been obtained for feeding close to the liquid surface, as indicated in Fig. 4.6 by position 1. Experimental results show the clear trend of decreasing particle size with increasing concentration $\bar{c}_{\text{BaCl}_2,0}$, starting at the size of 4.1 $\mu$m for $\bar{c}_{\text{BaCl}_2,0} = 0.002$ mol/l and decreasing to 1.0 $\mu$m for $\bar{c}_{\text{BaCl}_2,0} = 0.02$ mol/l. At low concentration levels the Bromley model and the Pitzer model give similar predictions. At a concentration of $\bar{c}_{\text{BaCl}_2,0} = 0.01$ mol/l predictions calculated with the Bromley and Pitzer model start to deviate more and more with further increase of concentration. This difference in model performance can be explained with help of Fig. 4.2, where lines of constant supersaturation are shown. At low supersaturation, corresponding to low concentration levels in Fig. 4.10, Fig. 4.2 shows similar predictions with Bromley and Pitzer model. But with increasing supersaturation the deviation between predictions of different thermodynamic models increases in Fig. 4.2. This explains why also in Fig. 4.10 the estimates of Pitzer and Bromley model are significantly different at higher concentrations. The good agreement of Pitzer model predictions and experimental data at high concentrations proves, that the Pitzer model is suitable to characterize highly concentrated solutions.
4.5. CONCLUSIONS

A detailed thermodynamic model for the aqueous $\text{Ba}^{2+}/\text{SO}_4^{2-}/\text{Na}^+/\text{Cl}^-$ system has been developed and presented. Based on this improved characterization of the solution composition, the nucleation and growth rate equations for barium sulfate precipitation have been reconsidered. New kinetic relationships for nucleation and growth have been derived by fitting experimental data in the literature. A comparison of experimental growth rate data and model results within a wide concentration range for stoichiometric and non-stoichiometric conditions has shown, that the new growth model gives predictions of satisfactory accuracy.

The new kinetics relationships have been applied in a mixing-precipitation model for a single feed semibatch process. Particularly when combined with the Pitzer activity model accurate estimates of mean particle size could be produced. However, for strongly non-stoichiometric conditions a lack of predictability remains (Fig. 4.9 and 4.10 at small concentration range), which results probably
from under-prediction of the rate of homogeneous nucleation and calls for further improvement of nucleation kinetics.

The large difference in mean particle size prediction between the thermodynamic models at high concentration highlights the significance of choosing a proper thermodynamic model under such conditions.

### 4.6 NOMENCLATURE CHAPTER 4

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Units</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>[mol kg$^{-1}$]</td>
<td>activity</td>
</tr>
<tr>
<td>$A_{DH}$</td>
<td>[kg$^{0.5}$ mol$^{0.5}$]</td>
<td>Debye-Hückel constant</td>
</tr>
<tr>
<td>$A_{G,j}$</td>
<td>[m$^2$ m$^{-3}$]</td>
<td>specific surface area of particles per unit volume in $j$</td>
</tr>
<tr>
<td>$c$</td>
<td>[mol l$^{-1}$]</td>
<td>molar concentration</td>
</tr>
<tr>
<td>$c_{i,0}$</td>
<td>[mol l$^{-1}$]</td>
<td>molar mean initial concentration of $i$</td>
</tr>
<tr>
<td>$d_{imp}$</td>
<td>[m]</td>
<td>impeller diameter</td>
</tr>
<tr>
<td>$E$</td>
<td>[s$^{-1}$]</td>
<td>Engulfment parameter</td>
</tr>
<tr>
<td>$f$</td>
<td>[-]</td>
<td>long range interaction function Eq. 4.8</td>
</tr>
<tr>
<td>$F_i$</td>
<td>[-]</td>
<td>ion interaction function in Eq. 4.6</td>
</tr>
<tr>
<td>$G$</td>
<td>[m s$^{-1}$]</td>
<td>growth rate</td>
</tr>
<tr>
<td>$g_{ex}$</td>
<td>[kJ]</td>
<td>Gibbs excess energy</td>
</tr>
<tr>
<td>$I$</td>
<td>[mol kg$^{-1}$]</td>
<td>ionic strength</td>
</tr>
<tr>
<td>$k_a$</td>
<td>[-]</td>
<td>surface shape factor of particles</td>
</tr>
<tr>
<td>$k_D$</td>
<td>[m s$^{-1}$ kg mol$^{-1}$]</td>
<td>mass transfer coefficient</td>
</tr>
<tr>
<td>$k_R$</td>
<td>[m s$^{-1}$]</td>
<td>integration rate coefficient</td>
</tr>
<tr>
<td>$K_{IP}$</td>
<td>[-]</td>
<td>ion-pair equilibrium constant</td>
</tr>
<tr>
<td>$K_{SP}$</td>
<td>[mol$^2$ m$^{-6}$]</td>
<td>thermodynamic solubility product</td>
</tr>
<tr>
<td>$L$</td>
<td>[m]</td>
<td>characteristic particle dimension</td>
</tr>
<tr>
<td>$m_i$</td>
<td>[mol kg$^{-1}$]</td>
<td>molal concentration of $i$</td>
</tr>
<tr>
<td>$M$</td>
<td>[kg kmol$^{-1}$]</td>
<td>molar mass</td>
</tr>
</tbody>
</table>
\( n \) \([\text{m}^{-3}]\) population density function
\( N_{\text{Stirrer}} \) \([\text{s}^{-1}]\) stirring rate
\( N_P \) [-] power number of stirrer
\( Q \) \([\text{m}^3 \text{s}^{-1}]\) flowrate
\( R \) \([\text{kJ K}^{-1} \text{mol}^{-1}]\) universal gas constant
\( R_{\text{max}} \) \([\text{l}^{-1} \text{s}^{-1}]\) constant in Eq. 4.12
\( R_N \) \([\text{l}^{-1} \text{s}^{-1}]\) nucleation rate
\( S_A \) [-] supersaturation ratio
\( t_{\text{circ}} \) \([\text{s}]\) circulation time
\( t \) \([\text{s}]\) fluid age with respect to beginning of circulation
\( T \) \([\text{K}]\) absolute temperature
\( V_i \) \([\text{m}^3]\) volume of \( i \)
\( X \) [-] volume fraction of micro mixed fluid
\( z_i \) [-] number of charges of \( i \)

**greek letters**

\( \alpha \) [-] volume ratio of mixed fluids
\( \varepsilon \) \([\text{m}^2 \text{s}^{-3}]\) local energy dissipation rate
\( \tau \) \([\text{m}^2 \text{s}^{-3}]\) average rate of energy dissipation in the tank
\( \gamma_i \) [-] activity coefficient
\( \gamma_{\pm} \) [-] mean ionic activity coefficient
\( \lambda_{ik} \) \([\text{mol}^2 \text{kg}^2]\) ion pair interaction function Eq. 4.6
\( \mu_{ikl} \) \([\text{mol}^3 \text{kg}^3]\) ion triplet interaction constant Eq. 4.6
\( \nu \) \([\text{m}^2 \text{s}^{-1}]\) kinematic viscosity
\( \nu_t \) [-] stoichiometric coefficient
\( \rho \) \([\text{kg m}^{-3}]\) density
4.7 REFERENCES CHAPTER 4


Experimental and simulation results for the mixing influenced barium sulfate precipitation process in a continuous stirred tank are presented. The influence of mixing on stirred tank precipitation is highlighted for different operating conditions, e.g. feed point position and agitation rate, by analysis of experimental data. The system behavior is explained using simulation results obtained with a detailed CFD based mixing-precipitation model. The performance of the model is evaluated by comparison with the experimental data.
5.1. INTRODUCTION

Mixing can affect the course of a precipitation process when some of the precipitation sub-processes, as chemical reaction and subsequent nucleation, are fast compared to mixing. It is well known that under such conditions precipitate properties can strongly depend on mixing related process operating conditions, e.g. the agitation rate, feed point position and feed addition rate. However, up to now the interplay between sub-processes mechanisms is not understood well enough to allow for the rational and systematic design of mixing sensitive precipitation processes.

To gain more insight into the nature of mixing-precipitation, processes of known kinetics have been studied extensively in the past through experiments [5.1], [5.2], [5.3], [5.4] and modeling [5.5], [5.6], [5.7], [5.8], [5.9], [5.10]. It has been shown that the process design based exclusively on experimental methods is rather cumbersome for mixing-sensitive processes [5.2], [5.4]. This can be attributed to the complexity of the interactions in such systems. Turbulent mixing influences the process at different length scales, i.e. by generation of supersaturation on the small scale and by large scale reactant transport through the vessel, the different particle formation mechanisms with nonlinear rates compete for reactants, and the process mechanisms have widely different time scales.

Detailed models of such complex systems have been presented in recent years for processes of practical relevance, such as precipitation in a pipe [5.5], [5.7] and in a Taylor-Couette reactor [5.6], where the number of modeled scales was reduced to those corresponding to the most relevant mechanisms involved.

The aim of the work presented in this chapter is to understand better which influence mixing can have on precipitation in particular for continuous stirred tank processes. Using the model system barium sulfate the influence of mixing on precipitation was studied experimentally and through simulations. In the examined process, precipitation of barium sulfate occurs upon mixing of aqueous BaCl₂ and Na₂SO₄:

\[
\text{BaCl}_2(aq) + \text{Na}_2\text{SO}_4(aq) \rightarrow \text{BaSO}_4(s) \downarrow + 2\text{NaCl}_{(aq)} \quad (5.1)
\]
As shown schematically in Fig. 5.1., aqueous solutions of concentrated BaCl₂ and of dilute Na₂SO₄ are mixed in the system by simultaneous feeding of both reactants, while withdrawing the suspension through the reactor outlet at the same time.

In section 5.2 of this chapter a Eulerian frame mixing-precipitation model is presented accounting for mixing mechanisms on the macro-, meso-, and micro-scale, and particle formation by nucleation and growth. The application of that model to a continuous stirred tank process is described in section 5.3, discussing in detail the implementation of the model in a computational fluid dynamics (CFD) code and explaining the simulation strategy used to solve the model equations. The experimental procedure and results are described in section 5.4 and section 5.5.1, respectively. Simulation results are presented in section 5.5.2 and are compared with experimental data in section 5.5.3, to evaluate the model performance for a wide range of operating conditions.
5.2. MIXING – PRECIPITATION MODELING

In mixing-precipitation processes particle formation is controlled by many simultaneously occurring sub-processes, as nucleation, growth, micro-, meso- and macro-mixing. A challenge in modeling of such processes is that all these mechanisms can influence the dynamics of the process, but occur at widely different length scales. Therefore, a high spatial resolution would be required to resolve the characteristics of a process in all the details. Due to the limitations in computational power this is hardly possible, and mixing-precipitation models have to compromise on the resolution. One has to choose the right level of modeling detail, in particular for each of the mixing mechanisms, to be able to formulate an overall process model with good prediction performance.

It was shown in chapter 4 that classical mixing models, such as the engulfment (E) model [5.11], can serve as feasible tools to predict the influence of mixing on precipitation processes. Although such models compromise on spatial resolution, especially for the macromixing by assuming a homogeneously mixed bulk, they can qualitatively capture the dynamics of mixing and allow to predict the influence of mixing on a process within a reasonable computational time.

Modern mixing models follow the approach of transport equation modeling using a rather fine spatial discretization of the mixing device to resolve the macro-flow motion in detail [5.12]. Commonly the Navier-Stokes, the continuity, the species mass balance and the population balance equations are solved in the Reynolds averaged form to reduce the computational effort. However, when using equations based on Reynolds averaging the well-known closure problem arises. This issue has already been addressed in chapter 3.3 for the modeling of mixing controlled chemical reaction processes. To briefly highlight this problem for a mixing influenced precipitation process, the result of Reynolds decomposition and averaging for the moment transformation of the population balance equation is shown:

\[
\frac{\partial \bar{m}_j}{\partial t} + \bar{u}_p \frac{\partial \bar{m}_j}{\partial x_i} + \bar{m}_j \frac{\partial \bar{u}_{pi}}{\partial x_i} = - \frac{\partial \bar{u}_{pi} \bar{m}_j}{\partial x_i} + \delta_j \bar{R}_N + \bar{j} \bar{G} \bar{m}_{j-1} \quad \text{for } j = 0, 1, 2, \ldots \quad (5.2)
\]
Here $\bar{m}_j$ is the average, and $m'_j$ is the local fluctuating component of the j-th moment of the number density particle size distribution (PSD), and $\bar{u}_{pi}$ is the average, and $u'_{pi}$ is the fluctuation of the i-th component of the particle velocity. Some of the averaged terms in Eq. 5.2 are unknown and have to be modeled to solve the equation. It is of particular importance to correctly describe the terms $\overline{R}_N$ and $G m_{j-1}$, which account for particle nucleation and growth, respectively. The values of both terms crucially depend on the local distributions of reactants concentration in solution. Therefore, information about the local mixture structure is required to be able to express these terms correctly. This information can be obtained by solving species transport equations and population balance Eqs. 5.2 in conjunction with a mixing model for the local fluid structure. Mixing models of such kind are the turbulent-mixer-model [5.13] and the spectral relaxation model [5.14].

In the following sections, a mixing-precipitation model based on the turbulent-mixer-model [5.13] and its application to a continuous precipitation process is presented. In section 5.5 results obtained using this model are compared with experimental data thus highlighting the strength of the modeling approach.

### 5.2.1. MIXING-PRECIPITATION MODEL TRANSPORT EQUATIONS

The mixing-precipitation model presented in this section follows a closure modeling approach for Reynolds averaged model equations. The closure of the equations characterizing the fluid motion, i.e. Navier-Stokes and continuity equations, is performed using a standard turbulence model, e.g. the $k$-$\varepsilon$ model. Transport equations for the ionic species and for the particle population are closed using the gradient diffusion approximation and a composition probability density function (PDF) method to overcome the problem related to the nucleation and growth terms in Eq. 5.2. The composition PDF is determined based on information about the local mixture structure, which is obtained using the turbulent-mixer-model.
By using the turbulent-mixer-model, one can describe in detail, how a passive non-reacting tracer $T$ undergoes mixing after its injection into the reactor [5.15]. The normalized concentration can be defined as

$$f = \frac{c_T}{c_{T0}}$$ (5.3)

where $c_T$ is the concentration of the tracer, and $c_{T0}$ is its initial or feed concentration. The change of average scalar concentration $\bar{f}$, which is equivalent to a mixture fraction, can be described by the following equation

$$\frac{\partial \bar{f}}{\partial t} + \bar{u}_j \frac{\partial \bar{f}}{\partial x_j} = \frac{\partial}{\partial x_j} \left( D_m + D_T \right) \frac{\partial \bar{f}}{\partial x_j}$$ (5.4)

where $D_m$ is the molecular diffusivity and $D_T$ the turbulent diffusivity. Eq. 5.4 describes the change of scalar concentration $f$, which occurs by the action of mixing on large scales.

