

Multi-instrumental data processing and natural gas hydrate crystallization modelling under flow

Vinicius Rodrigues de Almeida

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Traitement de données de multi-instruments et modélisation de la cristallisation des hydrates de gaz naturel dans un écoulement

Multi-instrumental data processing and natural gas hydrate crystallization modelling under flow

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LIST OF SYMBOLS

Symbol	Description	Unit
А	Hamaker constant	J
С	Concentration of gas into the liquid	mol/L
D_1	Diameter of the downward pipe	mm
D_h	Diameter of the slightly inclined pipe	mm
D_2	Diameter of the upward pipe	mm
d	Particle diameter	mm
E_{abs}	Absolute energy	aJ
$\overline{E}_{s,h}$	Average absolute energy (horizontal section) relative to a sensor s	aJ
F	Force	Ν
f	Molar fraction of natural gas	-
$\mathbf{f}_{\mathbf{c}}$	Collision frequency	Hz
\mathbf{f}_1	Fanning friction factor in the downward section	-
$\mathbf{f}_{\mathbf{h}}$	Fanning friction factor in the slightly inclined section	-
\mathbf{f}_2	Fanning friction factor in the upward section	-
g	Acceleration of gravity	m/s^2
h	Liquid bridge	m
$\mathbf{k}_{\mathbf{w}}$	Water conversion	-
L_1	Equivalent length of the downward pipe	m
L _h	Equivalent length of the slightly inclined pipe	m
L_2	Equivalent length of the upward pipe	m
L ₄	Liquid level measured by the differential pressure in the separator	m
Μ	Molar mass	g/mol
m	Mass	kg
$\mathbf{N}_{\mathbf{p}}$	Number of particles	-
$\mathbf{N}_{\mathbf{h}}$	Hydration number	-
n	Number of moles	moles
n _c	Number of mols of gas consumed for hydrate formation	moles
n _p	Number density of particles	-
р	Pressure	Ра
pc	Critical pressure	Pa

Q	Flow rate	L/s
r	Particle radius	m
Т	Temperature	°C
t	Time	S
T _c	Critical temperature	°C
t _d	Time since the beginning of the dissolution of gas	S
t _H	Time since the onset of hydrate formation	S
U_1	Flow velocity in the downward section	m/s
U_{h}	Flow velocity in the horizontal section	m/s
U_2	Flow velocity in the upward section	m/s
¥	Volume	m ³
V_r	Relative velocity	m/s
α	Fraction (in volume)	-
β	Fraction relative to the mixture	-
ε _r	Relative permittivity	-
ΔG	Free energy	J
Δp_1	Pressure drop in the downward section	kPa
Δp_h	Pressure drop in the slightly inclined section	kPa
Δp_2	Pressure drop in the upward section	kPa
Δp_4	Differential pressure in the separator	Pa
δt	Step of time	S
γ	Shear rate	s ⁻¹
μ	Chemical potential	J/mol
ρ	Density	kg/m ³
θ	Contact angle	rad
η	Viscosity	Pa·s
μ	Chemical potential	J/mol
τ_{C}	Response time between particle-particle collision	S
$ au_{\rm V}$	Momentum response time	S
ω	Pitzer's acentric factor	-

Superscripts

• •	T 1 . 1	/ ·	
1n1	Injected gas	(gas compensation	system)
mj	injected gas	(Sub compensation	by scom)

Subscripts

С	Continuous phase				
c	Critical				
D	Dispersed phase				
d	Dissolved gas				
cap	Capillary				
f	Free gas				
G	Gas phase				
Н	Hydrate phase				
i	Natural gas component				
m	mixture				
0	Oil phase				
S	Surface				
sat	Saturated				
shear	Shear (force)				
V	Volume				
VW	Van der Waals (force)				
W	Water phase				

