

**Experimental and theoretical study
of the flow, aggregation and deposition
of gas hydrate particles**

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Contents

Abstract	7
1 Organization of the thesis	9
1.1 Papers included in the thesis	9
1.2 Papers not included in the thesis	10
2 General Introduction	11
2.1 Hydrate structures and equilibria	12
2.2 Gas hydrate kinetics	14
2.3 Gas hydrate plugging scenarios	17
2.4 Gas hydrate prevention	19
3 Experiments and simulations with gas hydrates: literature overview	21
3.1 Experiments with gas hydrates	21
3.1.1 High-pressure systems	21
3.1.2 Model hydrates	23
3.2 Simulations with gas hydrates	25
3.2.1 Computational fluid dynamic models	27
3.2.2 Population balance models	29

4	Summary of papers included in the thesis	33
4.1	Paper 1	33
4.2	Paper 2	35
4.3	Paper 3	36
4.4	Paper 4	36
4.5	Paper 5	37
5	Concluding remarks and further work	41
	References	43

Abstract

Gas hydrate plugging is considered to be a very problematic topic during petroleum production and transportation. The phenomenon of hydrate plug formation involves inter-related effects related to different disciplines, namely multiphase flow, thermodynamics, surface chemistry and solid mechanics. At present the problem is not fully understood, although much information is becoming available about hydrates in general.

One of the challenging problem in gas hydrate research is the difficulty of reproducing industrial conditions on a laboratory scale as natural gas hydrates require high pressure to form, limiting the possibilities for gaining insight into the process by direct observation due to safety considerations. The scale of the process in combination with industrial flow conditions is not also absolutely repeated on a lab-scale.

The problem of limited direct information about the process can be alleviated by simplification of the experimental conditions such as the use of low-pressure models for the hydrates and shifting from pipeline systems to agitated vessels. In addition, computational fluid dynamics (CFD) models of the evolution of gas hydrates in pipelines can give valuable information. The present state-of-the-art of CFD-research is such that the models need to be validated experimentally. This can be done with the macroscopic parameters of the process (e.g. pressure, temperature and velocity), which are relatively simple to monitor even in a high-pressure system.

A CFD-model can predict the detailed behavior of hydrate particles, including their interactions with the continuous phase and with each other. This will help to understand, for instance, the mechanism of hydrate deposition in turbulent flow; or the agglomeration of particles in a pipeline during transportation.

This work includes both an experimental study of water-hydrate slurry behaviour in a lab-scale, low-pressure flow loop and a CFD model that mimics the experiment.

The experimental part of this dissertation is focused on the rheological behaviour of freon hydrate slurries: their apparent viscosity and yield stress were empirically examined in the low-pressure flow loop. Sampling of hydrate particles was carried out for determination of their size distribution and maximum hydrate volume fraction (i.e. the packing limit).

The numerical modelling part involves a step-by-step development of models for hydrate deposition and aggregation. Initially, a model built using the commercial CFD-package STAR-CD was validated using experimental data from the literature in terms of its ability to correctly predict deposition of particles in a quiescent fluid.

In parallel with this a population balance model (PBM) was developed and validated for prediction of hydrate particle nucleation, growth, aggregation and breakage in the pipeline.

Based on this modelling approach tested in the way described above, a CFD-model of the experimental rig was developed and tested in the homogeneous flow regime, where the rheology of the hydrate slurry was the factor determining the system behaviour. After this, the model was updated with the PBM expressions for hydrate particle size development and the process of deposition in a turbulent pipeline flow was studied.

Chapter 1

Organization of the thesis

This dissertation is written in an article-based form. The summary begins with an introductory part comprising a literature review, and this is followed by a discussion part, comprising a list of the research articles included in the thesis with a short discussion of each and conclusions from them. The introductory part consists of chapters 2, 3, while the discussion part is comprised in chapters 4 and 5.

Chapter 2 in the introductory part presents the state-of-the-art of research into the gas-hydrate problems. A review of the literature on experiments and simulations of hydrate-related phenomena is presented in chapter 3.

The scientific papers are presented in chapter 4. These are articles published or accepted for publication in peer-review journals and international conference proceedings and one article submitted for publication. The chapter is amplified with a brief summary of each research paper.

Chapter 5 includes the final remarks on the research work that has been performed.

1.1 Papers included in the thesis

1. Balakin, B.V., Pedersen, H., Kilinc, Z., Hoffmann, A.C., Kosinski, P., Hoiland, S., 2010. Turbulent flow of freon R11 hydrate slurry. *Journal of Petroleum Science and Engineering* 70, 177-182, doi:10.1016/j.petrol.2009.11.007.
2. Balakin, B.V., Hoffmann, A.C., Kosinski, P., Rhyne, L.D., 2010. Eulerian-Eulerian CFD model for the sedimentation of spherical particles in suspension

with high particle concentrations. *Engineering Applications of Computational Fluid Mechanics* 4(1), 116-126.

3. Balakin, B.V., Hoffmann, A.C., Kosinski, P., 2010. Population balance model for nucleation, growth, aggregation and breakage of hydrate particles in turbulent flow. *AIChE Journal*, doi:10.1002/aic.12122.
4. Balakin, B.V., Hoffmann, A.C., Kosinski, P., Hoiland, S., 2010. Turbulent flow of hydrates in a pipeline of complex configuration. resubmitted to *Chemical Engineering Science* after minor revisions.
5. Balakin, B.V., Hoffmann, A.C., Kosinski, P., 2010. Computational fluid dynamic model for deposition of adhesive hydrate particles in a pipeline. submitted to *Chemical Engineering Science*.

1.2 Papers not included in the thesis

1. Balakin, B.V., Hoffmann, A.C., Kosinski, P.J. and Rhyne, L.D., 2008. Eulerian-Eulerian simulation of sedimentation of uniformly-sized, non-Brownian spheres in viscous fluids *AIP Conference Proceedings* 1048, 723–726, doi:10.1063/1.2991030.
2. Aspenes G., Balakin, B., Borgund, A.E., Hoiland, S., 2009. Hydrate Agglomeration and Deposition Studies - the influence of pipeline wettability and flow. *Proceedings of Oil Field Chemistry Symposium*, Norway, Geilo.
3. Balakin, B.V., Hoffmann, A.C., Kosinski, P., 2009. Computational fluid dynamic model of gas hydrate deposition in a turbulent pipeline flow. *Proceedings of International Conference on Gas Hydrate Resources Development*, K.S. Basniev, A.E. Ermolaev, Y.F. Makogon, Russia, Moscow.

Chapter 2

General Introduction

Gas hydrates (Figure 2.1) are crystalline compounds of water and gas, visually similar to ice [1]. Any gas with relatively low molecular weight, or, actually, with relatively small molecular size, may be incorporated as "guest" into the water crystal cage, forming gas hydrate [2]. Most of the light hydrocarbons, noble gases and refrigerants fall into this category.



Figure 2.1: Burning cyclopentane hydrate [3]

The formation and stability of gas hydrates require relatively high pressures of 10–30 MPa and low temperatures from deep negative up to 20–25°C, however the typical temperatures of their stability are lower than 15–20°C [4, 5]. Gas hydrate stability in nature requires very specific pressure conditions, which can be found in deep sea floor deposits and permafrost, where the hydrates in addition may be preserved

from dissociation by an ice layer. Natural gas hydrates represent a possible energy source. The recovery of light hydrocarbons from hydrates may involve a technology for replacing methane by carbon dioxide in the clathrate structure [6, 7], or regular dissociation of hydrate in a deposit.

Hydrates may be formed artificially in water-gas systems brought into the thermodynamic zone of hydrate stability. Such systems are for instance found in the gas or petroleum industry, in which the hydrates constitute a severe problem posing as an unexpected impurity there, the handling of which is associated with high pumping costs and safety risks [2]. Some recent scientific trends in the hydrate field focus on employing hydrates for useful purposes, for example in technologies for natural gas transportation [8, 9], refrigeration [10, 11], water purification [12] and desalination [13, 14].