Mixing on the small scales is modeled by the variance $\sigma_s^2$ of the local distribution of $f$ around its average value $\bar{f}$ [5.12]:

$$\sigma_s^2 = \left( f - \bar{f} \right)^2 = \sigma_1^2 + \sigma_2^2 + \sigma_3^2$$ (5.5)

where the components $\sigma_1^2$, $\sigma_2^2$ and $\sigma_3^2$ characterize concentration fluctuations on different scales, where specific mixing mechanisms act. The first component $\sigma_1^2$ is related to the inertial-convective mixing range, whereas $\sigma_2^2$ and $\sigma_3^2$ correspond to viscous-convective and viscous-diffusive mechanisms, respectively. The evolution of the variance components and thereby the change of the local mixture structure can be modeled by the transport equation

$$\frac{\partial \sigma_i^2}{\partial t} + \bar{u}_j \frac{\partial \sigma_i^2}{\partial x_j} = \frac{\partial}{\partial x_j} \left( D_m + D_T \right) \frac{\partial \sigma_i^2}{\partial x_j} + R_{pi} - R_{Di}, \ (i = 1, 2, 3)$$ (5.6)
where $R_{P_i}$ and $R_{D_i}$ represent the production and dissipation rates of each variance component, respectively [5.13]. As shown elsewhere [5.12], the inertial-convective variance component $\sigma_1^2$ is produced by gradients of the mean scalar $\bar{f}$ according to

$$R_{P1} = -2u'_j f'_j \frac{df}{dx_j} = 2D_T \left( \frac{df}{dx_j} \right)^2.$$ \hspace{1cm} (5.7)

The changes in variance due to the inertial-convective mechanism can be modeled by [5.16]:

$$R_{D1} = R_{P2} = \frac{2}{k} \varepsilon \sigma_1^2; \hspace{1cm} (5.8)$$

whereas changes due to viscous-convective mechanisms, with rates $R_{P3}$ and $R_{D2}$, are modeled as [5.13]:

$$R_{D2} = R_{P3} = E \sigma_2^2 = 0.058 \left( \frac{E}{\nu} \right)^{1/2} \sigma_2^2. \hspace{1cm} (5.9)$$

Finally, the component $\sigma_3^2$ of the variance decays due to molecular diffusion at a rate given by [5.13]:

$$R_{D3} = 0.058 \left( \frac{E}{\nu} \right)^{1/2} \left[ 0.030 + \frac{17050}{Sc} \right] \sigma_3^2. \hspace{1cm} (5.10)$$

The mixing model, constituted of the system of Eqs. 5.5 to 5.10, is known as the multiple-time-scale turbulent mixer model [5.13]. This set of equations can fully characterize the local mixture structure and its evolution by turbulent mixing.

The information obtained from the mixing model can be used to describe the mixture structure with a probability density function (PDF) for $f$. For the process analyzed in this work the real shape of the composition PDF can be approximated with a Beta-function that is defined by [5.15]:
\[
\Phi(f) = \frac{f^{v-1}(1-f)^{w-1}}{\int_0^1 y^{v-1}(1-y)^{w-1} dy}
\]  
(5.11)

with \( v = \bar{f}\left[\bar{f}(1-\bar{f})/\sigma^2 - 1\right] \)
and \( w = \left[(1-\bar{f})/\bar{f}\right]v \)

Using the Beta-function \( \Phi(f) \), the local average nucleation rate term \( \bar{R}_N \) in Eq. 5.2 can be expressed as [5.15]:

\[
\bar{R}_N = \int_0^1 R_N(f)\Phi(f) df
\]
\[
= \int_0^1 R_N(c_{Ba^{++}}(f), c_{SO_4^{-}}(f), c_{Na^+}(f), c_{Cl^-}(f))\Phi(f) df,
\]  
(5.12)

where \( R_N(f) \) is the local nucleation rate, which is a function of the local ion concentrations \( c_{Ba^{++}}(f) \), \( c_{SO_4^{-}}(f) \), \( c_{Na^+}(f) \), and \( c_{Cl^-}(f) \) of barium, sulfate, sodium and chloride, respectively. Since sodium and chloride ion concentrations are not affected by the precipitation reaction they can be expressed as

\[
\frac{c_{Cl^-}(f)}{c_{Cl^-0}} = f
\]
\[
\frac{c_{Na^+}(f)}{c_{Na^+0}} = 1 - f
\]  
(5.13)
(5.14)

with the chloride ion concentration \( c_{Cl-,0} \) in the barium chloride feed and the sodium ion concentration \( c_{Na+,0} \) in the sodium sulfate feed. As shown elsewhere [5.7], the concentrations \( c_{Ba^{++}}(f) \) and \( c_{SO_4^{-}}(f) \) can be determined by an interpolation between the concentrations \( c_i^\infty(f) \) and \( c_i^0(f) \) for \( i = Ba^{++}, SO_4^- \) corresponding to the limiting cases of an instantaneous and of an infinitely slow precipitation:

\[
c_i(f) = c_i^\infty(f) + \frac{c_i^\infty - c_i^0}{c_i^\infty - c_i^\infty}[c_i^0(f) - c_i^\infty(f)] \quad \text{for} \quad i = Ba^{++}, SO_4^- \]  
(5.15)
Here \( \bar{c}_i \) is the average ion concentration, whose evolution is described by the following mass balance equation:

\[
\frac{\partial \bar{c}_j}{\partial t} + \bar{u}_i \frac{\partial \bar{c}_j}{\partial x_i} + \bar{c}_j \frac{\partial \bar{u}_i}{\partial x_i} = \frac{\partial}{\partial x_i} \left[ \left( D_{m,j} + D_T \right) \frac{\partial \bar{c}_j}{\partial x_i} \right] - \frac{k_a \rho_{BaSO_4}}{2 M_{BaSO_4}} \overline{Gm_2}
\]

for \( j = \text{Ba}^{++}, \text{SO}_4^- \) \( (5.16) \)

where \( D_{m,j} \) is the molecular diffusivity of ion \( j \), \( k_a \) is the surface shape factor of the crystals, and \( \rho_{BaSO_4} \) and \( M_{BaSO_4} \) are the density and molar mass of barium sulfate, respectively.

The terms \( \overline{Gm_j} \) in Eqs. 5.2 and 5.16, which account for the effects of particle growth, can be recast using the composition PDF function, when assuming that all moments are proportional to the solid-phase concentration \( [5.7] \):

\[
\overline{Gm_j} = \frac{\bar{m}_j}{\bar{c}_{BaSO_4}} \frac{1}{\phi(f)} \int_{0}^{f} \int_{-\infty}^{\infty} G(f)s_{BaSO_4}(f)\phi(f)df.
\]

Here \( \bar{c}_{BaSO_4} \) and \( c_{BaSO_4}(f) \) are the local average and local instantaneous barium sulphate solid concentrations, respectively. The instantaneous local concentration \( c_{BaSO_4}(f) \) can be determined from a local balance on the barium ion concentration.

The transport equation for the \( j \)-th moment of a particle population, given by Eq. 5.2, can be closed using Eqs. 5.12 and 5.17 and the gradient diffusion approximation for the scalar flux term resulting in

\[
\frac{\partial \bar{m}_j}{\partial t} + \bar{u}_{pi} \frac{\partial \bar{m}_j}{\partial x_i} + \bar{m}_j \frac{\partial \bar{u}_{pi}}{\partial x_i} = \frac{\partial}{\partial x_i} D_{pT} \frac{\partial \bar{m}_j}{\partial x_i} + \delta_j \bar{R}_N + j \overline{Gm_{j-1}}
\]

for \( j = 0, 1, 2, ... \) \( (5.18) \)

Here \( D_{pT} \) is the diffusivity coefficient for particles. Since particles produced in the continuous precipitation process are small, the local values of the particle turbulent diffusivity \( D_{pT} \) and particle velocity \( \bar{u}_{pi} \) can be approximated by the local values of fluid turbulent diffusivity \( D_T \) and velocity \( \bar{u}_i \), respectively \( [5.7] \).
5.2.2 AQUEOUS SOLUTION AND PARTICLE FORMATION KINETICS MODEL

The mixing-precipitation model presented in the previous section can fully describe a process, when correlations for particle formation kinetics are known. The kinetics and mechanisms of barium sulfate nucleation and growth have been studied rather thoroughly in the literature, but almost exclusively for the case of precipitation under stoichiometric conditions. During the course of a mixing limited process this condition is not fulfilled. It has been shown in chapter 4 that under such conditions the quality of the precipitation kinetics model depends crucially on the characterization of the driving force, i.e. supersaturation. It was also shown in chapter 4 that the Pitzer model, which accounts for all ion-pair and ion-triplet interactions in a solution for ionic strength values up to 6 M, gives the most appropriate characterization of an aqueous $\text{Ba}^{2+}/\text{SO}_4^{2-}/\text{Na}^+/\text{Cl}^-$ solution, when also taking the formation of $\text{BaSO}_4$ ion-pairs complexes into account.

Based on the Pitzer activity model the particle formation driving force can be expressed in terms of the dimensionless supersaturation ratio, whose definition for $\text{BaSO}_4$ precipitation is:

$$S_A = \left( m_{\text{Ba}^{2+}} m_{\text{SO}_4^{2-}} / K_{SP} \right)^{0.5} \gamma_\pm, \quad \gamma^2 = \gamma_{\text{Ba}^{2+}}^2 \gamma_{\text{SO}_4^{2-}}^2$$

(5.19)

where $K_{SP}$ is the solubility product, $m_i$ and $\gamma_i$ are the molality and the activity coefficient of the ionic species $i$, respectively, whereas $\gamma_\pm$ is the mean ionic activity coefficient.

As shown in chapter 4, a nucleation rate correlation based on the supersaturation ratio defined in Eq. 5.19 has been developed that can be written as follows:

$$R_N = R_{N,\text{hom}} + R_{N,\text{het}}$$

with

$$R_{N,i} = R_{\text{max},i} \exp \left( -A_i \frac{\ln^2 S_A}{S_A} \right), \quad (i = \text{hom, het}).$$

(5.20)
Here $R_{\text{max,het}} = 3.75 \times 10^{11} \text{ m}^{-3} \text{ s}^{-1}$ and $A_{\text{het}} = 40.0$, and $R_{\text{max,hom}} = 1.45 \times 10^{42} \text{ m}^{-3} \text{ s}^{-1}$ and $A_{\text{hom}} = 2254.0$ are the parameters characterizing heterogeneous and homogeneous nucleation, respectively.

As described in chapter 4, growth of BaSO$_4$ particles can be either integration or diffusion limited and is therefore characterized by a two step model accounting for both effects. The integration step is described by

$$G = k_r \left( \frac{c_{\text{Ba}^{2+},\text{int}} c_{\text{SO}_4^{2-},\text{int}}}{K_{SP}} \right)^{0.5} \left( \gamma^{-1} \right)$$

(5.21)

where the subscript int refers to interface solid/solution conditions. The model parameter $k_r$ has been estimated as $k_r = 9.1 \times 10^{-12} \text{ m s}^{-1}$. The diffusion step rate can be described as:

$$G = k_D \left( c_{i,\text{bulk}} - c_{i,\text{int}} \right) \left( i = \text{Ba}^{2+}, \text{SO}_4^{2-}, \text{BaSO}_4^0 \right)$$

(5.22)

with $k_D = 4.0 \times 10^{-5} \text{ (m s}^{-1})\text{(kg mol}^{-1})$, assuming the same mass transfer coefficient for all species.
5.3. APPLICATION OF THE MIXING-PRECIPITATION MODEL TO A CONTINUOUS STIRRED TANK PROCESS

It is described in the following, how the mixing-precipitation model presented in the previous section can be applied to the stirred tank process shown in Fig. 5.1. The finite volume based CFD software FLUENT 6.1 is employed to solve the model equations by discretizing the reactor domain into 500,000 cells. The flow-field was calculated using a standard $k$-$\varepsilon$ model since previous work [5.12] has shown for a similar stirred tank geometry that predictions of good accuracy can be obtained.

In principle the continuous process could be simulated directly by calculating the solution for the differential equations describing the flow-field, mixing model, reactant transport and population balance equations in conjunction with the precipitation kinetics model shown in the previous section. However, the direct calculation of the solution for all model equations and the entire reactor domain would require a very large computational time. Thus, an alternative approach has to be used to reduce the computational effort without however compromising on the predictive capability of the model. The computational burden has been reduced in three steps. First, an efficient implementation technique has been developed for the complex models of the liquid phase and of the precipitation kinetics. Secondly, the numerical effort is further reduced by applying the composition PDF closure only in regions of the reactor domain, where small-scale segregation occurs and influences the mixing-precipitation process. Third, a new simulation strategy has been developed to overcome the problem of slow convergence for the numerical solution of the reactant transport and population balance equations.

These three steps are explained in detail in the following sections. The simulation procedure is applied to a continuous stirred tank process for several different operating conditions and the results are presented in section 5.5.
5.3.1. IMPLEMENTATION METHOD FOR THE MODEL OF THE LIQUID PHASE AND OF THE PARTICLE FORMATION KINETICS

Mixing-precipitation processes of different complexity were studied in the past using CFD [5.5], [5.6], [5.7], [5.8]. Most commonly the kinetics of particle formation were described using correlations employing a concentration based driving force [5.6], [5.8]. In some cases simple activity models were used to express the driving force [5.5], [5.7]. In all these works [5.5], [5.6], [5.7], [5.8] the kinetics models are simple enough to allow for the computation of particle formation rates within a reasonable computational time. However, when using a complex liquid phase and kinetics model, as the one presented in section 2.2, the computational time, which is required to determine the particle formation rates, is significant. In such a case, the simulation of a mixing-precipitation process spends most of the computational time in determining the particle formation rates. Thus, the direct implementation of the particle formation kinetics presented in section 2.2 is only feasible in combination with a simplified mixing model, as shown in chapter 4.

For the implementation in conjunction with a complex CFD model a different approach has to be chosen. In the newly developed approach both supersaturation ratio and growth rate are calculated for a wide range of ion concentrations prior to a CFD simulation. The computed values are saved in two separate matrices, which serve as lookup tables in the CFD code. Thereby, it can be avoided to solve the liquid phase and kinetics model equations during the course of a CFD model simulation. Since both supersaturation and growth rate are functions of barium, sulfate, sodium and chloride concentrations, in principle a four dimensional lookup table should be used. However, it can be more convenient to use smaller lookup tables to reduce the size of computer memory required to save these tables. A three dimensional lookup table can be constructed exploiting the fact that the condition of electroneutrality should be fulfilled, which can be written as:
Using Eq. 5.23 supersaturation and growth lookup tables can be computed as a function of three parameters only, namely the barium ion concentration $c_{Ba^{++}}$, the sulfate ion concentration $c_{SO_{4}^{--}}$ and the chloride ion concentration $c_{Cl^{-}}$. The lookup tables are constructed by calculating all values of supersaturation ratio and growth rate after discretizing the parameter space logarithmically. Typically, 500 intervals are used to discretize the range of both barium and sulfate ion concentrations, whereas only 10 intervals are chosen to discretize the third dimension, since the functional dependence of growth rate and supersaturation on sodium and chloride ion concentration is rather weak. The upper and lower bounds for the ranges of all three parameters $c_{Ba^{++}}$, $c_{SO_{4}^{--}}$ and $c_{Cl^{-}}$ are chosen to cover the conditions occurring in all experiments presented in section 5.5.

For the simulation of a mixing-precipitation process using the CFD software FLUENT 6.1 the lookup tables, typically of a size around 50 MB, are saved in the heap memory of the computer. During the course of a simulation values of growth rates are determined directly from the lookup table using a linear interpolation method. Nucleation rates are calculated using Eq. 5.20 by determining the supersaturation ratio by linear interpolation between lookup table values.

Using the lookup table approach the calculation of nucleation and growth rates can be speeded up by a factor of about 2000 in comparison with a direct computation using the model equations.

5.3.2. APPLICATION OF THE COMPOSITION PDF-CLOSURE TO THE CONTINUOUS STIRRED TANK PROCESS

In principle, a continuous stirred tank process can be fully described by simultaneously solving all model equations in section 5.2 for the entire reactor domain in combination with properly chosen boundary conditions. The disadvantage of that approach is a high computational effort, since the numerical solution of integro-differential Eqs. 5.16 and 5.18 is time consuming. A more
efficient alternative is to solve consecutively first the mixing model equations and then the reactant and population balance equations, applying the PDF closure only in regions of the reactor domain, where small-scale segregation occurs and influences the process. This approach is possible for the process analyzed in this chapter, since the reactant and particle concentrations are rather dilute. Only under such conditions mixing is not influenced by the reaction and particle formation.