LIST OF ABBREVIATIONS

AA	Anti-agglomerant
AE	Acoustic Emission
CLD	Chord length distribution
FBRM	Focused beam reflectance measurement
HDD	Hits driven data
LDHI	Low dosage hydrate inhibitor
KHI	Kinetic hydrate inhibitor
PVM	Particle vision measurement
SRK	Soave-Redlich-Kwong
TDD	Time driven data
THI	Thermodynamic hydrate inhibitor

CHAPTER 1 - INTRODUCTION

Multiphase flow transportation in offshore pipelines is an important concern for the petroleum industry. The operational hazards involving oil and gas transportation in pipelines are studied in an engineering analysis process called *flow assurance*. The three main treats to flow assurance are *wax*, *hydrates*, and *asphaltenes* (Kaiser, 2020). Hydrate problems are common in deep-water production, and they are considered the biggest challenge in flow assurance nowadays (Cardoso et al., 2014). *Gas hydrates* are crystals composed by water and gas molecules, and they form in offshore scenarios of petroleum extraction due to the high pressures and low temperatures of these systems.

Figure 1 shows that the petroleum (with water, sand, and other impurities) is at high pressure and high temperature when it is extracted from the wells, outside of the hydrate formation domain (point A). As it flows in the pipeline, its temperature gradually decreases, since the water from the sea cools the pipeline. At some point, with low enough temperature, the mixture enters the hydrate thermodynamic formation domain (point B), and after some time, hydrates may form (point C). Hydrate formation is characterized by an immediate temperature increase (it is an exothermal process) and an absolute pressure decrease (hydrates store gas molecules while the system seeks for a lower level of energy). As the mixture remains flowing, the pressure decreases, so it will be outside of hydrate formation zone (starting from point D) until it reaches the end of the pipeline (point E).





The formation of gas hydrates inside oil and gas pipelines is undesirable and represents an important technical issue for the industry because it may cause blockage of pipelines. Avoiding hydrate blockages is necessary for two reasons. The first reason is the security threat and technical difficulties involved in removing the plugs, which can cause accidents. The second reason concerns the financial losses in case the production is interrupted due to a hydrate blockage incident.

There are two approaches to avoid hydrates blockage: *hydrate avoidance* and *hydrate management*. The first approach was the initial strategy adopted by the industry, where the pipelines will remain without hydrates during extraction. By its turn, the hydrate management approach allows operation with hydrates if the risk is acceptable. Due to the high costs of a completely hydrate avoidance, companies have been looking to migrate from hydrate avoidance are illustrated in Figure 2.



Figure 2. Hydrate avoidance versus hydrate management. Modified from Kinnari et al. (2015).

Currently in both strategies, chemical additives known as *hydrate inhibitors* are injected inside the pipelines to avoid plugs. There are three types of hydrate inhibitors: *thermodynamic hydrate inhibitor* (THI), *kinetic inhibitor* (KI) and *anti-agglomerant* or *hydrate dispersant* (AA). While the THIs are necessary in high doses (20-60 wt.% vs. water), the KIs and AAs can be effective at low doses (from 0.25 to 3 wt.% vs. water), and, because of that, they are frequent called *low-dosage hydrate inhibitors* (LDHIs).

THIs are the most common additives used on field, and they reduce the temperature of hydrate formation, working as hydrate avoidance inhibitors. THIs are well understood and predictable, but they are becoming more and more expensive, once the volume of this type of additive is proportional to the water fraction of the condensate mixture. During oil and gas extraction, water is injected inside the reservoir to maintain its pressure. Therefore, the water fraction increases over the years, so it does the amount of THI.

An alternative is the use of LDHIs, which include KIs and AAs. KIs are used to delay the beginning of crystallization and can be used for some systems where the time inside the thermodynamic formation zone of hydrates is short. However, KIs are for several scenarios unpredictable and/or ineffective, mostly when pipelines are very long. The AAs are designed to maintain the system flowable with hydrates, by controlling the size of hydrate particles. The role of AAs is therefore not to avoid hydrate formation, but to prevent agglomeration and in certain cases deposition in such way that the system continues flowing even if there are hydrate particles in the pipeline. Therefore, AAs will change the dispersion and the particles size distribution.