2.1 Hydrate structures and equilibria

In addition to the covalent bond between the oxygen and hydrogen in the water molecule, there are also two pairs of vacant electrons in the neighborhood of the oxygen molecule, which induce a weak positive charge in the vicinity of the hydrogen molecules. The resulting polarity forces the hydrogen and oxygen to be aligned in a hexagonal pattern, forming *hydrogen bonds* [1, 15]. The water molecules, connected via the hydrogen bonds, may form spatial cavities, which are occupied by the molecules of gas, forming gas hydrate.

The crystal structure of gas hydrate depends on the size of the "guest" molecule. Gas molecules of a size less than 0.6 nm form the cubic structure I [2, 4], presented in Figure 2.2. "Guests" such as methane, ethane, carbon dioxide and hydrogen sulfide form structure I hydrate. However, when methane and ethane are mixed in the system, they form structure II hydrate [16]. Larger molecules with sizes in the interval from 0.6 and 0.7 nm form structure II (Figure 2.2). Structure II hydrates are formed by propane, iso-butane etc. [16]. Gases with a molecular size between 0.7 and 0.9 nm form hexagonal structure H.

As mentioned before, normal conditions are unsuitable for the formation and stability of most types of hydrates [17, 18]. This is related to the fact that the system needs to be energetically intensive in order to incorporate the gas molecule into the water structure. Generally, the conditions of gas hydrate formation are given in P-T

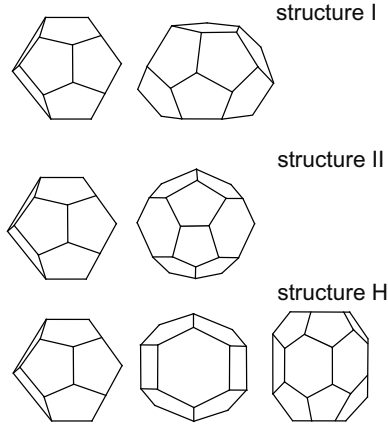


Figure 2.2: Water cages, forming different hydrate structures.
Redrawn from Aspenes [16]

diagrams, in which the hydrate equilibrium curve, presented in Figure 2.3, is drawn, such that the zone above the equilibrium curve is the region of hydrate thermodynamic stability. The equilibrium dependence of the pressure on system temperature is of polynomial type [2] (Figure 2.3).

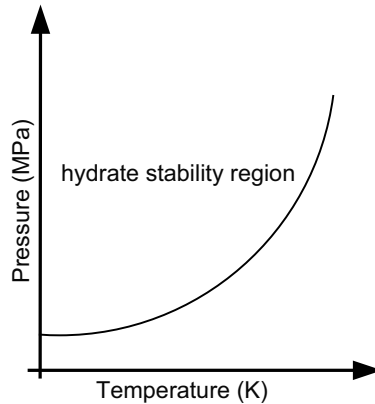


Figure 2.3: Example of hydrate equilibrium conditions

The hydrate equilibrium pressure is not only a function of temperature, but also depends on the "guest" gas. Katz [4] found experimentally that hydrate equilibrium characteristics are proportional to the gas specific gravity, i.e. to the ratio between the molar masses of the gas in question and air. Hence, having the equilibrium curve of a single-component gas, for instance methane, presented in Figure 2.4, it is

possible to find the corresponding dependence for multi-component mixtures with known specific gravity.

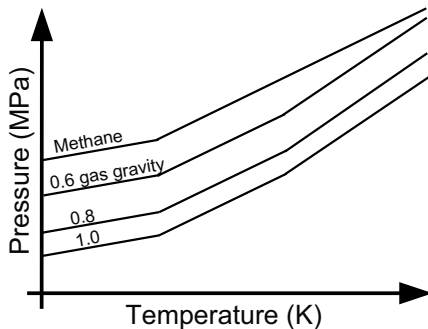


Figure 2.4: Illustration of gas gravity method. Redrawn from Sloan and Koh [2]

This technique, often called the "gravity method", is a classical approach for determining equilibrium conditions for gas hydrates, however it is not applicable for structure H hydrates or for the entire range of system temperatures. More precise correlations are also available in the literature for determination of gas hydrate equilibrium conditions. For example, Sloan and Koh [2] describe a technique based on a vapor-solid distribution coefficient, called the " K_{vsi} method" [19].

2.2 Gas hydrate kinetics

In the early stages of hydrate formation the *nucleation* occurs, i.e. the formation of a solid phase in the liquid-gas system [20, 21]. Initially, the solid pre-hydrate crystal, also named a nucleus, is unstable. This instability is explained by the amount of energy required for the nucleus to build onto its own surface. An increase in the surface of the particle thus results in an increase of the free energy of the solid phase relative to the homogeneous-mixture phase. However, in the hydrate-stable region, an increase in the volume of the particle will result in a decrease in the free energy of the solid phase. An equation describing the free energy of the solid phase relative to that of the homogeneous solution, ΔG_{hom} is then, if the particles are assumed to

be spherical [2]:

$$\Delta G_{hom} = \frac{4}{3}r^3\pi G_v - 4\pi r^2\sigma \quad (2.1)$$

where ΔG_{hom} is the change of Gibbs free energy of the system upon dissolution of the particles if no impurities are present, G_v is the energy release due the formation of solid per unit volume, r is the radius of hydrate nuclei and σ is the energy gain for the formation of new surface per unit surface. It follows from Equation 2.1, that there is a critical size, r_{cr} of the pre-hydrate particle at which the energy of the system is at an extremum. This size may be found by the standard procedure for the determination of extrema:

$$r_{cr} = \frac{2\sigma}{G_v}. \quad (2.2)$$

After the (pre-)hydrate particle has grown beyond its critical size, the system does not require additional energy for surface stabilization of the nuclei, thus further growth of the stable hydrate particles leads to a release of energy from the system.

The nucleation scenario described above, represents an idealized case of *homogeneous nucleation*, which takes place in highly supersaturated systems. However, the presence of impurities in the system (so called *nucleation centers* or *nucleation sites*) facilitates nucleation, which in that case is *heterogeneous* [20, 22]. Any solid contaminant, distinct liquid droplet or a gas bubble may form the center of heterogeneous nucleation, since the energy gain for the formation of hydrate nuclei on the surface of the impurity is lower compared to homogeneous nucleation. This is often expressed as:

$$\Delta G_{het} = f(a, b, c)\Delta G_{hom} \quad (2.3)$$

where $f(a, b, c)$ is a correction factor, which depends on the contact angles a, b, c [2] between the tangential line to the nuclei surface and the interphase (Figure 2.5).

A description of hydrate nucleation kinetics would not be complete without a description of the *induction time* [23] and *nucleation rate* [24]. The first term is a temporal measure of the period during which the system is in the thermodynamic stability range for hydrates before the actual formation of hydrates begins, i.e. the system is in a metastable state. This parameter depends on the level of system supersaturation and on the amount of impurities present reducing the energy barrier [20]. The length of the period also depends on the presence of kinetic inhibitors, described further below. The second term is the rate of production of pre-hydrate particles. Normally this is also assumed to be dependent on the supersaturation [25], but is also related to a variety of other system parameters: the gas molecule size, the geometrical characteristics of the system, the presence of impurities, the "history"

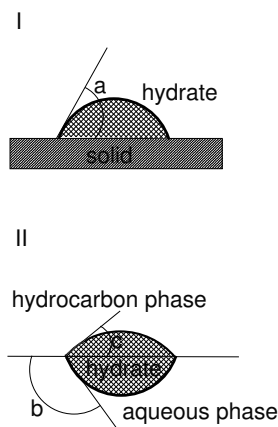


Figure 2.5: Nucleation on a distinct solid surface (I) and on an interphase between hydrocarbon and aqueous phases (II). Redrawn from Kashchiev and Firoozabadi [20]

of the water (previous superheating, ice/hydrate formation) and the turbulence intensity [2].