After computation of the flow field using a $k-\varepsilon$ model, the mixing model equations Eqs. 5.3 to 5.10 have to be solved using properly chosen boundary conditions. When choosing these conditions, it should be considered that the mixing model with the Beta-PDF is only suitable to describe mixtures, whose PDF shape can be approximated well by a Beta-function. For this reason, it crucial to correctly define the two components of the binary mixture, which correspond to $f = 0$ and $f = 1$. Here, two cases have to be distinguished for the different feed addition modes, i.e. the first case where both feed tubes are close to each other, i.e. mode (2) and (3), and the second case, where the feed tubes are far apart, i.e. mode (1). In the first case, mixing between the two fresh feeds should be described, since direct contacting of the feeds is dominant and mixing of fresh feed with the bulk is of negligible influence. Here, $f = 0$ and $f = 1$ correspond to the fresh sodium sulfate and barium chloride feed, respectively. In the second case, mixing between the bulk and the fresh barium chloride feed should be modeled, since barium can contact the sulfate only after dilution in the bulk. Thus, $f = 0$ and $f = 1$ correspond to the bulk and fresh barium chloride feed, respectively.

In the first case, the distributions of the average mixture fraction $\bar{f}$ and the variance components $\sigma_1^2$, $\sigma_2^2$ and $\sigma_3^2$ are calculated by solving Eqs. 5.6 to 5.10 with $\sigma_i^2(\text{BaCl}_2 \text{ feed }) = 0$ and $\sigma_i^2(\text{Na}_2\text{SO}_4 \text{ feed }) = 0$ as boundary conditions. In the second case, the procedure described in chapter 3.4.1.1 is used.

After the distributions of mixture fraction and total variance are determined, the Danckwerts' intensity of segregation [5.16] can be calculated for each point in the reactor as
The Danckwerts' intensity of segregation is used as a criterion to identify, where the PDF closure should be applied. In this work, the PDF closure is applied in regions of the reactor domain, where the intensity of segregation is larger than 0.01. When the segregation is smaller, the closure for the nucleation rate term \( \overline{R}_N \) in Eq. 5.18 is simplified to

\[
\overline{R}_N = R_N \left( \overline{c}_{Ba^{++}}, \overline{c}_{SO4^{--}}, \overline{c}_{Na^+}, \overline{c}_{Cl^-} \right)
\]  

(5.25)

and the closure for the growth related terms in Eqs. 5.16 and 5.18 is modified accordingly using

\[
\overline{Gm}_{j-1} = \bar{m}_{j-1} G \left( \overline{c}_{Ba^{++}}, \overline{c}_{SO4^{--}}, \overline{c}_{Na^+}, \overline{c}_{Cl^-} \right).
\]  

(5.26)

When calculating the average nucleation and growth rates as functions of local average ion concentrations, the numerical effort to solve Eqs. 5.16 and 5.18 can be significantly reduced in comparison to the PDF method. Typically, in the continuous stirred tank, shown in Fig. 5.1, strong segregation occurs only in a region close to the feed points. Thus, the simplified closure of Eqs. 5.25 and 5.26 can usually be applied to large parts of the reactor domain.
5.3.3. SIMULATION STRATEGY AND CONVERGENCE CRITERIA

One of the key problems in simulating mixing-precipitation processes using CFD is to identify a robust procedure for the computation of the numerical solution of model equations within reasonable computational time. This applies in particular to processes conducted in reactors of complex geometry, where the number of numerical cells is typically large. However, most works in literature analyze processes for simple reactor geometries [5.5], [5.7], [5.9], whereas only a few publications deal with processes operated in reactors of complex geometry [5.8], [5.10]. The problem in finding an efficient simulation procedure for solving the model equations is addressed in detail only in [5.10], where a complicated multi-step iteration procedure is presented.

In this work a new algorithm is proposed, based on which the numerical solution can be found within a reasonable computation time using only four main iteration cycles, referred to as step (I), (II), (III) and (IV) in the following. The method has been applied to process simulations for a wide range of stirred tank operating conditions and has been found to be robust in all cases. The procedure is described in detail in the following after briefly highlighting the reasons for difficulties in calculating the numerical solution of the model equations.

The problem in computing the numerical solution can be attributed to the characteristics of the species transport Eqs. 5.16 and population balances Eqs. 5.18. These equations can be strongly coupled and highly nonlinear, when supersaturation is high. This applies in particular, when supersaturation is so large that particle formation is dominated by homogeneous nucleation, where the functional dependence of nucleation rate on supersaturation is strongly nonlinear. On the contrary, at low supersaturation species transport Eqs. 5.16 and population balance Eqs. 5.18 are only weakly coupled, since nucleation and growth rates are small.

In the continuous stirred tank process, shown in Fig. 5.1, both kinds of characteristics can be identified for different parts of the reactor domain. Close to the feed pipes supersaturation is usually high and in the bulk fluid it is typically much smaller. The volume of fluid with elevated supersaturation close
to the feed points, further on referred to as feed plumes, is usually small in comparison to the volume of the bulk. Within the feed plumes high supersaturation results in high nucleation and growth rates, which in turn cause species transport and population balance Eqs. 5.16 and Eqs. 5.18 to be strongly coupled.

A standard way of solving highly nonlinear and strongly coupled equations in CFD is to introduce the under-relaxation factors $\delta_i$ that are used to update the values of the unknowns and are defined as follows:

$$
\delta_i = \frac{(y_{i,new} - y_{i,old})}{(y_{i,new,pred} - y_{i,old})} \text{ for } i = 1, \ldots, \text{number of equations} \quad (5.27)
$$

where $y_{i,old}$ is the value of a variable at the previous iteration step, $y_{i,new,pred}$ is the new value calculated by the algorithm at the new iteration, $y_{i,new}$ is the actual new value assigned to the variable and $i$ is the index number of equations in the system to be solved. When solving a system of equations, values between 0 and 1 can be selected independently for each $\delta_i$.

Different combinations of under-relaxation factors $\delta_i$ were explored to solve Eqs. 5.16 and Eqs. 5.18. When choosing values close to one for all $\delta_i$ (i.e. $\delta_i > 0.99$), the iterative computation has the tendency to diverge for any spatial distribution of the reactants and of the moments of the PSD assigned at the start of the computation. The stability of the iteration procedure could only be guaranteed, when the under-relaxation factors corresponding to species transport equations Eqs. 5.16 have been reduced to values smaller than one (i.e. $0.9 > \delta_i > 0.8$). This however resulted in excessively long computation times. Thus, the simple use of under-relaxation factors cannot be considered as a feasible approach to obtain the numerical solution for Eqs. 5.16 and 5.18.

As highlighted in the previous paragraphs, the tendency of the iterative computation to diverge can be due to the characteristics of the feed plume. When using small under-relaxation factors $\delta_i$ in order to avoid divergence problems, slow convergence is observed due to the characteristics of the bulk region, where the computed spatial distributions of reactants and moments of the PSD change slowly during the iteration.
This problem can be overcome by using an independent iteration routine to compute concentration changes in the bulk fluid. The four steps of the newly developed simulation procedure are outlined in the following.

In step (I), the flow-field and mixing model Eqs. 5.4 to 5.10 are solved. In these straightforward computations the solutions usually converge without problems. The residual values computed by the software FLUENT 6.1 during the course of the iteration procedure are used as convergence criteria [5.17].

In step (II), the regions of feed plumes and bulk fluid are identified and defined in the computational grid. For that purpose, the computation of concentration and moment distributions is started by performing several hundreds of iterations using small under-relaxation values for Eqs. 5.16 and 5.18 and a properly chosen initial solution. Typically, the result obtained is quite different from a fully converged solution. However, the intermediate solution can be used with sufficient accuracy to identify where strong concentrations gradients occur in the integration domain. Based on a certain limit value for the gradient in supersaturation, the integration domain is subdivided into regions defined as feed plumes and bulk. Fluid with a small supersaturation gradient is assigned to the bulk, and fluid with large gradients is assigned to the feed plumes.

In the next step, constraints for the bulk sulfate and barium ion concentrations are defined, which are applied for further iterations steps with the CFD model. Both sulfate and barium ion concentrations are set to constant values for the entire bulk region, which are defined as:

\[
\overline{c}_{SO_{4}^{2-}, bulk} = \overline{c}_{Ba^{2+}, bulk} = \frac{1}{V_{Bulk}} \int_{Bulk} \overline{c}_{SO_{4}^{2-}}
\]

(5.28)

Here \(V_{bulk}\) is the volume of the bulk region, \(\overline{c}_{SO_{4}^{2-}}\) is the local average sulfate ion concentration computed in the last iteration step before averaging, and \(\overline{c}_{SO_{4}^{2-}, bulk}\) and \(\overline{c}_{Ba^{2+}, bulk}\) are the average bulk concentrations of sulfate and barium ions, respectively. Eq. 5.28 applies only to equimolar mixing of barium chloride and sodium sulfate and has to be slightly modified when computing \(\overline{c}_{Ba^{2+}, bulk}\) for non-equimolar mixing of barium chloride and sodium sulfate solutions.
In step (III), the iteration procedure is continued keeping the barium and sulfate bulk concentrations at the values calculated by Eq. 5.28. At each iteration step the bulk average barium and sulfate concentrations are modified using an independent iteration routine of the CFD code to minimize the sulfate mass balance error $\Delta M_{SO_4^{--}}$. Based on that value the bulk average barium and sulfate concentrations are modified according to

$$\bar{c}_{SO_4^{--},bulk, next} = \bar{c}_{Ba^{++},bulk, next} = \left(1 + \delta \Delta M_{SO_4^{--}}\right) \bar{c}_{SO_4^{--},bulk}, \quad (5.29)$$

where $\bar{c}_{SO_4^{--}, bulk, next}$ and $\bar{c}_{Ba^{++}, bulk, next}$ are the bulk average sulfate and barium ion concentrations used for the next iteration step. The under-relaxation factor $\delta$ is set to a value between 0.001 and 0.01 depending on the value of the mass balance error $\Delta M_{SO_4^{--}}$. The sulfate mass balance error $\Delta M_{SO_4^{--}}$ between sodium sulfate feed inlet and reactor outlet is calculated with:

$$\Delta M_{SO_4^{--}} = \int_{\text{outlet}} \dot{m}_{\text{outlet}} \left(\bar{c}_{SO_4^{--}} + m_3 \frac{\rho_{BaSO_4}}{M_{BaSO_4}} k_v \right) dA - \dot{M}_{Na_2SO_4,feed} \bar{c}_{Na_2SO_4,feed} \quad (5.30)$$

Here $\dot{m}_{\text{outlet}}$ is the specific mass flowrate at the outlet, $\dot{M}_{Na_2SO_4,feed}$ is the total mass flowrate at the sodium sulfate inlet, $k_v$ is the volume shape factor of the particles and $\bar{c}_{Na_2SO_4,feed}$ is the sodium sulfate feed concentration. After performing several hundreds of iterations with the imposed constraints for the bulk sulfate and barium ion concentrations, the solution has converged to a mass balance error $\Delta M_{SO_4^{--}}$ of approximately 0.1 percent.

In step (IV), the constraints for barium and sulfate bulk concentrations are relaxed and several hundreds of additional iterations are performed. The solution usually converges rapidly, since the intermediate solution calculated in step (III) is close to the final result.

To monitor the convergence behavior during the iteration process several criteria are used. The change of all ion concentrations at the reactor outlet is observed. Furthermore the change of computed average particle size $d_{43}$ defined as:
\[ d_{43} = \frac{m_4}{m_3} \left( \frac{n}{k_d} \right)^{1/3} \]  

(5.31)

is monitored. In addition the mass balance errors \( \Delta M_{SO4^-} \) and \( \Delta M_{Ba^{++}} \), calculated using Eq. 5.30 and a corresponding equation for the barium mass balance, are checked. The solution is considered to be fully converged when the balance errors are smaller than 0.01 percent and no changes occur in the other observed parameters.

5.4. EXPERIMENTAL SECTION

5.4.1. EXPERIMENTAL SETUP

The setup for continuous stirred tank precipitation experiments is described in chapter 2.1.3. In Fig. 5.1 the different feed tube locations used for the work presented in this chapter are shown schematically. The sodium sulfate feed tube is always fixed at the same location in the impeller discharge and the barium chloride tube can be positioned at the three different locations F1,S, F2,S and F3,S, as defined in chapter 2.1.3. In the following, barium chloride feed addition at the feed points F1,S, F2,S and F3,S is referred to as feed addition mode (1), (2) and (3), respectively.

5.4.2 MATERIALS

Barium chloride dihydrate, puriss, p.a., and sodium sulfate decahydrate, puriss, p.a, were purchased from Fluka (Buchs, Switzerland). Barium chloride and sodium sulfate aqueous solutions were prepared using double distilled water.

5.4.3 EXPERIMENTAL PROCEDURE

Barium chloride and sodium sulfate solutions at concentrations \( c_{BaCl_{2} feed} \) and \( c_{Na_{2}SO_{4} feed} \) were obtained by dissolving the corresponding salts in double distilled
water. For each experiment, the reactor was initially filled with 6 liters of water. The precipitation experiment was started by simultaneously feeding barium chloride and sodium sulfate solutions through the two feed tubes into the reactor. Throughout the entire experiment suspension is withdrawn at the reactor outlet controlling the flow rate with an overflow regulator to keep the liquid level in the system constant. While feeding the solutions into the reactor, the particle size in the outlet stream was continuously analyzed in-situ using an FBRM device. The signal of average particle size $d_{av}$, calculated based on the measured chord length distribution, was observed to detect when steady state conditions were reached in the reactor. Once the measured particle size $d_{av}$ had stabilized at a constant value, a suspension sample was taken from the reactor. Samples were always taken at the same position in the impeller discharge stream. The suspension was analyzed immediately after sampling using the Multisizer 3 to determine the particle size distribution. Then, the sample was dried for image analysis by scanning electron microscopy.

5.5. DISCUSSION OF EXPERIMENTAL AND SIMULATION RESULTS

In the following, the experimental results obtained using the procedure defined in section 5.4 are discussed. The effects of changes in operating parameters, e.g. feed position, stirring rate and reactant concentrations, on the particle properties are presented in section 5.5.1. Simulation results are reported in section 5.5.2, discussing in detail the results obtained in the different steps of the simulation procedure outlined in section 5.3. The comparison of experimental and simulation results are presented in section 5.5.3.

5.5.1 DISCUSSION OF EXPERIMENTAL RESULTS

In this section experimental results obtained using the procedure defined in section 5.4 are discussed. Results obtained for three different feed locations, shown in Fig. 5.1, are presented sections. 5.5.1.1, 5.5.1.2 and 5.5.1.3 for
processes operated at various conditions. Finally, in section 5.5.4 the results obtained for the different feed point locations are compared.

5.5.1.1. EXPERIMENTAL RESULTS FOR FEED ADDITION MODE (1)

Experimental results presented in Fig. 5.2 to Fig. 5.4 were obtained for feed mode (1) shown in Fig. 5.1.