The use of AAs has been reported as effective for low water cut systems. However, for high water cuts, results are more variable from literature data using different pilot systems. The mechanisms of anti-agglomeration or dispersion of hydrates in flow lines when AAs are used are not well understood. The effect of AAs in flow lines are not well understood because hydrate formation and plugging mechanisms involve several complexes phenomena: crystallization, growth, agglomeration, breakage, deposition, settling, flow pattern, and others. Analyzing and quantifying these phenomena under flowing conditions represents a challenge, even at laboratory level. Part of these mechanisms occurs at microscopic scale (crystallization and growth), but the impact on the flow regime and the transportability of hydrates occurs when particles are at macroscopic scale (deposition, bedding, sloughing, viscosification, plugging).

Overall, several mechanisms of hydrate formation are known, and in recent years, more insights have been proposed in the literature. However, a completely description of all mechanisms has not yet been achieved. A satisfactory explanation on how the slurry flow behaves over time and space is not yet available. Most of the academic research focuses on oil-dominated systems, while industrial interest concerns water or gas-dominated systems. A better understanding on the suspension, the distribution of hydrate particles in the liquid phase, and how hydrate formation impacts water-oil flow pattern, is still needed.

A high-pressure flow loop with temperature control is an apparatus used in laboratory to study hydrate formation under flow. Due to the size of this type of apparatus and the complexity of the phenomena, the analysis of results is a challenge, and it requires a combination of different instruments and a careful implementation of data processing and calculation methods. This is where this thesis situates. It uses a multidisciplinary approach, combining an experimental work and the development of a software for data treatment and calculation methods to study hydrate formation for applications in flow assurance.

1.1. Objectives

The objective of this work is a flow loop (56 meters long, diameters of 15.7 mm and 10.2 mm) experimental study of gas hydrate formation and transport in oil-water dispersions (30, 50 and 80% water cut) without and with LDHI-AA (doses of 1.50 wt.% vs. water at 50% water cut and 0.94 wt.% vs. water at 80% water cut), carrying out tests with saline water (30 g/L of NaCl), Kerdane oil and natural gas. A new combination of different sensors has been used in the Archimedes flow loop apparatus installed at Mines Saint-Etienne to analyze the flow pattern and distribution of hydrates in the system, and a data processing application has been developed for data analysis and calculation procedures to extract information from the experiments. This work has three partial objectives:

- To understand better the different steps of hydrate blockage formation, hydrates transportability and its impact on the multiphase flow conditions.
- To test the effectiveness of a commercial LDHI-AA in avoiding plugs and understand how it changes the slurry flow and the transportability of the system for water continuous systems.
- To evaluate the applicability of acoustic emission, permittivity measurements and high-speed imaging to detect and track hydrate particles and the flow pattern in flow loop experiments, namely the continuous phase, hydrates fraction and deposition.

1.2. Motivation

Nowadays, petroleum extraction is moving to deep-sea scenarios, increasing the technical complexity and costs of production. In deep sea, as the lengths of pipelines are becoming longer, the required thermodynamic conditions for hydrate formation are attained, which is a challenge for engineers on this field to assure that the pipelines remain flowable. The costs and environmental issues associated with the overuse of THIs that are injected for hydrate avoidance are relevant for the petroleum industry.

Most of the work reported in the literature, including both experimental studies and mathematical models, concerns oil-dominated systems. Limited studies have attempt to explain mechanisms of hydrate blockage at high water cuts. For the industrial point of view, there is a growing interest in high water cuts, due to the increasing water fraction flowing in the pipelines as the wells become older.