In contrast to the stochastic process of hydrate nucleation, the growth of hydrates is widely described in the literature [26, 27]. Physically the growth [28] takes place through further incorporation of gas molecules into the water cages in the vicinity of the pre-formed nuclei. Gas hydrate growth rate is strongly dependent on the rate of diffusion of gas through the liquid to the surface of the particles. As a diffusional phenomenon, this depends on the area of gas-water interface and therefore the size of hydrate particles, and also on the P-T conditions of the system. In addition, the rate of gas diffusion is a function of the turbulence intensity [29] and physical properties of the carrier media.

The opposite process to growth, namely that of particle dissociation does not play a central role in the current work. However, this process is widely considered in the literature, so the author will skip the discussion of hydrate dissociation, and refer to information that may be found, for example, in [2, 30].

The processes of hydrate growth and dissociation are responsible for the variations in the hydrate phase volume in the system and the hydrate particle size, both of which are important in the context of flow assurance. However, hydrate particles are cohesive enough (especially wet particles) to form *aggregates* [31, 32], something that was shown, for example, by Changyu et al. [33] by in-situ pipeline experiments with model hydrates. In this context, micromechanical measurements of

hydrate-hydrate adhesion force, carried out by Aspenes [16] in a three-phase system of oil/water/hydrate-former, presents the possibility of an interparticle liquid bridge appearance, which force impacts the aggregate formation and is much higher than for "dry" hydrate particles. Gas hydrate breakage, attrition and secondary nucleation are also considered in the literature [25].

2.3 Gas hydrate plugging scenarios

The scenario of pipeline plugging with gas hydrates is system-dependent. For the petroleum industry where the pipeline is often filled with liquid phases (Figure 2.6), hydrates can form on the interface between oil and aqueous phases, often on the surface of water droplets dispersed in the oil phase. As a result, they may build a solid shell around the droplet [2] and further conversion of the water core of such particles is significantly hindered due to the very slow diffusion of gas molecules through the shell.

The presence of solid particles increases the apparent viscosity of a solid-liquid slurry [34, 35], and as a consequence the frictional pressure loss in the system is increased. Flowing solids may aggregate causing a further increase of the slurry viscosity [36]. After some time (Figure 2.6) the aggregates may form relatively large assemblies, the frictional resistance of which to flow cannot be overcome by the system agitator, so that a quiescent zone is formed in the pipeline. Finally, stationary aggregates are joined with each other and the pipeline walls, partly due to the formation of solid bridges, forming a stable monolith plug.

The scenario described above does not consider the case where the shells of the hydrate-covered water droplets are broken due to particle-particle/wall collisions and turbulent pulsations in the carrier flow. This process would likely enhance hydrate growth due to an increased amount of water/oil interface in the system.

In a gas-dominated system the hydrate-plugging scenario is different. This type of system, encountered in the natural gas industry, usually contains water in the vapor phase. During transport the pipeline wall is often at a temperature lower than the equilibrium temperature for gas-water vapor flow. This leads to water condensation on the walls of the channel (Figure 2.7), forming a gas-liquid flow of the annular type. Hydrate formation may thus be induced on the pipeline walls, in contrast to the scenario for the liquid-dominated system (Figure 2.6), where the hydrate

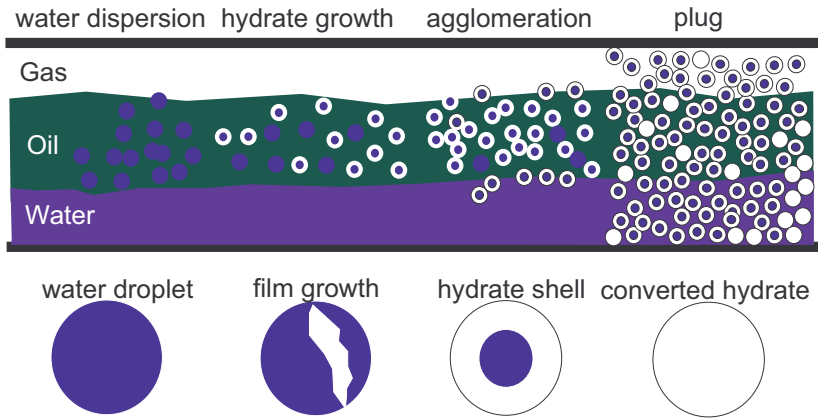


Figure 2.6: Gas hydrate formation in liquid-dominated system. Redrawn from Sum et al. [37]

particles are formed in the bulk. Moreover, the formed hydrate obstruction is of a different character, as a monolith hydrate layer forms from the walls [38]. Further water condensation on the hydrate layer makes it grow thicker, finally plugging the pipeline.

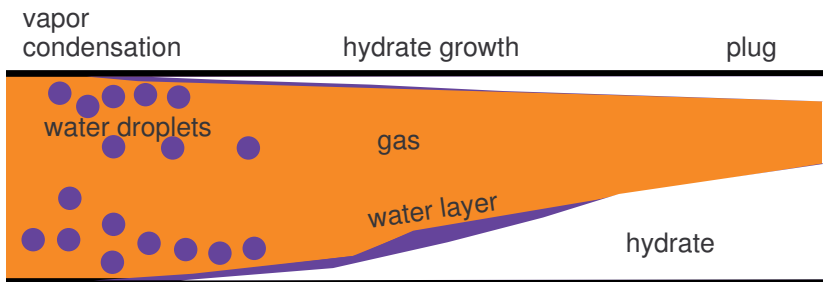


Figure 2.7: Gas hydrate formation in gas-dominated system. Redrawn from Musakaev et al. [39]

It is shown in another paper [40] that a hydrate obstruction stuck to the pipeline wall may be broken up due to erosion. The resulting free small fragments sediment in gas-liquid flow, building a plug located downstream, similar to the type of plug formed in a liquid-dominated plugging scenario.

2.4 Gas hydrate prevention

There are two ways of hydrate prevention used in industrial systems, which are based on the basic physics of hydrate formation. Both of them include an artificial adjustment of the process parameters, focused on escaping the conditions for hydrate formation:

1. Flow dehydration, which reduces the water amount in the system, so it would no longer contain the basic media for hydrate formation [2]. This may be done in the gas industry by causing the stream to flow through a dehydrator.
2. Manipulation to move the system's P-T conditions outside the hydrate-stable region. In industry the pipeline may be heated by an electrical cable mounted on it and/or it may be thermally insulated.

The mentioned techniques cannot be widely used in the industry due to the high costs and impracticality of keeping the system parameters on an artificial level only due to the hydrate formation problem.

Hydrate prevention may also be achieved by chemical methods, which are focused on the use of additives, which influence the event of hydrate formation or its kinetics. These inhibitors may be classified by their acting mechanism, composition, aim and physico-chemical properties [4]. In the current chapter we mention two different types of inhibitors, discriminated by the mechanism of their influence on hydrate behavior.

The first, and the oldest, type of inhibitors, are of the thermodynamic type [41]. The mechanism of their influence on hydrate formation is in the reduction of the thermodynamic activity of the water phase, which reduces the hydrate equilibrium temperature at a fixed gas phase pressure. Most commonly, such inhibitors are electrolytes which are dissolved in water: alcohols, glycols and aqueous solutions of inorganic salts [4]. The use of such inhibitors during off-shore production is associated with high logistical costs as significant volumes (10–30 % of water mass [4]).