As described in section 5.4.3., all experiments are conducted by simultaneously feeding aqueous barium chloride and sodium sulfate solutions into the reactor until steady state conditions are reached and sampling can be performed. In Fig. 5.2 the average particle size $d_{av}$, measured with an FBRM device in the reactor outlet stream, is shown as a function of time for an experiment with the operating parameters summarized in the caption of the figure. The particle size $d_{av}$ is reported from the onset of particle formation, which occurs rapidly after the start of feed addition, until the time when steady state conditions are established. After an initial increase in measured particle size $d_{av}$ a maximum is reached and the value of $d_{av}$ approaches asymptotically a constant value. It can be noticed that steady state conditions are established approximately after one hundred minutes, which corresponds to 3.4 times the mean residence time. Similar patterns of behavior in the measured particle size $d_{av}$ over process time could be observed for all reactor operating conditions explored in this work. However, the time required to reach steady state varied with changing process parameters. For experiments with high feed addition rate the time required to reach steady state was up to six times the mean residence time. Therefore, the standard procedure for all experiments was to perform sampling after seven mean residence times. In this way, it could be ensured that steady state conditions were always established at the time of sampling.

It is shown in Fig. 5.3 how the average particle size $d_{43}$ changes with increasing stirring rate. Experiments illustrated in Fig. 5.3. were performed at the operating conditions listed in the caption of the figure. The experimental error in measuring the particle size $d_{43}$ is about 1%, i.e. rather small; therefore error-bars are omitted in the presentation of experimental data. The reproducibility of the
experiments is in the range of a few percent, as it can be seen in Fig. 5.3 in the cases where runs at the same conditions were repeated. Experimental data indicate that the particle size \( d_{43} \) stays constant at a value around 24 \( \mu \)m for all agitation rates.

In Fig. 5.4 the influence of changing reactant concentrations on the average particle size \( d_{43} \) is illustrated. The reproducibility of the experiments is in the range of a few percent. As in Fig. 5.3, the measured particle size \( d_{43} \) has a constant value around 24 \( \mu \)m for all reactant concentrations.

\[ \text{Fig. 5.2. Time history of average particle size } d_{av} \text{ measured with an FBRM system in the reactor outlet stream.} \]

\[ \text{feed addition mode (1), } N_{\text{stirrer}} = 200 \text{ rpm,} \]

\[ c_{\text{Na}_2\text{SO}_4,0} = 0.002 \text{ mol/l, } c_{\text{BaCl}_2,0} = 0.1 \text{ mol/l,} \]

\[ q_{\text{feed,BaCl}_2} = 4 \text{ ml/min, } q_{\text{feed,Na}_2\text{SO}_4} = 200 \text{ ml/min.} \]
Fig. 5.3. Influence of agitation rate on $d_{43}$, feed addition mode (1).
$c_{Na_2SO_4,0} = 0.03 \text{ mol/l}, c_{BaCl_2,0} = 1.5 \text{ mol/l},$
$q_{feed,BaCl_2} = 4 \text{ ml/min}, q_{feed,Na_2SO_4} = 200 \text{ ml/min}$.

Fig. 5.4. Influence of reactant concentrations on $d_{43}$, feed addition mode (1).
$c_{BaCl_2,0} = 50 \times c_{Na_2SO_4,0}, N_{stirrer} = 200 \text{ rpm}.$
$q_{feed,BaCl_2} = 4 \text{ ml/min}, q_{feed,Na_2SO_4} = 200 \text{ ml/min}$.
5.5.1.2. EXPERIMENTAL RESULTS FOR FEED ADDITION MODE (2)

Experimental results presented in Fig. 5.5 and Fig. 5.6 were obtained for feed mode (2), as shown in Fig. 5.1.

In Fig. 5.5 the influence of mixing on the average particle size $d_{43}$ through changes in the agitation rate is shown by two series of experiments, each for constant sodium sulfate feed concentration. The open triangles in the figure indicate the experimental results for a sodium sulfate feed concentration of 0.03 mol/l, and the filled triangles refer to the data for a sodium sulfate feed concentration of 0.06 mol/l. For both sodium sulfate feed concentrations the particle size $d_{43}$ is not influenced by changes in stirring rate. For the lower sodium sulfate feed concentration the particle size $d_{43}$ has a value around 24 µm and for the higher concentration a value around 4 µm.

In Fig. 5.6 the influence of the flow rate ratio $\alpha$, which is defined as the ratio of sodium sulfate to barium chloride feed flow rate, on the particle size $d_{43}$ is illustrated. For all experiments presented in the figure the molar addition rates of sodium sulfate and barium chloride were kept constant at 0.012 mol/min and 0.006 mol/min, respectively. The sodium sulfate feed addition rate was 200 ml/min and both barium chloride concentration and feed flow rate were modified with changing values of $\alpha$ as described in the caption of Fig. 5.6. It is shown in Fig. 5.6 that changes in $\alpha$ do not significantly affect the average particle size $d_{43}$. For all experiments presented in the figure the particle size is approximately 3.5 µm.
Fig. 5.5. Influence of agitation rate on $d_{43}$, feed addition mode (2).

$c_{\text{BaCl}_2,0} = 1.5 \text{ mol/l},$

$q_{\text{feed, BaCl}_2} = 4 \text{ ml/min}, q_{\text{feed, Na}_2\text{SO}_4} = 200 \text{ ml/min}.$

Fig. 5.6. Influence of flow rate ratio $\alpha$ on $d_{43}$, feed addition mode (2).

$c_{\text{Na}_2\text{SO}_4,0} = 0.06 \text{ mol/l}, c_{\text{BaCl}_2,0} = 0.03 \text{ mol/l} \times \alpha,$

$q_{\text{feed, Na}_2\text{SO}_4} = 200 \text{ ml/min}, q_{\text{feed, BaCl}_2} = q_{\text{feed, Na}_2\text{SO}_4} / \alpha.$
5.5.1.3. EXPERIMENTAL RESULTS FOR FEED ADDITION MODE (3)

Experimental results presented in Fig. 5.7 to Fig. 5.11 were obtained for feed mode (3), as shown in Fig. 5.1.

In Fig. 5.7 the influence of mixing on the average particle size \(d_{43}\) through changes in the stirring rate is shown by two series of experiments, each for constant sodium sulfate feed concentration. The open diamond symbols in the figure indicate the experimental results for a sodium sulfate feed concentration of 0.03 mol/l, and the filled diamond symbols refer to the data for a sodium sulfate feed concentration of 0.06 mol/l. For the lower sodium sulfate feed concentration the reproducibility of the experiments is in the range of 20 % in terms of the particle size \(d_{43}\). For the higher sodium sulfate feed concentration the reproducibility is with 1 % much better, as it can be seen in Fig. 5.7, where symbols corresponding to different runs at the same conditions virtually coincide. For both feed concentrations the particle size \(d_{43}\) is not influenced by changes in agitation rate. For the lower sodium sulfate feed concentration the particle size \(d_{43}\) has a value around 11 \(\mu\)m and for the higher concentration a value of approximately 3 \(\mu\)m for all agitation rates between 200rpm and 600 rpm.

In Fig. 5.8 the influence of sodium sulfate and barium chloride feed addition rate on the particle size \(d_{43}\) is presented. The feed ratio \(\alpha\) is kept constant for all experiments presented in the figure and the sodium sulfate addition rate is modified from 200 ml/min to 3000 ml/min. As shown in the figure, the particle size \(d_{43}\) seems to be constant over the entire range of feed addition rates.

In Fig. 5.9 and Fig. 5.10 it is illustrated, how changes in \(\beta\), which is the ratio of the molar sodium sulfate feed addition rate to the molar barium chloride feed addition rate, influence the properties of particles. The ratio \(\beta\) is varied between 1 and 3, with \(\beta=1\) corresponding to mixing of equimolar amounts of reactants. As shown in Fig. 5.9 the particle size \(d_{43}\) has a value around 11 \(\mu\)m for equimolar mixing. With increasing \(\beta\), corresponding to increasing excess of sodium sulfate, the particle size decreases asymptotically to a value of 3.5 \(\mu\)m.
Although the particle size is affected by the ratio $\beta$, no influence on the coefficient of variation of the PSD can be observed in Fig. 5.10.

In Fig. 5.11 the influence of mixing on particle size by changes in the flow rate ratio $\alpha$ is visualized. It is shown that an increase in the flow rate ratio leads to a decrease in particle size. For small flow rate ratios the particle size $d_{43}$ is around 18 $\mu$m and it decreases to a value around 11 $\mu$m for $\alpha$ larger than 30.

![Graph showing the influence of agitation rate on $d_{43}$](image)

*Fig. 5.7. Influence of agitation rate on $d_{43}$, feed addition mode (3).*  
$c_{\text{BaCl}_2,0} = 1.5 \text{ mol/l},$  
$q_{\text{feed,BaCl}_2} = 4 \text{ ml/min}, q_{\text{feed,Na}_2\text{SO}_4} = 200 \text{ ml/min}.$
Fig. 5.8. Influence of reactant addition rates on $d_{43}$, feed addition mode (3).
$c_{Na_{2}SO_{4},0} = 0.03\ \text{mol/l}$, $c_{BaCl_{2},0} = 1.5\ \text{mol/l}$,
$N_{stirrer} = 200\ \text{rpm}$, $q_{\text{feed,BaCl}_{2}} = 0.02 \times q_{\text{feed,Na_{2}SO_{4}}}$.

Fig. 5.9. Influence of Na$_{2}$SO$_{4}$ to BaCl$_{2}$ feed ratio on $d_{43}$, feed addition mode (3).
$c_{Na_{2}SO_{4},0} = N_{Na_{2}SO_{4}} / N_{BaCl_{2}} \times 0.03\ \text{mol/l}$, $c_{BaCl_{2},0} = 1.5\ \text{mol/l}$,
$q_{\text{feed,BaCl}_{2}} = 4\ \text{ml/min}$, $q_{\text{feed,Na_{2}SO_{4}}} = 200\ \text{ml/min}$, $N_{stirrer} = 200\ \text{rpm}$. 
Fig. 5.10. Influence of Na$_2$SO$_4$ to BaCl$_2$ feed ratio on the coefficient of variation of the PSD, feed addition mode (3).

\[ c_{Na_2SO_4,0} = 0.03 \text{ mol/l}, \quad c_{BaCl_2,0} = \alpha \times c_{Na_2SO_4,0}, \]

\[ q_{\text{feed, Na}_2SO_4} = 200 \text{ ml/min}, \quad q_{\text{feed, BaCl}_2} = \frac{1}{\alpha} \times q_{\text{feed, Na}_2SO_4}. \]

Fig. 5.11. Influence of flow rate ratio $\alpha$ on $d_{43}$, feed addition mode (3).

\[ c_{Na_2SO_4,0} = 0.03 \text{ mol/l}, \quad c_{BaCl_2,0} = \alpha \times c_{Na_2SO_4,0}, \]

\[ q_{\text{feed, Na}_2SO_4} = 200 \text{ ml/min}, \quad q_{\text{feed, BaCl}_2} = \frac{1}{\alpha} \times q_{\text{feed, Na}_2SO_4}. \]
5.5.1.4. COMPARISON OF EXPERIMENTAL RESULTS OBTAINED FOR DIFFERENT FEED POINTS

Precipitation experiments were conducted for barium chloride feed addition at three different locations in the reactor, as indicated in Fig. 5.1. The influence of the feed location on the properties of the product particles is shown in Fig. 5.12 to Fig. 5.14.

In Fig. 5.12 two PSDs corresponding to experiments with the feed addition modes (2) and (3) are shown. Other operating parameters are identical for both experiments as summarized in the caption of Fig. 5.12. It can be clearly observed in that the PSDs are quite different; particles obtained for feed addition mode (2) are larger than for feed mode (3), but the shape of the two distributions is not significantly different.

The effect of feed addition location on particle size is also illustrated in Fig. 5.13. Here, the influence of mixing on the average particle size $d_{43}$ is shown for three series of experiments, each for a constant feed location but varying stirring rate. The boxes in the figure indicate the experimental results for feed addition mode (1), the triangles refer to the data for addition mode (2), and the diamond symbols indicate the results for feed addition mode (3). The other operating parameters are identical to those in Fig. 5.12. It can be noticed in Fig. 5.13 that the particle size is almost identical for addition modes (1) and (2) over the entire range of agitation rates from 200 rpm to 600 rpm with a $d_{43}$ value of approximately 24 µm. Particles produced in feed mode (3) are much smaller for all agitation rates.

The influence of feed location on particle properties, shown in Fig. 5.12 and Fig. 5.13 for equimolar mixing of reactants, can not be observed when feeding sodium sulfate solution in excess. This is visualized in Fig. 5.14 where two series of experiments are shown, each for a constant feed location but varying agitation rate. The filled triangles in the figure indicate the experimental results for feed addition mode (2), and the filled diamond symbols refer to the data for addition mode (3). It can be clearly seen that the particle size $d_{43}$ is almost identical for both feed addition modes over the whole range of agitation rates.
Fig. 5.12. Influence of feed point position on PSD.

\[ c_{Na2SO4,0} = 0.03 \text{ mol/l, } c_{BaCl2,0} = 1.5 \text{ mol/l, } N_{stirrer} = 200 \text{ rpm,} \]
\[ q_{feed,BaCl2} = 4 \text{ ml/min, } q_{feed,Na2SO4} = 200 \text{ ml/min.} \]

Fig 5.13. Influence of feed point position and agitation rate on \( d_{43} \).

\[ c_{Na2SO4,0} = 0.03 \text{ mol/l, } c_{BaCl2,0} = 1.5 \text{ mol/l,} \]
\[ q_{feed,BaCl2} = 4 \text{ ml/min, } q_{feed,Na2SO4} = 200 \text{ ml/min.} \]
5.5.2 DISCUSSION OF SIMULATION RESULTS

Based on the mixing-precipitation model described in section 5.2.1 a continuous stirred tank process can be simulated following the procedure outlined in section 5.3.3. Using two different examples, the results of the simulations are presented with particular focus on how convergence to the final solution is achieved by following the different steps of the numerical algorithm.

To be able to simulate the process with the finite volume based CFD software FLUENT 6.1, the reactor geometry, shown in Fig. 5.1, is discretized; typically, the reactor domain is subdivided into approximately 500,000 cells.

In step (I) of the numerical procedure presented in section 5.3.3, the flow-field is calculated using a standard $k-\varepsilon$ model. Results obtained using several different numerical grids were compared to confirm that the computed solution is grid independent.

Next, mixing model Eqs. 5.4 to 5.10 are solved. The obtained results are shown in Fig. 5.15 for process operating parameters listed in the caption of the figure.
In Fig. 5.15 a) the distribution of the mixture fraction $\bar{f}$ is shown, whereas Fig. 5.15 b) shows the distribution of the segregation index $I_S$, as defined in Eq. 5.24, for a cross section of the stirred tank. It can be noticed in Fig. 5.15 a) that gradients in mixture fraction are only visible very close to the feed point of the barium chloride feed pipe, where the inlet fluid is rapidly diluted in the bulk. The same pattern of behavior is shown by the distribution of the segregation index $I_S$ shown in Fig. 5.15 b). Significant segregation occurs at the barium chloride feed point, where the segregation index $I_S$ has a value around 0.4. Segregation at the sodium sulfate inlet corresponds to $I_S \approx 0.005$, i.e. negligibly small. It is worth noting that the color map for the segregation index in Fig 5.15 b) is scaled logarithmically. The segregation pattern shown in Fig. 5.15 is typical for small feed addition rates of barium chloride and sodium sulfate solutions. For higher addition rates segregation close to the feed points is more pronounced.

It is clearly noticeable in Fig 5.15 b) that the region with $I_S > 0.01$ is rather small. Since the PDF closure is only applied when $I_S$ is larger than that threshold value, the major part of the computational domain can be described with the simplified closure, as outlined in section 5.3.2.
Fig. 5.15. Distributions of (a) mixture fraction $\bar{f}$ (wall of small feed tube is not visualized), and (b) segregation index $I_s$.