The implementation and improvement of the current hydrate blockage avoidance strategies requires a better comprehension on how flow pattern and hydrate plug formation are

connected, how hydrates are dispersed in the system, what is the maximum transportability of hydrates based on the flow conditions, how the apparent viscosity changes, how much additive must be injected, among several other analyses that could be proposed. For that, one path is the development of a database of hydrate formation experiments combining different instruments that can be used for modeling the different steps of hydrate formation and hydrate blockage, which is where the discussion of this thesis is limited. However, it creates a base for future advanced treatments that could be created as predictive tools in hydrate management, based on mathematical models, statistics, and machine learning (or other artificial intelligence) techniques.

1.3. Organization of the thesis

<u>Chapter 2</u> contains the <u>literature review</u>. The focus is flow assurance and the mechanisms of hydrate formation in oil-water systems. It is also presented the basic notions of gas hydrates, liquid-liquid, solid-liquid flows, and some techniques for hydrate blockage prevention. The contributions of this work are discussed.

<u>Chapter 3</u> presents the <u>materials and methods</u> used in this work. It contains the description and schematics of the flow loop apparatus used in the experiments, the instruments, and the experimental protocol. It also presented the <u>calculation methods</u> for gas dissolution, oil density, and water conversion.

<u>Chapter 4</u> analyzes the <u>liquid-liquid flow</u> before hydrate formation. A combination of permittivity, water-cut and viscosity analysis is presented, compared to some images of the flow obtained with a camera.

<u>Chapter 5</u> presents the results of hydrate formation with and without a commercial AA. It discusses the <u>mechanisms of hydrate formation</u> and <u>hydrate plug formation</u> for both cases.

<u>Chapter 6</u> presents two simplified <u>models</u> to calculate the apparent flowing <u>hydrate</u> <u>fraction</u> based on density measurements and an <u>additional treatment with absolute energy</u> comparing it to the frictional pressure drop.

Chapter 7 presents the relevant conclusions and ideas for future works.

As supplementary material, there are six Appendices. Appendix A presents details of the Archimède Data Processing and Visualization Application, software that was developed to treat and visualize the data from the experiments using the Archimède flow loop. Appendix B contains a simplified PVT model from literature used in this work for the calculation methodologies. Appendix C has data of solubility experiments for some of the components of the natural gas in Kerdane oil. Appendix D contains the calculated Reynolds number and apparent viscosity for the experiments. Appendix E contain additional results of experiments not presented or not discussed in the thesis. Finally, Appendix F contains the calculated water conversion and hydrate fraction for all the experiments.

1.4. Highlights in French - Résume du Chapitre 1 en Français

Le transport d'écoulement polyphasique dans les pipelines en l'eau profonde est une préoccupation importante pour l'industrie pétrolière et gazière. Les dangers opérationnels pour ce scénario sont étudiés dans un processus d'analyse technique appelé *maintien de l'écoulement*. Les problèmes d'hydrates sont courants dans la production en eau profonde, et ils sont considérés comme le plus grand défi de l'assurance de flux. Les hydrates de gaz sont des cristaux composés de molécules d'eau et de gaz, et ils se forment dans des scénarios d'extraction de pétrole en haute mer en raison des hautes pressions et des basses températures de ces systèmes.

La formation d'hydrates de gaz à l'intérieur des oléoducs et des gazoducs n'est pas souhaitable et représente un problème technique important pour l'industrie, car elle peut provoquer le blocage des pipelines. Il existe deux approches pour éviter le blocage des hydrates : l'évitement des hydrates et la gestion des hydrates. Dans la première stratégie, les pipelines resteront sans hydrates pendant l'extraction. A son tour, l'approche de gestion des hydrates permet un fonctionnement avec des hydrates si le risque est acceptable. En raison des coûts élevés d'un évitement complet des hydrates, les entreprises ont cherché à passer de l'évitement des hydrates à la gestion des hydrates, avec l'utilisation des additives l'antiagglomérant ou dispersant d'hydrate (AA), que peuvent être efficaces à faibles doses (entre 0.5 et 3 poids% d'eau). Les AA sont conçus pour maintenir le système fluide avec les hydrates, en contrôlant la taille des particules d'hydrates. Le rôle des AA n'est donc pas d'éviter la formation d'hydrates, mais d'empêcher l'agglomération et dans certains cas le dépôt de telle sorte que le système continue de circuler même s'il y a des particules d'hydrate dans la canalisation. Les AA vont donc modifier l'émulsion et la distribution granulométrique.