The second type of hydrate inhibitors are *kinetic* [2, 42], which are of the low dosage type (0.5–1.0 % of water mass [4]). The mechanism of their influence on hydrate formation is based on the increase of the *induction time* up to time scales comparable to the residence time of the system, i.e. so long that a significant amount of the

hydrate is not formed in the line. This effect is believed to be caused by inhibitor-specific adsorption onto the surface of the hydrate nuclei, preventing further growth (so-called *lock-and-key model* [43]). The kinetic inhibition involves such types of polymers or copolymers as polyvinylpyrrolidone (PVP), polyvinylcaprolactam (PV-Cap). Some of these low-dosage inhibitors, in addition to all their positive features, does not meet the ecological and toxicity requirements and thus cannot be widely used due to environmental considerations. Moreover, the kinetic inhibitors which meet the environmental requirements are not effective enough in the northern regions due to high subcoolings.

Inhibition methods focus on the full or partial prevention of gas hydrate appearance as a solid phase in the system. However, several modern directions in the hydrate field suggest that hydrate particles may be transported in the pipe without the formation of a plug. This can be done with the use of anti-agglomerants, which would hinder the aggregation of hydrate particles. The apparent viscosity of such a liquid-hydrate slurry may be kept on a suitable level, limiting the frictional pressure loss to a tolerable value. One of the promising anti-agglomerants considered nowadays are acids naturally occurring in some crude oils [44, 45].

It has been experimentally shown [31] that the cohesion and adhesion of hydrate particles decrease with a reduction in the system temperature. The Cold Flow concept [46] is based on this principle, stating that the system can be immersed deep inside the hydrate-stable zone, converting all free water into hydrate phase, and the slurry is transported with the particles having low cohesivity. It was also shown by Groysman et al. [32] and Aspenes [16] that the plugging tendency of gas hydrate is a function of pipeline material, something that should also be considered during the design of industrial systems.

Chapter 3

Experiments and simulations with gas hydrates: literature overview

There is a wide range of scientific literature focused on the rheological, thermodynamic, kinetic and other aspects of hydrate problems. The current chapter presents a brief overview of experimental and theoretical research, performed by other authors in the field of pipeline hydrate flow assurance and related areas.

3.1 Experiments with gas hydrates

Experimental research papers dedicated to the flow of gas hydrate may be divided in two categories dependent on the type of hydrate used. One category is studies of clathrates formed by natural gas, is performed in high-pressure equipment, focusing on the kinetics of hydrate formation and the rheology of hydrate slurries. The other category consists of papers studying low-pressure model hydrates. Such studies are easier to conduct and sometimes yield visual in-situ information on hydrate flow patterns. The two categories are separately distinguished below.

3.1.1 High-pressure systems

A classical example of experimental investigation of a hydrate slurry pipeline flow may be found in Gaillard et al. [47]. The authors examined the formation of methane hydrate in a flow loop filled with water and pressurized methane. Hydrate formation

kinetics were studied as a function of system temperature, pressure, fluid velocity and hydrate-former volume fraction. A technique for hydrate growth rate prediction depending on these parameters was developed on the basis of the experimental results. Moreover, the influence of kinetic inhibitors and anti-agglomerants on hydrate formation kinetics and flow was considered in the work, although studies of gas hydrate flow assurance were not performed.

Similar work was done by Delahaye et al. [48] who considered a flow loop filled with a water-CO₂ hydrate slurry. The development of the system pressure and temperature were studied as a function of the following hydrate formation process: either by system cooling after pressurization or by gas injection after cooling. The hydrate slurry rheological properties were estimated on the basis of pressure drop behaviour as a function of the velocity. The dependence of the apparent viscosity of the slurry on the hydrate volume in the system (it was varied in the interval 0–20 %) was investigated. The variation found was similar to that in a previous study [49, 50]. However, the paper did not include visualisation of the flow patterns and granulometry.

Sinquin et al. [36] studied the rheological properties of a four-phase mixture of oil, water, gas and hydrate. The experiments were performed in a large-scale flow loop in both laminar and turbulent flow regimes. A dependence of the apparent viscosity of the suspension on the hydrate volume fraction was found in the laminar flow regime. The interaction of hydrate particles with the pipeline wall was studied for the turbulent flow regime in terms of the friction factor [51] as a function of hydrate volume fraction. In addition, the study [36] related the rheology of the hydrate slurry to its granulometry, as described later in the theoretical part of this chapter. However, the authors' quantitative estimates for the development of the hydrate particle size in the system were not confirmed by direct measurements.

All the above-mentioned papers mainly deal with hydrate formation kinetics and rheology of hydrate slurries. However, there is a need for more in-depth understanding of the slurry morphology and particularly of hydrate particle behaviour in agitated and flowing hydrate-containing systems. Experimental studies to gain such understanding were initially carried out in closed agitated systems, since the visualization of the pressurized multiphase system is less complex there. Herri et al. [52] studied the kinetics of methane hydrate formation in a pressurized reactor. The temporal behaviour of mean particle size and the number of particles was studied by a *turbidimetry* [53] technique. The rate of hydrate former consumption was recorded during the experiments. Herri et al. found that the hydrate particle size is

strongly dependent on the degree of turbulence induced in the fluid phase.

The work by Greaves et al. [54] uses a similar approach in a closed agitated system, filled with oil-in-water emulsion and a pressurized gas phase. The authors used an improved experimental set-up: a *focused beam reflectance method* (FBRM) [55]-probe for the determination of particle Chord Length Distribution (CLD) [56] and a digital video-camera, covered with a hydrophobic material. The distribution of hydrate particle chords was obtained in combination with in-situ photographs of water-oil-hydrate slurry. It was observed during the experimental study that hydrate particles could agglomerate relatively fast in a system with high water-cut.

A recent article by Darbouret et al. [57] focuses on hydrate granulometry in two flow loops (lab-scale and pilot-scale), filled with oil-in-water emulsion and gas. The FBRM/CLD-measurement technique was again used in the experiments, and the authors found a relation between a decrease in the slurry velocity and an increase in the hydrate particle size. Moreover, based on combined pressure drop and FBRM-measurements the authors succeeded to distinguish between hydrate particle growth and the aggregation process. Details of the calculation of actual particle sizes from the measured CLDs are given in the paper.

3.1.2 Model hydrates

The use of hydrates [58, 59] which are stable at atmospheric pressure [16], significantly simplifies the investigation of the flow assurance problem. An advantage of using this type of hydrate lies in the possibility of arranging for a sampling procedure, which provides the researcher with direct information about the hydrate fractal geometrical parameters. Moreover, the imaging of in-situ behaviour of a hydrate slurry is a key reason for using model hydrates. Early studies with model hydrates, however, focus on the same parameters as studies on pressurized systems: macroscopic aspects of flow assurance.

Berge et al. [60] measured permeability and porosity of a plug formed by freon R11 (CCl_3F [61, 62]) hydrate (Figure 3.1). The authors determined the porosity by saturating a porous plug with brine, which was then melted for the determination of actual water and hydrate-former volumes. The permeability was calculated on the basis of pressure loss measurements for water flow through the plug. The dependence of the permeability as a function of the porosity was determined, the porosity was estimated to be in the range of 34–60 %.