$c_{Na_2SO_4,0} = 0.06 \text{ mol/l}, \quad c_{BaCl_2,0} = 1.5 \text{ mol/l},$

$q_{\text{feed,BaCl}_2} = 4 \text{ ml/min}, \quad q_{\text{feed,Na}_2SO_4} = 200 \text{ ml/min}, \quad N_{\text{stirrer}} = 200 \text{rpm}.$

In the next step of the numerical procedure, referred to as step (II) in section 5.3.3, the computational domain is subdivided into the regions of feed plumes and bulk fluid. For that purpose the computation of concentration and moment distributions is started by performing several hundreds of iterations for the solution of Eqs. 5.16 and 5.18, and the gradient in supersaturation is calculated and used as criterion for the domain decomposition. The result is illustrated in Fig. 5.16 for the same operating conditions as those in Fig. 5.15. Here, two regions within the computational domain identified as feed plumes are shown in red, and the remaining part of the computational domain is assigned to the bulk.
In step (III) of the numerical procedure, the solution for species and particle population transport equations (Eqs. 5.16 and 5.18) is computed resolving concentrations gradients only in the feed plumes while assuming a homogeneously mixed bulk. Average barium and sulfate ion concentrations in the bulk are calculated as outlined in section 5.3.3. Computation results based on that approach are visualized in Fig. 5.17 a). Here, the supersaturation distribution in the reactor is shown for the same operating parameters.

In step (IV) the solution for species and particle population transport equations is computed resolving concentrations gradients within the entire reactor domain. The result is presented in Fig. 5.17 b) in terms of the supersaturation distribution in the reactor. The difference between the distributions shown in Fig. 5.17 a) and b) is rather small. The peak supersaturation value in Fig. 5.17 a) is $S = 76$, i.e. only slightly smaller than the maximum value $S = 81$ observed in Fig. 5.17 b). The difference is so small due to the low feed addition rates, which make the reactants be rapidly diluted in the bulk fluid.
In case of higher addition rates, the results obtained in step (III) and step (IV) are more different, as it can be seen in Fig. 5.18. Here, supersaturation distributions are shown for feed addition mode (3) and addition rates of 500 ml/min and 10 ml/min for sodium sulfate and barium chloride solutions, respectively. Although the predicted maximum supersaturation values obtained in step (III) and (IV) are \( S = 379 \) in Fig. 5.17 a) and \( S = 381 \) in Fig. 5.17 b), i.e. rather similar, the distribution patterns are rather different.

**Fig. 5.17.** Supersaturation distribution, feed addition mode (1).

- \( c_{Na2SO4,0} = 0.03 \text{ mol/l}, \ c_{BaCl2,0} = 1.5 \text{ mol/l}, \ N_{stirrer} = 200 \text{ rpm}, \)
- \( q_{feed,BaCl2} = 4 \text{ ml/min}, \ q_{feed,Na2SO4} = 200 \text{ ml/min}. \)
- a) accounting for concentration gradients in feed plumes only, simulation step (III), as defined in section 5.3.3.
- b) accounting for concentration gradients in the entire domain simulation step (IV), as defined in section 5.3.3.
Fig. 5.18.  Supersaturation distribution, feed addition mode (3).
\[ c_{Na_2SO_4,0} = 0.03 \text{ mol/l}, \ c_{BaCl_2,0} = 1.5 \text{ mol/l}, \ N_{stirrer} = 200 \text{ rpm}, \]
\[ q_{feed,BaCl_2} = 10 \text{ ml/min}, \ q_{feed,Na_2SO_4} = 500 \text{ ml/min}. \]

a) accounting for concentration gradients in feed plumes only, simulation step (III), as defined in section 5.3.3.

b) accounting for concentration gradients in the entire domain simulation step (IV), as defined in section 5.3.3.

In Fig. 5.19 a) and b) nucleation and growth rate distributions, as computed in the step (IV) of the simulation procedure, are presented for operating parameters equal to the ones of Fig. 5.15 and Fig. 5.17. In agreement with the supersaturation distribution shown in Fig. 5.17 b) the nucleation rate has its maximum values close to the feed point of barium chloride. A similar distribution pattern is shown in Fig. 5.17 b) for the growth rate.
Fig. 5.19. Nucleation (a) and growth rate distributions, feed addition mode (1).

\[ c_{Na_{2}SO_{4},0} = 0.03 \text{ mol/l}, \quad c_{BaCl_{2},0} = 1.5 \text{ mol/l},\quad N_{stirrer} = 200 \text{ rpm}, \]
\[ q_{feed,BaCl_{2}} = 4 \text{ ml/min}, \quad q_{feed,Na_{2}SO_{4}} = 200 \text{ ml/min}. \]

5.5.3. COMPARISON OF EXPERIMENTAL AND MODELING RESULTS

In this section the simulation results and the experimental data described in section 5.5.1 are compared and discussed for three different feed positions (see sections 5.5.3.1, 5.5.3.2 and 5.5.3.3). Simulation results are exploited to explain the experimental observations whenever possible.

5.5.3.1. COMPARISON OF EXPERIMENTAL AND SIMULATION RESULTS FOR ADDITION MODE (1)

The experimental data presented in Fig. 5.3 and Fig. 5.4 indicate that in the case of feed mode (1) the particle size \( d_{43} \) is similar for all operating conditions analyzed in this work. The same behavior can be predicted with the model. This
is shown in Fig. 5.20, where experimental data and model results for the influence of agitation rate on the particle size $d_{43}$ are compared. The solid and the dashed line in Fig. 5.20 represent simulation results obtained in step (III) and (IV) of the simulation procedure, respectively. As discussed in detail in section 5.5.2 for the supersaturation distributions of the process, predictions obtained in step (III) and (IV) tend to agree well, when the feed addition rates of barium chloride and sodium sulfate are small. Accordingly, also predictions for $d_{43}$ obtained in steps (III) and (IV) are quite similar, as shown in Fig. 5.20.

In order to explain why the particle size $d_{43}$ in Fig. 5.20 does not change with increasing agitation rate, the corresponding supersaturation distributions are analyzed in the following. In Fig. 5.21 the spatial distribution of supersaturation is visualized by showing the iso-supersaturation surface for $S=30$, in Fig. 5.21 a) for an agitation rate of 200 rpm and in Fig. 5.21 b) for an agitation rate of 600 rpm. It can be noticed that the size of the feed plumes decreases with increasing agitation rate. This can be explained by the two facts that the local fluid velocity is proportional to the stirrer speed $N_{\text{stirrer}}$ and the micromixing
intensity is proportional to $N_{\text{stirrer}}^{3/2}$. Thus, an increase in agitation rate results in the shrinking of the feed plumes.

The supersaturation is smaller than $S=100$ at any agitation rate, which is shown in the precipitation diagram in Fig. 5.22. Here, processes are visualized for agitation rates of 200 rpm and 600 rpm and otherwise identical operating parameters as in Fig. 5.20. The circles in Fig. 5.22 indicate barium and sulfate ion concentrations at different locations in the reactor as computed with the CFD model in step (IV). Black symbols refer to a process with a stirring rate of 200 rpm, red symbols correspond to 600 rpm agitation rate and the solid lines are iso-supersaturation lines. The area in the diagram, which is occupied by symbols corresponding to specific operating conditions, is referred to as the operating region in the following. It can be noticed that the operating regions are similar for both agitation rates, with the region corresponding to 600 rpm shifted slightly towards smaller supersaturation levels. As for Fig. 5.21, this can be
again explained by the faster dilution of the reactants in the bulk at higher agitation rate.

However, the difference in supersaturation profiles has only a small impact on the rate of particle formation, especially because under these conditions particle formation is dominated by heterogeneous nucleation. Contrary to homogeneous nucleation, which is controlling for $S > 280$, as shown in Fig. 4.3, the heterogeneous nucleation rate depends only weakly on the supersaturation. Therefore, a change in agitation rate has only a small influence on the rate of particle formation and thereby on the average particle size $d_{43}$.

**Fig. 5.22.** Operating diagram, feed addition mode (1).

$c_{Na_{2}SO_{4},0} = 0.03$ mol/l, $c_{BaCl_{2},0} = 1.5$ mol/l,

$q_{feed,BaCl_{2}} = 4$ ml/min, $q_{feed,Na_{2}SO_{4}} = 200$ ml/min, $k_a = 47.0$. 
5.5.3.2 COMPARISON OF EXPERIMENTAL AND SIMULATION RESULTS FOR ADDITION MODE (2)

The experimental data presented in Fig. 5.5 and Fig. 5.6 for feed addition mode (2), show that the particle size $d_{43}$ is not altered when modifying mixing conditions in the reactor by changing either the agitation rate or the flow rate ratio.

It is shown in Fig. 5.23 that experimental data for the average particle size $d_{43}$ can be predicted well by the model. A constant particle size of 23 $\mu$m is calculated for the entire range of agitation rates from 200 rpm to 600 rpm. The small deviations between model prediction and experimental data are in the range of the experimental uncertainty, which is considered to be similar to that of the data shown in Fig. 5.20.

In Fig. 5.24 supersaturation distributions are presented, calculated for process parameters corresponding to Fig. 5.23. Fig. 5.24 a) and Fig. 5.24 b) show the distributions corresponding to agitation rates of 200 rpm and 600 rpm, respectively. The supersaturation pattern in both figures clearly indicates that barium chloride and sodium sulfate are transported from the feed inlets in the radial direction by the impeller discharge. Due to the small distance between the two feed tubes, sodium sulfate and barium chloride solutions can get in contact immediately after entering the reactor and before the sodium sulfate solution is completely diluted in the bulk. This effect is more pronounced for small agitation rates, where the dilution of the feed in the bulk is relatively slow. This is confirmed by Fig. 5.24 where the maximum supersaturation for 200 rpm ($S = 175$) is visibly larger than for 600 rpm ($S = 130$).

Since this supersaturation level is smaller than the threshold for homogeneous nucleation, changes in agitation rate have a negligible impact on the average particle size $d_{43}$, as shown in Fig. 5.23. An increase in agitation rate from 200 rpm to 600 rpm leads only to small modifications of the operating region in the precipitation diagram, as shown in Fig. 5.25.
Fig. 5.23. Comparison of experimental and simulation results for the influence of agitation rate on $d_{43}$, feed addition mode (2).
$c_{Na_{2}SO_{4},0} = 0.03 \text{ mol/l}$, $c_{BaCl_{2},0} = 1.5 \text{ mol/l}$,
$q_{\text{feed},BaCl_{2}} = 4 \text{ ml/min}$, $q_{\text{feed},Na_{2}SO_{4}} = 200 \text{ ml/min}$, $k_a = 47.0$.

Fig. 5.24. Supersaturation distribution, feed addition mode (2).
$c_{Na_{2}SO_{4},0} = 0.03 \text{ mol/l}$, $c_{BaCl_{2},0} = 1.5 \text{ mol/l}$,
$q_{\text{feed},BaCl_{2}} = 4 \text{ ml/min}$, $q_{\text{feed},Na_{2}SO_{4}} = 200 \text{ ml/min}$, $k_a = 47.0$,
a) $N_{\text{stirrer}} = 200 \text{ rpm}$  b) $N_{\text{stirrer}} = 600 \text{ rpm}$. 
5.5.3.3. COMPARISON OF EXPERIMENTAL AND SIMULATION RESULTS FOR ADDITION MODE (3)

In the following, simulation results and experimental findings for processes operated in feed addition mode (3) are compared and discussed.

In Fig. 5.26 the influence of mixing on the particle size $d_{43}$ by changes in the flow rate ratio $\alpha$ is illustrated. For small flow rate ratios up to $\alpha = 25$ experimental data for $d_{43}$ can be predicted by the model. However, the decrease in the measured particle size from 18 µm to 11 µm for flow rate ratios larger than $\alpha = 25$ is not captured by the model, which predicts an almost constant particle size over the whole range of $\alpha$ values. This model behavior can be explained by analyzing the calculated supersaturation distributions for processes.
having different flow rate ratios. In Fig. 5.27 the calculated operating regions are shown for two different values of $\alpha$. The black and the red circles in the figure correspond to $\alpha=7.5$ and $\alpha=50$, respectively. When comparing both operating regions, it can be clearly noticed that parts of the operating region are shifted towards larger barium concentrations for $\alpha=50$. However, the range of supersaturation is similar for both processes with a maximum value around $S=400$. This is due to the characteristic of the Pitzer activity model, which is reflected in the shape of the iso-supersaturation lines. The bend of the iso-supersaturation lines towards larger concentrations with increasing mixture asymmetry, e.g. further away from the diagonal of the precipitation diagram, determines that an increase of $\alpha$ does not lead to an increase in supersaturation. Since the nucleation rate model used in this work assumes a functional dependence of the nucleation rate on supersaturation only, similar particle formation rates are predicted by the model for processes with $\alpha=50$ and $\alpha=7.5$. This in turn leads to similar predictions for the average particle size $d_{43}$, since the particle growth rate is not significantly different in the two cases. The mismatch between experimental data and model predictions for large values of $\alpha$ was already observed for semibatch precipitation processes, as shown in Fig. 4.9 in chapter 3. The error in model prediction can most probably be attributed to the simplifying assumption for the nucleation rate model. There is experimental evidence that nucleation kinetics for barium sulfate are strongly influenced by the ionic strength of a solution [5.18],[5.19] and changes in the ratio of barium to sulfate concentration [5.18], [5.20] at equal supersaturation. However, up to now no experimental nucleation rate data of sufficient accuracy are available to derive nucleation rate model equations accounting for these effects.

In Fig. 5.28 the influence of stirring rate on the particle size $d_{43}$ is presented. Model predictions and experimental data exhibit no influence of agitation rate on the particle size $d_{43}$ over the whole range of stirring rates from 200 rpm to 600 rpm. As shown in Fig. 5.26 for $\alpha=50$ and $N_{\text{stirrer}}=200$ rpm, experimental values for $d_{43}$ in Fig. 5.28 are overpredicted by the model also for different agitation rates. The negligible influence of agitation rate on the process is reflected in the operating diagrams shown in Fig. 5.29. In this figure black and
red circles correspond to agitation rates of 200 rpm and 600 rpm, respectively. It is clearly noticeable in the figure that the operating regions for both agitation rates are quite similar. The operating regions differ only slightly in size. Due to higher intensity of mixing at elevated agitation rates freshly fed fluid is diluted faster in the bulk, which is reflected in the shrinkage of the operating region for a larger agitation rate.

In Fig. 5.30 the influence of feed addition rates on the particle size $d_{43}$ is visualized. For all experiments presented in the figure the feed rate ratio is kept constant at $\alpha = 50$. Experimental data for $d_{43}$ indicate an almost constant particle size over the range of sodium sulfate feed addition rate $q_{Na2SO4}$ from 200 ml/min to 2000 ml/min. As in Fig. 5.26 for $\alpha = 50$ and $q_{Na2SO4} = 200$ ml/min, the model over predicts the particle size $d_{43}$ also for the higher addition rates $q_{Na2SO4}$ presented in Fig. 5.30. The trend of a slightly decreasing particle size with increasing addition rates observed in the simulations is not in contradiction with the experimental findings, where such small changes can not be resolved due to the experimental uncertainty.

Changes in addition rates influence the process due to two different effects. First, an increase of the addition rate increases the flux of barium chloride and sodium sulfate into the reactor. Thereby, concentrations in the reactor should be increased, which in turn leads to an increase in supersaturation and particle formation rates, causing a smaller particle size. Secondly, an increase of addition rates leads to a decrease in mean residence time, which also causes a decrease in average particle size. The first effect of increasing concentration with increasing addition rates is visualized in Fig. 5.31, where the operating regions for different addition rates are shown. The black and the red circles in Fig. 5.31 correspond to sodium sulfate addition rates of 200 ml/min and 1500 ml/min, respectively. It is clearly shown in the figure, that the operating region representing the larger addition rate is shifted towards larger concentrations.