L'utilisation des AA a été signalée comme efficace pour les systèmes de coupure de bas niveau d'eau. Cependant, pour les systèmes de coupure d'eau haute, ils ne sont apparemment pas très efficaces. Les mécanismes d'anti-agglomération ou de dispersion d'hydrate dans les conduites d'écoulement lorsque les AA sont utilisés ne sont pas bien compris. Les AA ne sont pas bien compris car la formation d'hydrates et les mécanismes de colmatage impliquent plusieurs phénomènes complexes : cristallisation, croissance, agglomération, rupture, dépôt, décantation, modèle d'écoulement, etc. L'analyse de ces phénomènes dans des conditions d'écoulement représente un défi, même au niveau du laboratoire. Une partie de ces mécanismes se produit à l'échelle microscopique (cristallisation et croissance), mais l'impact sur le régime d'écoulement et la transportabilité des hydrates se produit lorsque les particules sont à l'échelle macroscopique (dépôt, litière, mue, viscosification, colmatage).

Une description complète de tous les mécanismes n'a pas encore été réalisée. Une description satisfaisante du comportement de l'écoulement de la suspension dans le temps et dans l'espace n'est pas encore disponible. La plupart des recherches universitaires se concentrent sur les systèmes dominés par le pétrole, tandis que l'intérêt industriel concerne les systèmes dominés par l'eau ou le gaz. Une meilleure compréhension de la suspension, de la distribution des particules d'hydrate dans la phase liquide et de l'impact de la formation d'hydrates sur le schéma d'écoulement eau-huile est encore nécessaire.

Un flowloop haute pression avec contrôle de température est un appareil utilisé en laboratoire pour étudier la formation d'hydrates sous écoulement. En raison de la taille de ce type d'appareil et de la complexité des phénomènes, l'analyse des résultats est un défi, et elle nécessite une combinaison de différents instruments et une mise en œuvre minutieuse des méthodes de traitement et de calcul des données. C'est là que se situe cette thèse. Il utilise une approche multidisciplinaire, combinant un travail expérimental et le développement d'un logiciel de traitement des données et de méthodes de calcul pour étudier la formation d'hydrates pour des applications en assurance d'écoulement.

L'objectif de ce travail est une étude expérimentale en boucle d'écoulement de la formation et du transport d'hydrates de gaz dans les émulsions huile-eau avec et sans antiagglomérant (doses 1,50 poids% eau pour 50% fraction d'eau, et 0,94 poids% eau pour 80% fraction d'eau), en réalisant des tests avec de l'eau, l'huile et du gaz naturel. Une nouvelle combinaison de différents capteurs a été utilisée dans l'appareil de boucle d'écoulement d'Archimède installé à Mines Saint-Etienne pour analyser le régime d'écoulement et la distribution des hydrates dans le système, et un logiciel de traitement des données a été développée pour analyser les données et mettre en œuvre des procédures de calcul. Ce travail a quatre objectifs partiels :

- Mieux comprendre les différentes étapes de la formation du blocage des hydrates, la transportabilité des hydrates et son impact sur les conditions d'écoulement multiphasique.
- Tester l'efficacité d'un LDHI-AA commercial pour éviter les bouchons et comprendre comment il modifie le débit de lisier et la transportabilité du système pour les systèmes à eau continue.

• Evaluation of the applicability of acoustic emission, permittivity measurements and high-speed imaging to detect and track hydrate particles and the flow pattern in flow loop experiments.

CHAPTER 2 - LITERATURE REVIEW

This chapter gives a brief presentation about crystallization of gas hydrates and a review about mechanisms of hydrate plug formation in water-oil systems. The approaches to avoid hydrate blockage, some future perspectives and the contributions of this thesis are discussed.