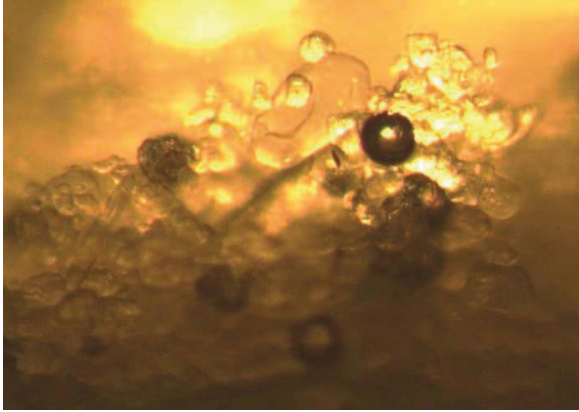


Figure 3.1: Agglomerated freon hydrate particle in water media.
The picture is acquired by the author

Also the rheology of model hydrates has been studied. Darbouret et al. [63] considered the laminar flow of water with tetra-*n*-butylammonium (TBAB, $C_{16}H_{36}BrN$ [64]) hydrate in a pipeline system. Series of pressure drop measurements were done for accurate determination of the slurry viscosity. TBAB hydrates of structure I and II were formed by adding variable amounts of hydrate-former. It was observed that the slurry rheology depended on the type of hydrate in the system, and the rheological expression could be correlated for both hydrate structures by the dependence reported by Graham et al. [65]. In addition, it was stated, that the slurry behaved as a Bingham fluid, exhibiting a yield stress. The yield stress was found to depend on the hydrate volume fraction to the third power in consistency with Thomas' et al. [66] empirical observations. However, this paper again did not present a study of the hydrate flow morphology and the turbulent flow regime was not investigated.

A parallel to the above-mentioned study was presented in a conference paper by Wang et al. [67] who considered a water-solid system with the hydrate of 1,1,1,2-tetrafluoroethane (HCFC, $C_2H_2F_4$ [11]). Hydrate formation kinetics were examined in combination with plugging taking place for a certain hydrate concentration. The history of the plugging process is shown in the paper in terms of the slurry mass flow rate and the pressure drop. In a full paper on the same work [10] the authors describe the morphology (Figure 3.2) of the slurry flow pattern. The gas hydrate slurry frictional pressure loss was also presented in the paper, as well as a correlation for the pipeline friction factor as a function of solid concentration is presented. In addition, sampling was described in the article. Sampled particle size distributions (PSD) were found by filtration of the slurry through metal sizers. However, the

PSDs presented in Wang et al. were not normalized, and it is difficult to draw any conclusions about the mechanisms governing the size change in the system.

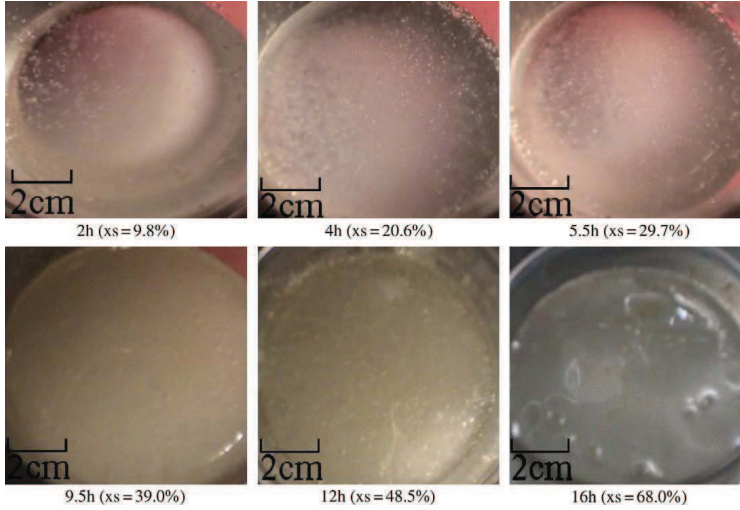


Figure 3.2: Slurry flow morphology in the transversal cross-section of a pipeline. The data is presented for different hydrate volume fractions x_s [10]

In-situ laser granulometry was done by Changyu et al. [33] for a water-solid slurry of freon R12 hydrate (CCl_2F_2 [68]). The temporal behaviour of the mean particle size and the hydrate volume fraction were observed for different flow rates. It was found that the hydrate formation was intensified with increasing flow velocity since the hydrate-former diffusion is enhanced by the turbulence. Conversely, the mean particle size was reduced with increasing the flow rate due to breakage of hydrate aggregates.

3.2 Simulations with gas hydrates

Gas hydrate flow assurance is generally considered as a fluid dynamical problem, which can be solved using the basic equations of fluid mechanics. The carrier (liquid) phase flow is in general described by the Navier-Stokes equations [69, 70]:

$$\nabla(\vec{u}) = q, \quad (3.1)$$

$$\rho \left(\frac{\partial \vec{u}}{\partial t} + \vec{u} \cdot \nabla \vec{u} \right) = -\nabla p + \mu \nabla^2 \vec{u} + f, \quad (3.2)$$

where \vec{u} is the velocity vector, ρ is the density, p is the pressure, μ is the viscosity and q, f are mass and momentum source terms respectively. The exact solution of Equations (3.1-3.2) may be found for a finite number of cases, simplifying the equations and thereby imposing certain limitations to the process they describe. However, they can be solved numerically for a wide range of scenarios by the use of finite-differencing techniques available in literature [71, 72].

When a second phase is dispersed in the fluid and the computational grid is coarse relative to the particles of the dispersed phase, which it normally is, as in the current work, Equations (3.1) and (3.2) are modified to take into account the presence of the second phase [73], as described in the thesis papers.

The dynamics of the hydrate phase may be calculated by two approaches: Eulerian-Lagrangian (details may be found in [74, 75], for instance) and Eulerian-Eulerian (for example, described in [73, 76]). In the Eulerian-Lagrangian method [77] the particles are considered as separate physical objects immersed in the liquid, and Newton's second law is applied directly to each particle. In this way it is possible to follow the motion of every particular particle in a Lagrangian reference frame. The technique makes it possible to distinguish between different mechanisms of particle-particle, particle-wall and particle-fluid interactions on a per-particle level. However, the Eulerian-Lagrangian technique is computationally expensive, hence simulations of industrial cases, which involve billions of particles [78, 79], are complicated.

The Eulerian-Eulerian approach models a dense hydrate phase as a quasi-liquid media, the properties of which are modified in a way so that the interphase and intra-phase interactions are modelled as source terms, included in the Navier-Stokes equations [80]. This approach is less computationally expensive than the Eulerian-Lagrangian one, although its drawback is in the use of averaged source terms, which gives rise to less accurate implementation of the physical phenomena.

There is a variety of possible expressions for the source term f in Equation 3.2 which represents the forces acting between the hydrate and liquid phases. The hydrate-fluid interaction involves both drag [74], buoyancy [81], lift [82, 83] and virtual mass mechanisms [84], although the dominating force is the drag. Several commonly used drag force expressions may be found in the recent work by Mazzei [85], who has compared simulations using each of them with experimental data.

The stress terms, which in the Navier-Stokes equations are the first and the second terms on the right-hand-side of Equation (3.2), arise in the dispersed phase mainly from particle-particle interaction. These terms may be modelled in three different ways within the Eulerian-Eulerian method. The first, and the oldest, way of modelling the shear stress terms involves the apparent viscosity of the multiphase mixture, from where the so-called *solid viscosity* may be derived, assuming the mixture is homogeneous [86]. A method of modelling the normal pressure term in the dispersed phase involves the use of *solid pressure force* [87, 88], which avoids the particulate phase from densification above the solid *packing limit* [89]¹. Another technique for modelling the stress terms is based on *granular temperature* [90, 91] of the particulate material, which is the measure of its velocity oscillations, and is an analogue to the kinetic theory of gases. Based on the computed *granular temperature*, the method calculates the bulk and shear viscosities of the solid phase.