In Fig. 5.32 and Fig. 5.34, the comparison of experimental data and model predictions is shown for changes in $\beta$. As already shown in Fig. 5.26, the model overpredicts the particle size $d_{43}$ for $\alpha = 50$ and a feed ratio $\beta = 1$. This also applies to model predictions up to a feed ratio $\beta = 2$, as shown in Fig. 5.32. For
\[ \beta = 3 \] the experimental value of \( d_{43} \) is slightly underpredicted by the model. The decrease in particle size \( d_{43} \) with increasing feed ratio \( \beta \) can be attributed to a significantly increasing supersaturation. This is shown in Fig. 5.33, where the spatial supersaturation distribution in the reactor is shown for \( \beta = 2 \). The maximum supersaturation shown in this figure is \( S = 730 \), i.e. significantly larger than \( S = 400 \) observed for \( \beta = 1 \) (see Fig. 5.27). In both cases supersaturation is larger than the threshold value for homogeneous nucleation, which controls the particle formation process. Thus, the difference in supersaturation for different feed ratios \( \beta \) corresponds to significantly different nucleation rates, thus leading to decreasing particle size with increasing \( \beta \). Although, the average particle size \( d_{43} \) changes with increasing feed ratio \( \beta \), no influence on the shape of the PSD can be observed. This is reflected in Fig. 5.34, where the coefficient of variation (CV) of the PSD is shown as a function of \( \beta \). Experimental data as well as simulation results report an almost constant value of CV for the entire range of \( \beta \). The experimental value for CV around 0.4 is slightly misestimated by the model, which predicts CV \( \approx 0.49 \) for all values of \( \beta \) shown in Fig. 5.34.
Fig. 5.26. Influence of flow rate ratio $\alpha$ on $d_{43}$, feed addition mode (3).

$c_{Na_{2}SO_{4},0} = 0.03 \text{ mol/l}, c_{BaCl_{2},0} = \alpha \times 0.03 \text{ mol/l}, N_{\text{stirrer}} = 200 \text{ rpm},$
$q_{\text{feed,Na}_{2}SO_{4}} = 200 \text{ ml/min}, q_{\text{feed,BaCl}_{2}} = 1 / \alpha \times q_{\text{feed,Na}_{2}SO_{4}}, k_a = 8.17.$

Fig. 5.27. Operating diagram, feed addition mode (3).
$c_{Na_{2}SO_{4},0} = 0.03 \text{ mol/l}, c_{BaCl_{2},0} = 1.5 \text{ mol/l}, N_{\text{stirrer}} = 200 \text{ rpm},$
$q_{\text{feed,BaCl}_{2}} = 4 \text{ ml/min}, q_{\text{feed,Na}_{2}SO_{4}} = 200 \text{ ml/min}, k_a = 8.17.$
Fig. 5.28. Influence of agitation rate on $d_{43}$, feed addition mode (3).

$c_{Na_{2}SO_{4},0} = 0.03 \text{ mol/l}, c_{BaCl_{2},0} = 1.5 \text{ mol/l},$
$q_{\text{feed,BaCl}_{2}} = 4 \text{ ml/min}, q_{\text{feed,Na}_{2}SO_{4}} = 200 \text{ ml/min}.$

Fig. 5.29. Influence of agitation rate on operating diagram, feed addition mode (3).

$c_{Na_{2}SO_{4},0} = 0.03 \text{ mol/l}, c_{BaCl_{2},0} = 1.5 \text{ mol/l},$
$q_{\text{feed,BaCl}_{2}} = 4 \text{ ml/min}, q_{\text{feed,Na}_{2}SO_{4}} = 200 \text{ ml/min}.$
Fig. 5.30. Influence of feed addition rate on $d_{43}$, feed addition mode (3).
$c_{NaSO_4,0} = 0.03 \text{ mol/l}, c_{BaCl_2,0} = 1.5 \text{ mol/l},$
$q_{feed,BaCl_2} = 0.02 \times q_{feed,NaSO_4}, N_{stirrer} = 200 \text{ rpm}.$

Fig. 5.31. Influence of feed addition rate on operating diagram, feed addition mode (3).
$c_{NaSO_4,0} = 0.03 \text{ mol/l}, c_{BaCl_2,0} = 1.5 \text{ mol/l},$
$q_{feed,BaCl_2} = 0.02 \times q_{feed,NaSO_4}, N_{stirrer} = 200 \text{ rpm}.$
Fig. 5.32. Influence of Na\textsubscript{2}SO\textsubscript{4} to BaCl\textsubscript{2} feed ratio on \(d_{43}\) feed at \(F_{3,\text{BaCl}_2}\).

\[
N_{\text{Na}_2\text{SO}_4} / N_{\text{BaCl}_2} = 0.03 \text{ mol/l, } c_{\text{Na}_2\text{SO}_4,0} = 0.06 \text{ mol/l, } c_{\text{BaCl}_2,0} = 1.5 \text{ mol/l,}
\]

\[q_{\text{feed, BaCl}_2} = 4 \text{ ml/min, } q_{\text{feed, Na}_2\text{SO}_4} = 200 \text{ ml/min, } N_{\text{stirrer}} = 200 \text{ rpm.}\]

Fig. 5.33. Supersaturation distribution, feed addition mode (3).

\[
c_{\text{Na}_2\text{SO}_4,0} = 0.06 \text{ mol/l, } c_{\text{BaCl}_2,0} = 1.5 \text{ mol/l, } N_{\text{stirrer}} = 200 \text{ rpm,}
\]

\[q_{\text{feed, BaCl}_2} = 4 \text{ ml/min, } q_{\text{feed, Na}_2\text{SO}_4} = 200 \text{ ml/min.}\]
In the following, results obtained for different feed addition modes, but otherwise identical operating parameters will be compared. For experimental data this comparison is illustrated in Fig. 5.13, where data for $d_{43}$ are shown by three series of experiments, each for a constant feed location but varying agitation rate. The simulation results corresponding to the three series in Fig.5.13 are presented in Fig. 5.20, Fig. 5.23 and Fig. 5.28 for feed addition modes (1), (2) and (3), respectively. It is evident that results obtained for feed addition mode (3) are different in comparison with those for mode (1) and (2), which are almost identical. Experimental data and simulation results for the particle size $d_{43}$ indicate that particles produced in feed addition mode (3) are always smaller.

Such behavior can be explained by comparing the spatial supersaturation distributions and operating regions for the different addition modes. In Fig. 5.17
and Fig. 5.24 a) supersaturation profiles for processes with identical operating parameters but the different feed addition mode (1) and (2) are shown. The supersaturation pattern in both figures indicates that barium chloride and sodium sulfate feed are transported in radial direction by the impeller discharge. Due to the small distance between the two feed tubes in addition mode (2) sodium sulfate and barium chloride solutions can contact immediately after entering the reactor and before the sodium sulfate solution is completely diluted in the bulk. Direct contacting of barium chloride and sodium sulfate feed does not occur for feed addition mode (1), where both reactants contact after dilution through the bulk. That difference in behaviors explains why the generated supersaturation is higher for feed addition mode (2) than for mode (1).

The effect of direct feed contacting is even more pronounced for processes with feed addition mode (3), where the distance between the feed tubes is smaller than for feed mode (2). Therefore, supersaturation reached in feed mode (3) is typically higher than for mode (2). This is shown in Fig. 5.35, where three operating regions for processes with identical operating parameters but different feed addition mode are visualized. The black, blue and red symbols correspond to feed addition modes (1), (2) and (3), respectively.

Although the supersaturation level is different for feed addition modes (1) and (2), the size of particles produced is similar in both cases, as can be seen in Fig. 5.13, where data for identical operating parameters but different feed addition mode are compared. This can be explained by the fact that for both feed modes supersaturation is smaller than the threshold for homogeneous nucleation.
5.6. CONCLUSIONS

The precipitation of barium sulfate upon mixing of barium chloride and sodium sulfate has been investigated experimentally and through simulations for a continuous stirred tank process.

A CFD based closure model for the mixing-precipitation process describing all relevant phenomena from the micro- to the macroscale, was presented. It was discussed in detail how this model can be applied to the process simulation of a continuous stirred tank process. In particular it was addressed, how a complex liquid phase and precipitation kinetics model can be implemented in a CFD code allowing computational efficient process simulations. Furthermore, a newly developed numerical procedure was presented, which is suitable to solve the
population balance and reactant transport equations effectively. The procedure was found to be robust and computational efficient for all tested cases.

Continuous stirred tank precipitation experiments were conducted for a wide range of operating conditions varying the feed point locations, agitation rate, feed addition rate and reactant concentrations. Experimental results revealed that the average size of the product particles is particularly sensitive to the relative positions of the feed inlets. For all operating parameters analyzed in this work the particle size was insensitive to mixing, when feed tubes of barium chloride and sodium sulfate were placed far apart from each other. By placing the feed tubes very close to each other, the particle size could be clearly influenced. This could be shown by modifying the feed flow ratio, which led to a change in particle size.

The CFD closure model was found to predict experimental data with reasonable accuracy for operating conditions corresponding to low supersaturation or small ratios of feed flow rates. For large flow rate ratios the model typically overpredicted the average size of product particles. This is most likely due to the assumption for the nucleation rate model that the nucleation rate is a function of supersaturation only. Experimental work published in the literature has shown that the barium sulfate nucleation rate strongly increases with increasing ionic strength or an increasing deviation of the barium to sulfate concentration ratio from one [5.18],[5.19],[5.20]. This could explain the experiment-model mismatch observed here. However, to be able to account for these effects in an improved nucleation model a wider experimental database of nucleation rate measurements would be necessary, which is not available up to now.

Although the model does not always predict the particle size correctly, it gives a lot of insight into the continuous stirred tank process, which can not be obtained based on experiments only. The distribution of reactants by the action of the macro-flow is captured precisely, since the fluid in the reactor is characterized with a rather fine spatial discretization in all three dimensions. Also small scale mixing effects are accounted for and therefore realistic spatial distributions of particle formation kinetics in the reactor can be obtained. Thus, simulations with the CFD closure model give detailed information, which is essential for the optimization of the reactor design and for the scale-up.
5.7 NOMENCLATURE CHAPTER 5

\( c_i \) [mol m\(^{-3}\)] \quad \text{local concentration of} \ i

\( c_{T0} \) [mol m\(^{-3}\)] \quad \text{initial or feed concentration of a passive non-reacting tracer}

\( c_T \) [mol m\(^{-3}\)] \quad \text{local concentration of a passive non-reacting tracer}

\( c_i^\infty \) [mol m\(^{-3}\)] \quad \text{local concentration of substance} \ i \ \text{for instantaneous precipitation}

\( c_i^\infty \) [mol m\(^{-3}\)] \quad \text{local average concentration of substance} \ i \ \text{for an instantaneous precipitation}

\( \overline{c}_i \) [mol m\(^{-3}\)] \quad \text{local average concentration of substance} \ i \ \text{in bulk}

\( c_{i,0} \) [mol m\(^{-3}\)] \quad \text{feed concentration of substance} \ i \ \text{in bulk}

\( D \) [m] \quad \text{inner reactor diameter}

\( D_m \) [m\(^2\) s\(^{-1}\)] \quad \text{molecular diffusivity}

\( D_T \) [m\(^2\) s\(^{-1}\)] \quad \text{turbulent diffusivity}

\( d_{imp} \) [m] \quad \text{impeller diameter}

\( d_{in,j} \) [m] \quad \text{inner diameter of feed tube} \ j

\( d_{outlet} \) [m] \quad \text{inner diameter of reactor outlet}

\( d_{sh} \) [m] \quad \text{impeller shaft diameter}

\( E \) [s\(^{-1}\)] \quad \text{local engulfment parameter}

\( f \) [-] \quad \text{local dimensionless concentration of non-reacting tracer}

\( \overline{f} \) [-] \quad \text{local average dimensionless concentration of non-reacting tracer}

\( F_i \) [-] \quad \text{feed point} \ i

\( \overline{G} \) [m/s] \quad \text{local average growth rate}

\( G \) [m/s] \quad \text{local growth rate}

\( H_{liq} \) [m] \quad \text{height of water level above the bottom of the vessel}

\( H_{imp} \) [m] \quad \text{height of impeller above the bottom of the vessel}

\( I_S \) [-] \quad \text{Danckwerts' intensity of segregation}

\( k \) [m\(^2\) s\(^{-2}\)] \quad \text{kinetic energy of turbulence}
\( k_s \) [-] surface shape factor of particles
\( k_v \) [-] volume shape factor of particles
\( k_d \) [m s\(^{-1}\) kg mol\(^{-1}\)] mass transfer coefficient
\( k_r \) [m s\(^{-1}\)] integration rate coefficient
\( K_{SP} \) [mol\(^2\) m\(^{-6}\)] thermodynamic solubility product
\( \bar{m}_j \) [m\(^l\) m\(^{-3}\)] local average \( j \)-th moment of PSD
\( m'_j \) [m\(^l\) m\(^{-3}\)] local fluctuation of \( j \)-th moment of PSD
\( \dot{m}_{\text{outlet}} \) [kg s\(^{-1}\) m\(^{-2}\)] specific mass flowrate at the outlet
\( M \) [kg kmol\(^{-1}\)] molar mass
\( \dot{M} \) [kg s\(^{-1}\)] mass flowrate
\( N \) [s\(^{-1}\)] stirring rate
\( q_i \) [ml min\(^{-1}\)] feed addition rate of \( i \)
\( R_{Di} \) [s\(^{-1}\)] dissipation rate of variance component \( i \)
\( R_{Pi} \) [s\(^{-1}\)] production rate of variance component \( i \)
\( R_N \) [m\(^3\) s\(^{-1}\)] local nucleation rate
\( \bar{R}_N \) [m\(^3\) s\(^{-1}\)] local average nucleation rate
\( S_A \) [-] supersaturation ratio
\( S_C \) [-] Schmidt number
\( \bar{u} \) [m s\(^{-1}\)] local average velocity
\( \bar{u}_{pi} \) [m s\(^{-1}\)] local average particle velocity
\( u'_{pi} \) [m s\(^{-1}\)] local fluctuation of particle velocity

**Greek letters**

\( \alpha \) [-] ratio of sodium sulfate to barium chloride feed addition rate
\( \beta \) [-] ratio of the molar barium chloride feed addition rate to molar sodium sulfate feed addition rate
\( \delta \) [-] under-relaxation factors
\[ \Delta M_i \quad [-] \quad \text{mass balance error for substance } i \]

\[ \varepsilon \quad [m^2 s^{-3}] \quad \text{local energy dissipation rate} \]

\[ \gamma_i \quad [-] \quad \text{activity coefficient} \]

\[ \gamma_{\pm} \quad [-] \quad \text{mean ionic activity coefficient} \]

\[ \sigma_i^2, \sigma_S^2 \quad [-] \quad \text{dimensionless concentration variances} \]

\[ \nu \quad [m^2 s^{-1}] \quad \text{kinematic viscosity} \]

\[ \rho \quad [kg m^{-3}] \quad \text{density} \]

### 5.8 REFERENCES CHAPTER 5


6. SIMULATION OF A SEMIBATCH STIRRED TANK MIXING-PRECIPITATION PROCESS USING A CFD BASED MODEL

Simulation results for a barium sulfate mixing-precipitation process in a semibatchwise operated stirred tank are presented. The results are obtained with a detailed CFD based mixing-precipitation model accounting for mixing from the small to the large scales using a PDF-closure model. The influence of mixing on stirred tank precipitation is shown by varying different operating conditions, e.g. agitation rate and reactant concentrations. CFD simulation results are compared with experimental data and E-model simulation results as presented in chapter 4, thereby assessing the features of the different models.
6.1. INTRODUCTION

Semibatch stirred tank precipitation is a widely used process in the fine chemicals and pharmaceutical industry. Although the requirements for precipitate properties are often high, up to now no standard design procedures could be established for such process, which allow for a rational process development leading to a product of desired properties. Commonly the process design is based on empirical methods and is usually rather time consuming. This is in particular the case, when the precipitation is fast and turbulent mixing is influencing the course of a process. Under such conditions the model based process design seems to be most promising to account for the complex interactions between all the mechanisms involved.