3.2.1 Computational fluid dynamic models

Bondarev et al. [92] simulated the formation of a methane hydrate layer on a cold pipeline wall under the conditions of gas flow. Euler equations for the gas phase were explicitly solved on a regular one-dimensional grid. Hydrate formation was considered in those computational cells, where the equilibrium conditions were satisfied. The growth of the hydrate layer was modelled as a Stefan problem [38, 93] with the latent heat of hydrate formation [94] as a parameter. The impact of the hydrate layer on the flow of the gas was taken into account in the model as a decrease in the pipeline equivalent diameter due to the growth of the hydrate obstruction. The simulation results, obtained by the authors [92] showed a non-uniform axial distribution of the hydrate layer in the pipe. It was shown that the layer expanded in the flow direction as the gas was cooled during transport due to both heat exchange with the pipeline wall and the Joule-Thomson effect [2]. A periodic behaviour of the system was observed in the simulations: the gas hydrate layer initially formed on the wall, acting as thermal insulation for the core of the gas flow. This insulation effect causes the flowing fluid to be heated and the hydrate layer to be partly dissociated. A steady-state solution was found in the system: a large hydrate obstruction was found to block the pipeline in the outlet region, while the hydrate layer thickness

¹A more complete discussion of these terms and their physical meaning is given in the thesis papers. The model for the two-phase mixture used in this work is based on the assumption that the two phases constitute two interpenetrating and interacting continua, both sharing a common pressure. The "solids pressure" is in addition to this shared pressure and its introduction breaks the symmetry between the two phases [73].

along the length of pipeline was still insufficient to create a blockage there. However, the simulation results [92] were not validated with experimental data.

A similar approach was used in the work by Sean et al. [95] for the process of hydrate dissociation in the laminar flow of an incompressible fluid. The simulation model considered only the carrier phase flow, while the dissolution of the hydrate phase was modelled via the *moving mesh* principle [96]: the hydrate particle, which was large compared to the computational mesh, was modelled as a wall boundary condition, the cells of which were deleted according to the rate of hydrate dissociation. The model was equipped with a scalar representing the diffusion of methane released from hydrate decomposition. A dissociation rate constant, which was obtained generally in an experimental study, was more precisely defined using the model data on the spatial distribution of methane. However, it was found that the rate constant did not depend on either the carrier phase flow rate or the system pressure, but a strong temperature dependence was found both in the experiments and the model [95]. A finite element model of hydrate dissociation in a porous medium was formulated by Nazridoust et al. [97]. The static system considered by Nazridoust et al. was not directly focused on the problem of flow assurance. However, the model included thermal and diffusional aspects of hydrate decomposition and it was validated with experimental data.

Jassim et al. [98] studied the deposition of hydrate particles in a pipeline flow of a gas. In contrast to the article by Bondarev et al. [92], the article of Jassim et al. dealt with hydrates formed in the bulk space. The model involved the solution of Euler equations for the pure carrier phase. A simulation of the Lagrangian type [78] was developed for the prediction of particle dynamics using the pre-computed velocity field. Backward coupling, i.e. the influence of the hydrate phase on the gas flow, was not implemented into this model. The simulation results presented in the work [98] showed particle velocity profiles and the efficiency of particle deposition dependent on the particle mean size. The model was validated with experimental data.

A three-dimensional Eulerian-Eulerian model for the behaviour of hydrate bed in pipeline bends was recently developed by Shabani et al. [99]. The solid stress exerted by the particulate phase on the pipeline wall was incorporated in the model via a friction factor correction, following a model of Churchill [100]. The solid stress in the bulk of the suspension was coded using a rheological expression for slurry viscosity, proposed by Thomas [66]. It was shown by Shabani et al. that a hydrate slug passing through a bend significantly increased the pressure drop. The simulation results were in agreement with corresponding experimental data.

3.2.2 Population balance models

The examples of simulations of multiphase flows involving hydrates presented above do not deal with hydrate particle size evolution, which determines the value of inter- and intra-phase momentum transport terms. The problem of particle cohesivity may be directly solved in the Eulerian-Lagrangian method by substituting adhesional interaction into the force balance for each separate particle [101–104]. However, this approach is not yet widely used in the hydrate field due to the difficulty of quantifying the adhesion force experimentally and the technical problems associated with the potential well definition in the code only recently having been overcome [103, 104]. Further research work is on-going for the development of a Eulerian-Lagrangian model for hydrate particle dynamics.

Another approach is normally used in connection with the Eulerian-Eulerian method [105]. As compared to the Eulerian-Lagrangian technique mentioned above, the Eulerian-Eulerian approach does not deal with each separate particle, but accounts for the general evolution of particle size distribution depending on the flow parameters and the particle material properties. The method was developed by Smoluchowski [106, 107] (also called *population balance principle* - PBM) in order to account for the statistics of the change of the amount of particles in a certain size band of their PSD due to the rate of their "birth" and "death" in this interval [108]². A "birth" event (Figure 3.3) is the increase of the amount of particles in a given size band due to nucleation, growth or agglomeration of smaller particles or due to dissociation or fragmentation of larger particles. A "death" event is the decrease of the number of particles in the given size band due to the same phenomena, except for nucleation.

The equation for the change of the PSD may be given by [25]:

$$\frac{df}{dt} + G \cdot \frac{\partial f}{\partial r} = B(r) - D(r), \quad (3.3)$$

where r is the particle size, $f(r)$ is the number density function, G is the growth or dissociation rate (negative for dissociation) and $B(r)$, $D(r)$ are the rates of particles "birth" and "death" respectively [109].

²Note that the terms "birth" and "death" are used somewhat differently in the PBM literature than in the mathematical literature on stochastic processes. In the latter a "birth"- "death" process is a very specific process in which only transfers to the neighboring states is allowed

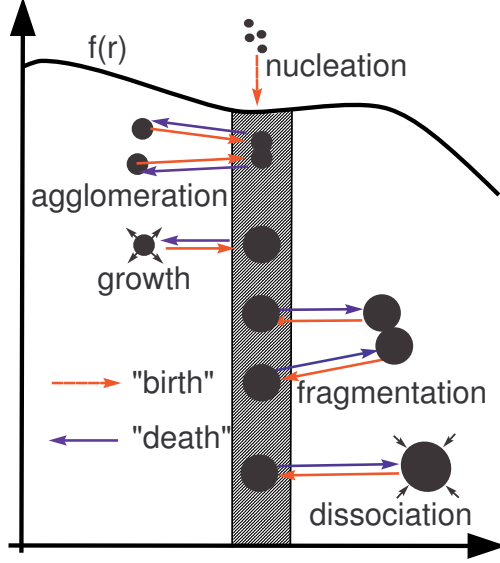


Figure 3.3: Schematic representation of the population balance principle

Equation 3.3 may be simplified by the application of a moment transformation:

$$M_j = \int_0^{\infty} r^j f(r) dr, \quad (3.4)$$

where M_j is the j^{th} moment of particle size distribution. In this way Equation 3.3 may be reduced to a set of ordinary differential equations:

$$\frac{dM_j}{dt} = j \cdot GM_{j-1} + \int_0^{\infty} r^j [B(r) - D(r)] dr, \quad (3.5)$$

in which the first four PSD-moments physically represent the number of particles, their size, area and volume [106, 110]. The kinetic terms B and G are set to be dependent on interparticle collision rate, particle adhesion force and particle/agglomerate strength [111, 112]. The spatial distribution of PSD-moments may be accounted for by the expansion of the substantial derivative [113, 114]:

$$\frac{\partial M_j}{\partial t} + \nabla \cdot (M_j \vec{u}) = j \cdot GM_{j-1} + \int_0^{\infty} r^j [B(r) - D(r)] dr, \quad (3.6)$$

where \vec{u} is the velocity.

The model by Englezos-Bishnoi-Malegaonkar [115, 116] is a typical example of im-

plementation of the population balance principle to the hydrate field. The model is developed for an agitated system filled with a water-hydrate mixture pressurized by natural gas. The nucleation of the hydrate phase is considered in the model [115] as a singular event just at the beginning of the process, forming an number of particles proportional to the difference between the initially consumed amount of gas and its equilibrium concentration in the presence of hydrate. The initial size of the hydrate nuclei was calculated using the expression for critical radius presented in Equation (2.2). The growth rate of the hydrate particles is set to be dependent on their surface area, the concentration of hydrate-former in the water phase, and on a growth rate constant, determined by fitting the results to experimental data. The transport of hydrate-former through the water phase is considered as a step-by-step process of dissolution, diffusion through the water phase and consumption on the hydrate surface.