In literature different types of models were proposed to describe such processes [6.1], [6.2], [6.3], [6.4], [6.5], [6.6]. In most cases small-scale mixing mechanisms were characterized with the E-model, as presented in chapter 4, whereas macro-mixing is described by simplified models [6.4], [6.5], [6.6]. Mixing-precipitation models, which use a detailed characterization of the macro-mixing are presented in [6.1], [6.2], [6.3], but in these cases small-scale mixing effects are neglected. However, it was shown in chapter 4 and 5, that accounting for such effects can be crucial to capture the system behavior correctly.

The aim of this chapter is to present a mixing-precipitation model for a semibatch process, which accounts for all mixing effects from the micro- to the macro-scale. The CFD based model resolves macro-mixing in detail and is therefore well suited for reactor design optimizations. The model shown in section 5.2 is employed and the application of this general model to a semibatch process is discussed in section 6.2. The barium sulfate semibatch precipitation process, which is presented in chapter 4, is simulated for single feed addition in the impeller discharge, as shown in Fig. 6.1. CFD modeling results are presented in section 6.3 and are compared in section 6.4 with experimental data and modeling results obtained with the E-model, shown in chapter 4. Thereby the performance of both models is assessing.
6.2. APPLICATION OF THE MIXING-PRECIPITATION MODEL TO A SEMIBATCH STIRRED TANK PROCESS

In the following it is described, how the mixing-precipitation model presented in section 5.2 can be applied to the stirred tank process shown in Fig. 6.1.

Contrary to the continuous stirred tank precipitation analyzed in chapter 5, the semibatch process has to be characterized by a time dependent simulation, which can significantly increase the computational burden. It is described in chapter 3 for competitive homogeneous reaction, how the numerical effort can be reduced in a semibatch reactor by approximating the time evolution by a series of continuous processes. However, that approach is less accurate and more difficult to implement for a precipitation process. Here, reaction and particle formation are not confined to a small region close to the feed pipes as it is the case for the competitive homogeneous reactions. Typically, nucleation and growth occur throughout the reactor and the overall dynamics of the particle
formation can be significantly influenced by changes in the bulk. These changes cannot be captured easily through a series of continuous processes. Therefore, the semibatch precipitation is modeled by fully resolving its time evolution.

For the semibatch process the macro flow field, mixing model, and reactant and PSD moment model equations are solved sequentially, as already described for the continuous process in section 5.3. After discretizing the reactor domain into 600,000 cells, the flow-field is calculated using a standard $k-\varepsilon$ model employing the finite volume based CFD software FLUENT 6.1, which is also used further on to solve the other model equations. The flow field can be assumed as constant during the whole feed addition time, since the volume of feed is small in comparison with the entire fluid volume.

In a second step, mixing model eqs. 5.3 to 5.10 are solved as described in chapter 3.4.1.1 for the double feed semibatch process. That approach is also applicable here, because the reactor operating conditions are similar to the ones analyzed in chapter 3. Again, the feed addition time is very large in comparison with the time scales for all mixing mechanisms from the micro- to the macro-scale. As discussed in chapter 3.4.1.1, a quasi-steady-state situation can be assumed at any time shortly after the feed addition has started. Thus, the spatial mixture fraction distribution can be computed using a steady state simulation.

To enable the application of the same computational procedure for the single feed as used for the double feed process, a virtual feed point is created in the computational domain, which is located far away from the feed pipe shown in Fig. 6.1. This virtual feed point is not modeled as it having the real geometry of a feed pipe, since this would influence the flow field simulation. Instead, it is only defined by applying locally the boundary condition $f_{\text{virtual feed point}} = 0$. This condition is used together with the second boundary condition $f_{\text{sodium sulfate feed}} = 1$ at the feed inlet to compute the spatial distribution of the mixture fraction $\bar{f}$, as described in chapter 3.4.1.1. The computed distribution of $\bar{f}$ is renormalized and then the distributions of the variance components are determined as explained in chapter 3.4.1.1. Thereby, all information is obtained, that is required to express the Beta-PDF at every location in the computational domain. As discussed in section 3.4.1.1, the Beta-
PDF describes mixing between the fresh feed entering the reactor and the bulk fluid at any time during the feed addition.

In the third step, reactant and PSD moment transport equations are solved using the kinetics model and the PDF closure described in chapter 5.3.1 and 5.3.2. When computing the time dependent solution for the spatial distributions of reactants and PSD moments, the numerical instabilities, which are observed in the simulation of a continuous process, do not occur. Thus, the computational procedure applied for the simulation of a semibatch process is simpler than the one presented in section 5.3.3 for the continuous process. In case of the semibatch process, all the model equations can be solved using under-relaxation values equal to one and fast convergence within each time step can be achieved.

The time stepping procedure has been optimized to allow for an accurate process characterization within reasonable computation time. The convergence criteria presented in section 5.3.3 were used to judge on the quality of the time stepping procedure. After testing several methods to discretize the feed addition time, a standard procedure was established. The feed addition time is divided into two distinct phases: first, a short time period after the start of feed addition, where the spatial reactant and PSD moment distributions change rapidly until distribution patterns are established. These change only slowly afterwards during the rest of the feed addition time, which is in turn referred to as the second phase. For the operating conditions analyzed in this chapter, the first part of the feed addition time is approximately one percent of the total. This first part is typically discretized into 200 time intervals, and the rest of feed addition time is subdivided into another 1000 intervals. Using this time discretization the entire feed addition can be simulated accurately within a computation time of approximately 100 hours, when using a 2.4 GHz Xeon single processor computer with 2 GB of RAM.
6.3 DISCUSSION OF SIMULATION RESULTS

Based on the mixing-precipitation model described in section 5.2.1 a semibatch stirred tank process can be simulated following the procedure outlined in section 6.2. Using one example, the results of a typical semibatch process simulation are presented in the following.

After discretizing the reactor geometry, shown in Fig. 6.1, the flow-field is calculated using a standard $k$-$\varepsilon$ model and mixing model equations are solved as described in sections 6.2 and 3.4.1.1. The obtained results are shown in Fig. 6.2 for process operating parameters listed in the caption of the figure. In Fig. 6.2 a) the spatial distribution of the renormalized mixture fraction $\tilde{f}^*$, defined by eq. 3.26, is shown and in Fig. 6.2 b) the distribution of the total variance $\sigma_s$ is visualized using a logarithmically scaled color table. It can be noticed in both figures that segregation occurs only in a small region close to the feed pipe.

In the next step of the numerical procedure, the time dependent solutions for the spatial reactant and PSD moment distributions are calculated. A typical result is presented in Fig. 6.3, where the time evolution of the supersaturation distribution is shown by a time series of six spatial distributions, which are labeled chronologically in the figure from 1 to 6. The operating conditions of the presented semibatch process are listed in the caption of the figure and correspond to the ones of Fig. 6.2. The volume ratio $\alpha$ and the average initial concentrations $\bar{c}_{i,0}$ listed in the caption are defined by eqs. 4.27 and 4.29, respectively. For the sodium sulfate feed addition rate of 8.2 ml/min and the volume ratio $\alpha = 50$ the duration of feed addition is 1625.8 sec when mixing equimolar amounts of barium chloride and sodium sulfate. All supersaturation distributions shown in Fig. 6.3 are plotted using the same logarithmically scaled color table. It can be noticed in the figure that already shortly after the start of feed addition high supersaturation is established close to the feed point. In distribution 1, which corresponds to a time of 4.3 sec after the start of feed addition, a maximum supersaturation of $S=580$ is achieved, which is never exceeded. Major changes can be recognized in the supersaturation of the bulk fluid. In distribution 3, corresponding to $t=83.9$ sec, the highest bulk
supersaturation of the whole time sequence is reached. When further increasing time the supersaturation visibly decreases. In distribution 6, corresponding to the end of feed addition at $t = 1625.8$ sec, the bulk and the peak supersaturation are significantly smaller in comparison with distributions 1 to 5.

**Fig. 6.2** Distributions of (a) mixture fraction $f^*$ (feed tube wall is not visualized), and (b) total variance $\sigma_s$.

$q_{\text{feed, Na}_2\text{SO}_4} = 8.2 \text{ ml/min}, N_{\text{stirrer}} = 180 \text{ rpm}.$
Fig. 6.3. Time series of supersaturation distributions representing the entire feed addition time of 1625 sec.

\[
\bar{c}_{\text{Na}_2\text{SO}_4,0} = \bar{c}_{\text{BaCl}_2,0} = 0.02 \text{ mol/l},
\]

\[
q_{\text{feed, Na}_2\text{SO}_4} = 8.2 \text{ ml/min}, N_{\text{stirrer}} = 180 \text{ rpm}, \alpha = 50.
\]
In Fig. 6.4 the time evolution of the average supersaturation in the reactor is visualized for the entire duration of a precipitation process with operating conditions equal to the ones in Fig. 6.2 and 6.3. The results of two simulations are shown. The solid line corresponds to results obtained with the numerical procedure outlined in section 6.2 using the PDF-closure model, as described in section 5.3.2 to account for small scale mixing effects. The dashed line corresponds to results obtained without a PDF-closure model, thus neglecting the small scale mixing influences. The six points in time, which correspond to the spatial distributions shown in Fig. 6.3, are also indicated in Fig. 6.4. The simulation results in Fig. 6.4 highlight the trend also observed in Fig. 6.3, i.e. the average supersaturation is first increasing and then decreasing continuously until the end of feed addition. Afterwards the supersaturation rapidly decreases to reach equilibrium conditions. Results obtained with both simulation approaches show the same pattern of behavior with the main difference that average supersaturation starts to decrease earlier when neglecting small scale mixing effects.

![Graph showing time evolution of average supersaturation during precipitation process.](image)

**Fig. 6.4.** Time evolution of average supersaturation during the precipitation process, feed addition time of 1625 sec.

\[ \overline{c}_{Na_2SO_4,0} = \overline{c}_{BaCl_2,0} = 0.02 \text{ mol/l}, \]

\[ q_{feed, Na_2SO_4} = 8.2 \text{ ml/min}, \ N_{stirrer} = 180 \text{ rpm}, \ \alpha = 50. \]
Such behavior of the average supersaturation can be explained by the evolution of reactant concentrations in the system. Initially only barium chloride is present in the reactor. From the start of feed addition the sodium sulfate concentration is continuously increased which results in an increasing supersaturation. Then the process is dominated by the decrease in reactant concentrations due to the particle formation, which leads to a decrease in supersaturation. The effect of decreasing reactant concentrations later during the feed addition is shown in Fig. 6.5. Here the average barium chloride concentration in the reactor is shown as a function of time. The solid and dashed lines correspond to the two simulation approaches as presented in Fig. 6.4. The average barium chloride concentration in Fig 6.5 is normalized with the corresponding initial concentration. It can be recognized that the decrease in barium chloride concentration in Fig 6.5 is observed at the same time, where the average supersaturation starts to decrease in Fig. 6.4. The strong decrease in supersaturation towards the end of the feed addition, which can be also observed in distribution 6 of Fig. 6.3, can be explained by the fact that barium chloride concentration approaches the value of zero.

![Fig. 6.5. Time evolution of average barium chloride concentration in the reactor, feed addition time of 1625 sec.](image)

\[
\frac{c_{BaCl_2}}{c_{BaCl_2,0}} = \frac{c_{Na_2SO_4}}{c_{Na_2SO_4,0}} = 0.02 \text{ mol/l},
\]

\[
q_{\text{feed, Na}_2\text{SO}_4} = 8.2 \text{ ml/min}, \quad N_{\text{stirrer}} = 180 \text{ rpm}, \quad \alpha = 50.
\]
Figs. 6.6 and 6.7 show the time evolutions of the number of particles and average particle size $d_{43}$, respectively. The solid and the dashed lines correspond to the results obtained with and without the PDF-closure, as in Figs. 6.4 and 6.5. In Fig. 6.6 the difference between the two simulation approaches is quite pronounced. When accounting for small scale mixing effects in the simulation, the calculated number of particles is significantly smaller compared to the case where small scale mixing is neglected. This can be explained by analyzing the spatial distributions of the small scale segregation and the supersaturation. Fig. 6.2 b) and Fig. 6.3 indicate that small scale segregation as well as supersaturation have a strong maximum close to the feed point. Since the supersaturation has a value of up to $S = 580$ at this location, homogeneous nucleation is locally the dominating mechanism. The nucleation rate at the feed point is so high that the evolution of the total number of particles in the system is dominated by particle formation at this location. Therefore, segregation in the small region close to the feed point strongly influences the process which is reflected in the difference between the two simulation approaches presented in Fig. 6.6.

![Graph showing time evolution of the number of particles](image)

**Fig. 6.6.** *Time evolution of the number of particles in the reactor during the precipitation process, feed addition time of 1625 sec.*

- $c_{\text{Na}_2\text{SO}_4,0} = c_{\text{BaCl}_2,0} = 0.02 \text{ mol/l},$
- $q_{\text{feed, Na}_2\text{SO}_4} = 8.2 \text{ ml/min}, N_{\text{stirrer}} = 180 \text{ rpm}, \alpha = 50.$
Likewise the predicted difference in the number of particles in the reactor, the computed average particle sizes $d_{43}$ also differ, as shown in Fig. 6.7.

### 6.4 COMPARISON OF SIMULATION RESULTS AND EXPERIMENTAL DATA

In the following, the effect of changing agitation rate and reactant concentration on the average particle size $d_{43}$ obtained in the semibatch process is discussed.

In Fig. 6.8 the influence of agitation rate on the particle size $d_{43}$ is illustrated. The box symbols represent experimental data [6.4]; the solid line corresponds to simulation results obtained with the CFD-model using the PDF-closure, whereas the dashed line corresponds to the model predictions obtained with the mixing-precipitation model based on the E-model, as presented in chapter 4. Both experimental data and simulation results indicate a constant particle size of approximately 4.1 $\mu$m for the whole range of agitation rates. Model predictions
obtained with both models are almost identical. To explain why the particle size is not influenced by changes in the agitation rate, the spatial supersaturation distributions for 180 rpm and 420 rpm are visualized in Fig. 6.9 and Fig. 6.10 at \( t = 280 \) sec. Fig. 6.9 shows the iso-supersaturation surfaces at \( S = 30 \), where figure a) and b) corresponding to 180 rpm and 420 rpm, respectively. It can be readily observed that the sodium sulfate feed is diluted faster at the higher agitation rate, since the volume enclosed by the iso-supersaturation surface is much smaller for 420 rpm than for 180 rpm. The level of supersaturation is quite similar at both agitation rates, as observed in Fig. 6.10. The maximum supersaturation of \( S = 240 \) at 180 rpm, as shown in Fig. 6.10 a), is only slightly larger than the one for 420 rpm, which is \( S = 230 \), as shown in Fig. 6.10 b). Since in both cases the supersaturation is smaller than the threshold for homogeneous nucleation, the number of particles produced under both conditions is only insignificantly different. Therefore, also the particle size \( d_{43} \) is similar at different agitation rates.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig6_8.png}
\caption{Influence of agitation rate on average particle size \( d_{43} \).
\( \bar{c}_{\text{Na}_2\text{SO}_4,0} = \bar{c}_{\text{BaCl}_2,0} = 0.0045 \text{ mol/l}, \)
\( q_{\text{feed, Na}_2\text{SO}_4} = 8.2 \text{ ml/min, } \alpha = 50. \)}
\end{figure}
Fig. 6.9. Iso-supersaturation $S = 30$, $t = 280$ sec.
$\overline{c}_{Na2SO4,0} = \overline{c}_{BaCl2,0} = 0.0045$ mol/l,
$q_{\text{feed, Na2SO4}} = 8.2$ ml/min, $\alpha = 50$.
\begin{itemize}
  \item[a)] $N_{\text{stirrer}} = 180$ rpm
  \item[b)] $N_{\text{stirrer}} = 420$ rpm.
\end{itemize}

Fig. 6.10. Supersaturation distributions, $t = 280$ sec.
$\overline{c}_{Na2SO4,0} = \overline{c}_{BaCl2,0} = 0.0045$ mol/l,
$q_{\text{feed, Na2SO4}} = 8.2$ ml/min, $\alpha = 50$.
\begin{itemize}
  \item[a)] $N_{\text{stirrer}} = 180$ rpm
  \item[b)] $N_{\text{stirrer}} = 420$ rpm.
\end{itemize}
In Fig. 6.11 the influence of reactant concentrations on the particle size $d_{43}$ is presented. The box symbols represent experimental data [6.4], the solid line represents simulation results obtained with the CFD-model using the PDF-closure, the dotted line those obtained with the CFD-model not using the PDF-closure, and the dashed line those obtained with the mixing-precipitation model based on the E-model, as presented in chapter 4. The experimental average sizes clearly decrease with increasing reactant concentrations. The modeling results obtained with all three types of models indicate a decrease in particle size when comparing the minimum concentration of 0.0045 mol/l and the maximum concentration of 0.02 mol/l shown in the figure. However, only the CFD-model in combination with the PDF-closure predicts a continuous decrease in $d_{43}$ over the whole concentration range, whereas the other two models predict that the particle size is first increasing and then decreasing, i.e. they exhibit a maximum. At low concentrations within the range from 0.0045 mol/l to 0.0125 mol/l the CFD-model with the PDF-closure gives the best prediction for the values of $d_{43}$. At higher concentrations the E-model based mixing-precipitation model gives the best prediction of $d_{43}$, whereas the CFD-model with the PDF-closure...
overpredicts the experimental value. At small concentrations the different models give the same predictions for the average particle size $d_{43}$. Here, small scale mixing is obviously not affecting particle formation. This is also visualized in Figs. 6.12 and 6.13, where CFD simulation results are shown for the time evolutions of the number of particles in the reactor and of the average particle size, respectively. As in Fig. 6.6 and 6.7, the dashed line in the figure symbolizes model predictions obtained without the PDF-closure and the solid line represents results which were obtained with the PDF-closure. In both Fig. 6.12 and 6.13 the end of feed addition is indicated by a vertical dashed line. It is clearly noticeable in both figures that model predictions are almost identical for both simulation approaches. This result indicates that small scale mixing is not important at low concentrations, which is contrary to the situation at larger concentrations, where accounting for small scale mixing phenomena in the model leads to quite different predictions, as it can be seen in Fig. 6.4 to 6.7. The negligible small scale mixing influence at low concentrations can be understood when analyzing a typical spatial supersaturation distribution, as it is shown in Fig. 6.9 a) and 6.10 a). Since the maximum value in supersaturation close to the feed point is smaller than the threshold for homogeneous nucleation, the nucleation rates are rather low and small scale segregation at the feed point cannot influence the course of particle formation. Thus CFD model predictions with and without the PDF-closure yield similar results.
Fig. 6.12. Time evolution of the number of particles in the reactor during the precipitation process, feed addition time of 1625 sec.
\[ \bar{c}_{\text{Na}_2\text{SO}_4,0} = \bar{c}_{\text{BaCl}_2,0} = 0.045 \text{ mol/l}, \]
\[ q_{\text{feed, Na}_2\text{SO}_4} = 8.2 \text{ ml/min}, N_{\text{stirrer}} = 180 \text{ rpm}, \alpha = 50. \]

Fig. 6.13. Time evolution of average particle size \( d_{43} \) during the precipitation process, feed addition time of 1625 sec.
\[ \bar{c}_{\text{Na}_2\text{SO}_4,0} = \bar{c}_{\text{BaCl}_2,0} = 0.0045 \text{ mol/l}, \]
\[ q_{\text{feed, Na}_2\text{SO}_4} = 8.2 \text{ ml/min}, N_{\text{stirrer}} = 180 \text{ rpm}, \alpha = 50. \]
6.5 CONCLUSIONS

In this chapter it has been shown how the CFD-based mixing-precipitation model, presented in section 5.2, can be applied to the semibatch stirred tank process shown in Fig. 6.1. Although the feed addition time for the analyzed process is rather long, meaningful results could be obtained when fully resolving the feed addition process using a transient simulation. The comparison of CFD model predictions and experimental data indicates, that the trends of changes in the particle size $d_{43}$ with modified operating parameters can be qualitatively predicted, when accounting for small scale mixing-influences. At small concentrations the predictions are quantitatively correct, but at higher concentrations the CFD based mixing-precipitation model overpredicts the experimental findings.

The comparison of results obtained with the CFD model and the much simpler E-model based mixing-precipitation characterization in Fig. 6.8 and 6.11 shows that the prediction quality is not significantly different for the two models. The key advantage of the CFD model is that additional insight into the process can be obtained, since detailed information about the time evolution of the spatial distributions of reactants and the PSD moments is determined. That information allows to conclude that particle formation by nucleation close to the feed point is controlling the dynamics of the process, when reactant concentrations are high. On the contrary, at low concentrations the feed point region is less important for the dynamics of the process. As shown in section 6.4, small scale mixing effects do not influence the barium sulfate precipitation under these conditions.
6.6 REFERENCES CHAPTER 6


7. CONCLUDING REMARKS
In this work the influence of turbulent mixing on precipitation and parallel chemical reaction processes in stirred tank reactors was investigated experimentally and through simulations. Both semibatchwise and continuously operated processes were analyzed for a wide range of operating conditions. The key aim of both experimental and simulation work was to establish a better understanding of the interaction between mixing and precipitation. In particular, the focus was on developing modeling tools, which allow to predict the influence of turbulent mixing on precipitate properties.

Mixing-precipitation models of different complexity were presented in this thesis, which differ mainly in their level of modeling detail for the three identified categories of sub-process mechanisms, which are: first, all the mechanisms which contribute directly to the particle formation; second, the small-scale mixing mechanisms; third, the large scale mixing mechanisms. By using different combinations in the level of modeling detail, hence of their accuracy for these three categories of mechanisms, the performance of the overall process models could be evaluated. Overall model performance was assessed by comparing the simulation results obtained with different types of models with experimental data for a wide range of stirred tank operating conditions.

Most of the experimental work was performed with the model substance barium sulfate, which was precipitated by mixing aqueous solutions of barium chloride and of sodium sulfate. Precipitation experiments were conducted in a baffled flat bottom stirred tank reactor equipped with a Rushton turbine. In chapter 2 of this thesis the developed experimental setup has been described in detail. The reactor unit was designed to ensure that precipitation experiments could be conducted in a controlled and reproducible manner and accurate process simulations are possible for the chosen geometry.

In chapter 3 a reactive mixing process involving two parallel chemical reactions with nonlinear reaction rates has been investigated experimentally and through simulations. Contrary to the kinetics of a precipitation process those for homogeneous chemical reactions are well known. This has the obvious advantage that the quality of process simulation results mainly depends on the
accuracy of the mixing characterization, which can be assessed by comparing simulation and experimental results for different types of models.

By performing a time-scale analysis for the used semibatch stirred tank process, it was shown to be essential for the modeling that mixing mechanisms in a wide range of time and length scales are accounted for. Two different reactive mixing models, both describing all relevant phenomena from the micro- to the macroscale, were applied to predict the yields of the parallel reaction for various process operating conditions. The classical E-model as well as the CFD closure model were both found to predict experimental data with similar, rather satisfactory accuracy. It is worth noting that the model performance of the closure model and of the E-model can be expected to differ for processes with higher feed addition rates than those analyzed in this work. Under such conditions, the effects of turbulent diffusion that are neglected in the E-model become significant and the CFD based model works better than the E-model.

The simulations with the E-model have the obvious advantage of being faster than with the CFD closure model. On the other hand, the CFD closure model has the advantage of characterizing the process in greater detail capturing precisely how reactants are distributed by the action of the macro-flow. Thus, simulations with the CFD closure model give detailed information, which is essential for the optimization of the reactor design and for the scale-up.

The focus of the work presented in chapter 4 is the development of an accurate characterization for all the mechanisms, which contribute directly to the particle formation. The relevant mechanisms for the precipitation of the model substance barium sulfate are analyzed in depth to formulate accurate kinetics models. The precise characterization of particle formation kinetics is known to be rather difficult. Thus, the definition of the kinetics models is a critical step, especially when aiming at an overall process model, that can be used to exactly predict the behavior of a mixing-precipitation process.

Barium sulfate precipitation is known to be dominated by nucleation and particle growth under the operating conditions analyzed in this work. In order to be able to express proper kinetics models for these mechanisms, an accurate driving force model is essential. Different activity based solution models for the aqueous
Ba\(^{2+}\)/SO\(_4^{2-}\)/Na\(^{+}\)/Cl\(^{-}\) system were evaluated and the Pitzer model was found to be the best model to describe the solution composition and the particle formation driving force, when also accounting for complex formation effects in the solution. Based on this liquid phase model, new kinetic relationships for nucleation and growth have been derived by fitting classical experimental data reported in the literature. A comparison of experimental growth rate data and model results within a wide concentration range has shown, that the new growth model gives predictions of satisfactory accuracy.

The new kinetics relationships have been applied in a mixing-precipitation model for a single feed semibatch process. Particularly when combined with the Pitzer activity model accurate estimates of mean particle size could be produced. The large difference in mean particle size prediction between the thermodynamic models at high concentration highlights the significance of choosing a proper thermodynamic model under such conditions. However, for strongly non-stoichiometric conditions the predictive capability of the model is not yet satisfactory, possibly due to the under-prediction of the rate of homogeneous nucleation. This calls for further improvement of the nucleation kinetics.

In chapter 5 the precipitation of barium sulfate upon mixing of solutions of barium chloride and sodium sulfate has been investigated experimentally and through simulations for a continuous stirred tank process. The key focus of the work presented in this chapter is the development of a detailed process model using the precipitation model presented in chapter 4 in combination with a CFD based mixing model, that describes all relevant phenomena from the micro- to the macroscale. In this chapter it was discussed in detail how this model can be implemented in a CFD code. In particular it was addressed, how the complex liquid phase and precipitation kinetics model can be implemented allowing for computational efficient process simulations. Furthermore, a newly developed numerical procedure was presented, which is robust and suitable to solve the population balance and the reactant transport equations effectively.

Continuous stirred tank precipitation experiments were conducted in a newly designed and built setup for a wide range of operating conditions varying the
feed point locations, agitation rate, feed addition rate and reactant concentrations. Experimental results revealed that the average size of the product particles is particularly sensitive to the relative positions of the feed inlets. Only when feed tubes of barium chloride and sodium sulfate were placed very close to each other, the particle size was clearly influenced by the mixing conditions in the reactor. This could be shown by modifying the feed flow ratio, which led to a change in particle size. In future work, some other feed configurations should be investigated, which can increase the sensitivity of the process to mixing. In this respect, it could be promising to use a premixed feed of barium chloride and sodium sulfate solutions.

The CFD closure model was found to predict experimental data with reasonable accuracy for operating conditions corresponding to low supersaturation or small ratios of feed flow rates. For large flow rate ratios the model typically overpredicted the average size of product particles. This is most likely due to the assumption for the nucleation rate model that the nucleation rate is a function of supersaturation only. Additional effects as the functional dependence of the interfacial tension on the ionic strength and on the barium to sulfate concentration ratio should be considered to improve the nucleation model. However, to be able to account for these effects a larger experimental database of nucleation rate measurements also under non-stoichiometric conditions would be necessary, which is not available up to now.

Although the model does not always predict the particle size correctly, it gives detailed insight into the continuous stirred tank process, which can not be obtained based on experiments only. The distribution of reactants by the action of the macro-flow is captured precisely, since the fluid in the reactor is characterized with a rather fine spatial discretization in all three dimensions. Since small scale mixing effects are accounted for, realistic information about the spatial distributions of particle formation kinetics in the reactor can be obtained.

In chapter 6 it has been shown how the general CFD-based mixing-precipitation model, which was presented in chapter 5, can be applied to a semibatch stirred tank process. By fully resolving the feed addition process in time using a transient simulation, the dynamics of the process can be captured. The presented
comparison of CFD model predictions and experimental data indicates, that the trends of changes in the particle size $d_{43}$ with modified operating parameters can be qualitatively predicted, when accounting for small scale mixing-influences. However, the model predictions are quantitatively only correct at small concentrations, whereas at large concentrations the model tends to overpredict the experimental values for the average particle size.

The comparison of results obtained with the CFD and the E-model based mixing-precipitation model shows that the prediction quality is not significantly different for the two models. This is in agreement with the findings in chapter 3, where both E-model and CFD closure model predicted similar behaviors for mixing influenced competitive reaction processes in the semibatch reactor. As for the mixing-reaction modeling the key advantage of the CFD mixing-precipitation model is that a detailed insight into the time evolution of the spatial reactant and the PSD moment distributions can be obtained. Only based on this information it is possible to conclude that particle formation by nucleation close to the feed point is controlling the dynamics of the process, when reactant concentrations are high. On the contrary, at low concentrations the feed point region is less important for the dynamics of the process and small scale mixing effects do not influence the barium sulfate precipitation.

One area of future work with regard to the presented stirred tank mixing-precipitation models is of course a more detailed characterization of the nucleation kinetics. The accuracy of the particle formation kinetics characterization can be clearly considered as the bottleneck for the overall process model. Nucleation kinetics of a model system should be determined based on a large experimental database, which covers a wide reactant concentration range including stoichiometric as well as non-stoichiometric conditions. In this work, the nucleation rates for non-stoichiometric conditions had to be extrapolated using stoichiometric data, which has clearly led to the disagreements between experimental data and mixing-precipitation model predictions. However, up to now standard procedures for measuring the nucleation rates at high supersaturation are not fully established. Special care has to be taken to ensure rapid reactant mixing, which guarantees that the
dynamics of particle formation are not masked by turbulent mixing. Additional difficulty is imposed by the fact that currently no measurement techniques are available, which can resolve the early stages in the evolution of particle formation in-situ. Therefore nucleation rate measurements often rely on rapidly stopping an ongoing precipitation to perform offline analysis, which can lead to significant errors.

Another area of future work certainly is the extension of the mixing-precipitation model to other particle formation mechanisms. In practical applications particle formation is rarely controlled by nucleation and growth exclusively. However, accounting for secondary particle formation mechanisms such as agglomeration and breakage requires the usage of other techniques than the computationally efficient method of moments to solve the population balance equation.
CURRICULUM VITAE

Lars Vicum

May 31st, 1972  born in Hannover, Germany

08/85 - 05/92  Gymnasium Großburgwedel; Burgwedel, Germany

08/92 - 08/96  Study of process engineering
                Universität Hannover, Germany

08/96 - 08/98  University of Wisconsin - Madison, USA
                Graduation as Master of Science, Mechanical Engineering

08/98 – 12/99  Study of process engineering
                Universität Hannover, Germany
                Graduation as Dipl.- Ing. Maschinenbau

07/00 – 07/05  Research assistant at the Institute of Process Engineering
                Swiss Federal Institute of Technology Zürich
                Separation Processes Laboratory
                Ph.D. studies under the supervision of Prof. Dr. M. Mazzotti

Zürich, 2005