The population balance technique was used in reference [115] for estimation of hydrate particle surface area, including the first three moments of particle size distribution in the analysis. The simulation results were in agreement with the respective experimental data via the growth rate constant, which later, however, had been found to be overpredicted, as shown by Skovborg [117].

In addition to the limitations shown in [2], the model of Englezos-Bishnoi- Malegaonkar [115, 116] does not consider an impact of the flow field on the aggregation/breakage of hydrate particles. In spite of this, there is a wide range of papers, which use this model, for instance the simulations of hydrate dissociation performed by Clarke and Bishnoi [118].

The model by Herri et al. [25] builds on the Englezos-Bishnoi-Malegaonkar technique and deals with a similar agitated system. However, the nucleation is here considered as a continuous production of zero-sized particles, depending on supersaturation [119]. The growth rate calculation is dependent on the second moment of the particle size distribution as in the Englezos-Bishnoi-Malegaonkar model, but the growth rate constant is set to be dependent also on the flow properties according to Armenante and Kirwan [120]. In addition, the population balance model was updated with the expressions for particle "birth" and "death" rate due to agglomeration, breakage, attrition and secondary nucleation, which were tuned by fitting to experimental the data presented in [52]. It was shown that aggregation gives rise to a particle size change comparable the change caused by particle growth. However, the PBM-model works with an system-average shear rate, while in reality the flow field in the vicinity of the impeller [121] and the vessel walls may be significantly

different [122, 123]. Moreover, the model was uncoupled in terms of the influence of the particulate phase PSD-moments on the carrier flow field.

In this sense, the work by Sinquin et al. [36], where the flow rheology was set to be dependent both on the hydrate volume fraction and on the particle size via the packing limit, may be considered to be a further development in terms of flow assurance modelling. The particle size was calculated with the use of an analytical expression [124], which relates the size to the shear rate and the particle-particle adhesion force. Although this approach is not of the population balance type and since it is not possible to mimic both the kinetics and the spatial distribution of PSD-moments, it has been used in an integrated flow simulator for prediction of the pressure drop in a hydrated pipeline [36]. The model-predicted pressure drops were in agreement with the experimental data.

At the end of this review the author of the current thesis concludes that there is a need for a PBM-model which takes into account more information about the flow pattern. This information can be acquired by CFD-simulations of the hydrate slurry flow. The model needs to be validated with experimentally obtained information on flow rheology, granulometry and kinetics.

Chapter 4

Summary of papers included in the thesis

4.1 Paper 1

Balakin, B.V., Pedersen, H., Kilinc, Z., Hoffmann, A.C., Kosinski, P., Hoiland, S., 2010. Turbulent flow of freon R11 hydrate slurry. *Journal of Petroleum Science and Engineering* 70, 177–182

This work is focused on an experimental study of freon hydrate slurry behaviour in a low-pressure flow loop. Particle-laden flow morphology transitions from a slug-type stream to a homogeneously mixed slurry are described in relation to the mean flow velocity in the rig.

Multiphase flow pressure drops were measured for a range of flow velocities and hydrate volume fractions in the turbulent flow regime. Further analytical treatment of the pressure drop data made it possible to estimate the apparent viscosity of the suspension and the yielding stress for a range of hydrate volume fractions. It was found in the work that the dependence between the slurry viscosity and the volume fraction of hydrate is of the Roscoe-Brinkman type (Figure 4.1) [34], while the yielding stress (Figure 4.2) follows the dependence proposed by Thomas [66] and Darbouret [63].

A sampling procedure was developed for the determination of hydrate agglomerate size: the particles were isokinetically sampled from the pipeline to a beaker for further microscopical investigation. Micro-photographs (Figure 3.1) were treated

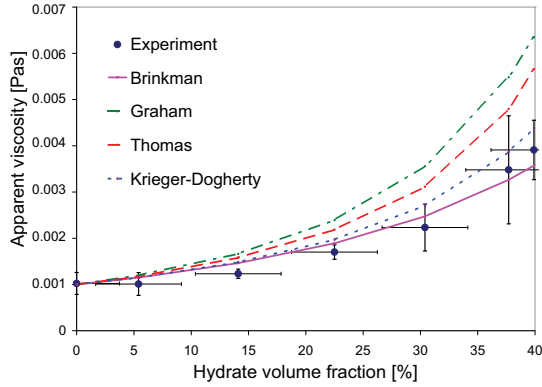


Figure 4.1: Slurry apparent viscosity as a function of hydrate volume fraction (comparison with expressions given by Brinkman [34], Krieger-Dougherty [125], Graham [63] and Thomas [86])

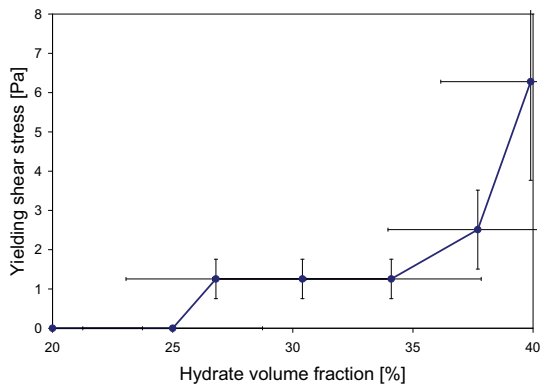


Figure 4.2: Yielding shear stress as a function of hydrate volume fraction

with the software package ImagePro for determination of the mean particle size and the sphericity of aggregates. The packing limit value for the hydrate bed was calculated from the granulometry data.

4.2 Paper 2

Balakin, B.V., Hoffmann, A.C., Kosinski, P., Rhyne, L.D., 2010. Eulerian-Eulerian CFD model for the sedimentation of spherical particles in suspension with high particle concentrations. *Engineering Applications of Computational Fluid Mechanics* 4(1), 116–126

This article deals with validation of a CFD model based on the commercial software STAR-CD on a well-defined two-phase process, namely that of particles sedimentation in a quiescent fluid. A Eulerian-Eulerian CFD model is built implementing an apparent viscosity for the suspension, coded by an expression of the Roscoe-Brinkman type. The experimental data that are used for the model validation, are taken from the literature [126]; the simulation results are compared with the experimental in terms of the average settling velocity, which reduces with an increase of the solid volume fraction, as presented in Figure 4.3.

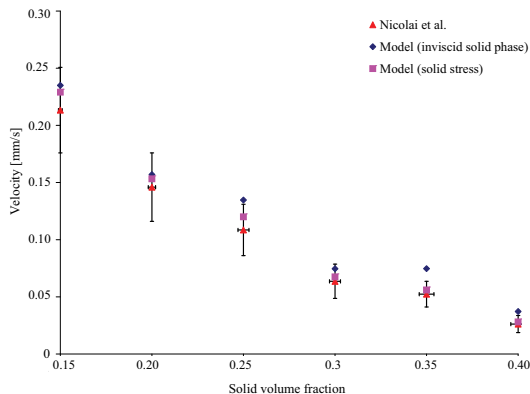


Figure 4.3: Time-averaged velocity of settling front as a function of solid volume fraction. Simulation results are presented both neglecting solid stress and accounting for it, and are compared with experimental data by Nicolai et al. [126]

In spite of the apparent simplicity of the studied problem, the formation of convective instabilities during the sedimentation of packed suspensions is widely described in the literature [127, 128]. This phenomenon is reproduced by the model, exhibiting fluctuations in the flowpattern similar to those observed by Nicolai et al. [126] in experiments.

4.3 Paper 3

Balakin, B.V., Hoffmann, A.C., Kosinski, P., 2010. Population balance model for nucleation, growth, aggregation and breakage of hydrate particles in turbulent flow. *AIChE Journal*, DOI 10.1002/aic.12122

This paper studies the recirculative flow of a water-hydrate mixture a hydrate particle population balance. It tracks the development of the hydrate phase in the system pump/pipeline used in the experimental study of Wang et al. [10], from the early beginning of the process, when the hydrate-former is injected to the system up to the first plugging event, when the pump was no longer able into circulate the slurry. The flow loop was divided into two compartments: pump and pipeline, each of which were assigned different turbulence intensities, calculated analytically. The population balance model was then developed building on the work by Herri et al. [25], including the "birth" and "death" sources, having their origin in the nucleation, growth, aggregation and breakage of hydrate particles. Two possible scenarios for particle nucleation were considered: continuous nucleation and a single nucleation-event as proposed by, for example, Englezos and Bishnoi [115].

It is shown in the work that the use of growth and nucleation is not adequate for a proper prediction of actual particle size, but the combination of all five possible size-changing factors results in a model which is in good agreement with the experimental data. The aggregation and breakage term constants, found by fitting the model data to the experimental results, are shown to be of similar value for the two different scenarios for nucleation mentioned above, supporting the relevance of their quantification. Particle size distributions were reconstructed from model-predicted PSD-moments (Figure 4.4). They are in suitable agreement with the experimental data of Wang et al. [10].

4.4 Paper 4

Balakin, B.V., Hoffmann, A.C., Kosinski, P., Hoiland, S., 2010. Turbulent flow of hydrates in a pipeline of complex configuration. resubmitted to *Chemical Engineering Science* after minor revisions

This article is focused on CFD-simulation of the experiments described previously in section 4.1 of this chapter for the homogeneous flow regime, i.e. for flow conditions

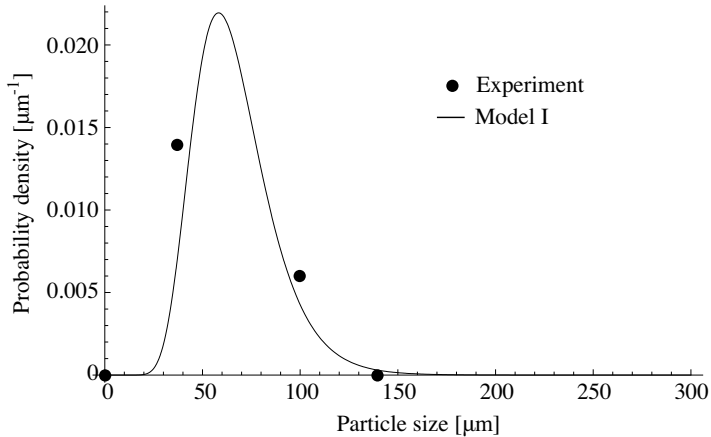


Figure 4.4: Hydrate particle size distribution for 9.8 vol.% hydrate in the rig. Simulation results are compared with experimental data [10]

where the hydrate is distributed almost homogeneously over the pipe. The model is based on the Eulerian-Eulerian principle with the viscosity of the solid phase fitted to the experimental data (Figure 4.1) of slurry rheology. The mean particle size used in the article is assumed to be constant. The geometry of the process mimics a part of the experimental rig.

The model is validated with experimental data (section 4.1) in terms of pipeline pressure drops and visual observations of the flow patterns developed in the rig. In addition, the article provides insight into the details of the flow structures developed in the rig (Figure 4.5), and provides a discussion of the reasons for their formation.

4.5 Paper 5

Balakin, B.V., Hoffmann, A.C., Kosinski, P., 2010. Computational fluid dynamic model for deposition of adhesive hydrate particles in a pipeline. submitted to *Chemical Engineering Science*

The work is focused on the process of hydrate-bed formation in the low-pressure flow loop. Experimental investigations were performed for determination of the behaviour of the particulate bed in the rig. In addition to experiments a CFD-model, described in section 4.4, was updated with an extra solid stress expression, which avoids the densification of the particulate phase above the packing limit. The

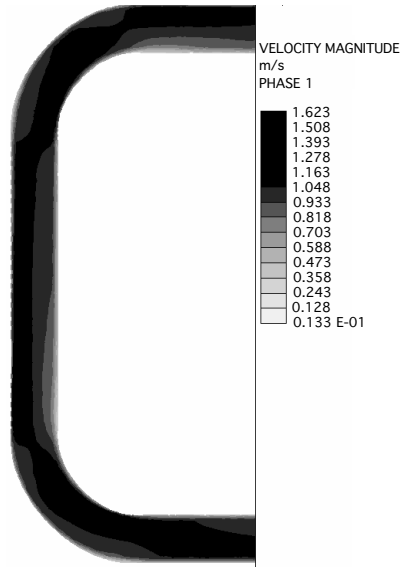


Figure 4.5: Contours of the carrier phase velocity magnitude in the midline cross-section of the flow loop

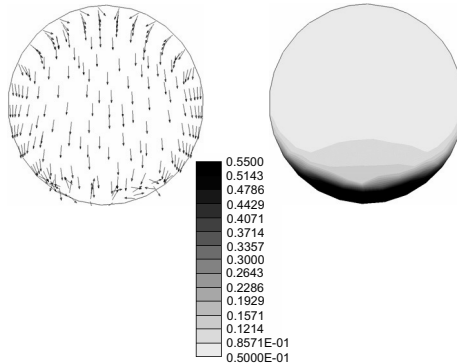


Figure 4.6: Vectors of water velocity together with contours of hydrate volume fraction

rheological expression used in this work includes the packing limit value, determined experimentally. Hydrate particle size evolutions were modelled using the PBM-approach described in section 4.3. On basis of the PBM-results, a subroutine for mean particle size prediction was incorporated into the CFD-model.

The simulations results for the updated model predict a dependence between hydrate bed thickness and mean flow velocity, which is in good agreement with the

experiments. Moreover, the model quantifies the distribution of particles in the bed for a range of flow velocities (Figure 4.6). The PBM-model, which was used for the determination of the mean particle size in the rig was validated with the data from the sampling described in section 4.1 of this chapter.

Chapter 5

Concluding remarks and further work

It was shown in the dissertation, that the gas hydrate flow assurance phenomenon can be analyzed by a predictive numerical tool, which involves both CFD and PBM principles. The papers included in this thesis demonstrate the ability of the developed models to mimic experimentally observed flow patterns, particle sizes and their distributions, dissipative energy losses and a variety of other parameters, which influence hydrate particle agglomeration and deposition.

The CFD-models used in the current work involve modification of hydrate particle size for the determination of its influence on the formation of hydrate beds in the vicinity of a pipeline knee. The PBM-models implement more precise definitions of flow patterns than was done previously in the hydrate literature.

The last article included in the dissertation describes an attempt to account for the variation of the particle size with the shear rate by using an analytical expression [36, 124]. The inter-particle cohesion force, used in this analytical expression, was determined using the compartmental PBM-model with the spatially-averaged shear stress. While this is a useful exercise there is no doubt that the use of a PBM-model, which is coupled with CFD-predictions, done on a per-cell basis (Equation 3.6), results in a better simulation and a prediction the spatial distribution of particle sizes.

The approach described in the thesis involves the prediction of particle size and the incorporation of this particle size into the inter-phase momentum exchange. However, the shear stress in the solid phase, caused by the particle interaction and

expressed in terms of the apparent viscosity of the suspension, is not dependent on the particle size. This may represent a deficiency in the model, since it is shown in the literature [36, 129] that the apparent viscosity of a hydrate slurry may depend on the particle size via a so-called *effective volume fraction*, which depends on the mean particle size and the particle fractal dimension. This volume fraction is often used in a rheological expression of the Krieger-Dougherty type [34] instead of the packing limit used here.

In addition, the current CFD-model does not include the thermal aspects of hydrate nucleation, growth and dissociation phenomena. The author concludes, therefore, that there is a need for further work on the proposed Eulerian-Eulerian model, which should be updated at least in terms of these three above-mentioned problems.

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