2.1. Gas hydrates

As explained in Chapter 1, gas hydrates are crystalline compounds of water and gas. They are organized in spatial blocks called *cages*. A cage is formed by a polyhedron network of water molecules with a gas molecule trapped inside it. The gas molecule is called *guest*, while the water molecule is called *host*. Guest molecules can be methane, propane, butane, and some other types of light natural gases.

There are three *hydrates structures* found in nature, as illustrated in Figure 3, called structure I (s-I), structure II (s-II) and structure H (s-H). As explained by Sloan et al. (2011), the structures differ from each other the way how the cages are formed, number of water molecules, size and how they are connected. There is one particular basic cage, the 5^{12} (12 pentagonal faces), which forms a building block for the three types of structures. There are no chemical bonds between hosts and guests molecules, but the presence of the guest keeps the cage stable.

The basic cage 5^{12} cannot be the unique in a building block structure, because strains would be too strong only with pentagonal faces. The bond strains can be relieved by the inclusion of hexagonal faces. For the structure s-I, the addition of two hexagonal faces form connecting $5^{12}6^2$ cages, with both the 12 original pentagonal faces and 2 additional hexagonal, strain-relieving faces. For structure s-II, there are four additional hexagonal faces, forming the building block $5^{12}6^4$. The structure s-H, by its turn, is more complex and formed by $4^35^66^3$ and $5^{12}6^8$ connecting cages. Hydrate formation can be described by the general equation:

$$G + N_h H_2 0 \rightleftharpoons G \cdot N_h H_2 0 \tag{1}$$

where G is a light natural gas molecule and N_h is the *hydration number*, that is, the ratio between the number of water molecules and gas molecules consumed for hydrate formation.



Figure 3. The three repeating unit crystals structures and their consecutive cages. Adapted from Sloan et al. (2011).

The type of structure formed depends on the size of the guest (gas) molecule. Only relatively small guests, no larger than 10 Å, can occupy water cavities. Methane, ethane, and carbon dioxide are examples of light natural gas molecules that form s-I, having 4.2-6 Å diameters. Guest molecules with less than 4.2 Å, such as nitrogen and some others, form s-II. Larger guests (6-7 Å), such propane and iso-butane, also form s-II. Only structures I and II are found in oil and gas production. As explained by Ke et al. (2019), due to the high pressures in oil and gas pipelines, only one guest molecule is expected to occupy each cavity, despite some (rare) exceptions may eventually exist. A comparison between the three common hydrate structures is shown in Table 1.

Hydrate structure	lydrate structure s-I		s-II		s-H		
System	Cubic		Face-centered cubic		Hexagonal		
Cage	Small	Large	Small	Large	Small	Medium	Large
Type of cages	5 ¹²	$5^{12}6^2$	5 ¹²	5 ¹² 6 ⁴	5 ¹²	4 ³ 5 ⁶ 6 ³	5 ¹² 6 ⁸
Water molecules	46		136		34		
per unity							
Examples of gases	Methane	e, Ethane,	ne, Nitrogen, Propa		CH ₄ +2.2-dimetybutane,		
Examples of gases	CO_2		Butane, O ₂		Xe + Cycloheptane		

Table 1. Characteristics of the common hydrate structures. Adapted from Sloan and Koh(2008) and Melchuna (2016).

A combination of different gases, which is the common case for natural gas in oil and gas fields, may lead to a transition for one structure to another (s-I and s-II), the coexistence between the two, or an initial formation of s-I and gradual transition to s-II. For example, adding a small amount of propane to methane changes the hydrate structure from s-I to s-II (Ke et al., 2019). The reason is that propane molecules are larger than methane molecules, and they can help stabilize the large cavity, $5^{12}6^4$, of s-II hydrate structure. Then, it will be easier to have a structural stability for type s-II than s-I, which also leads to a decrease on the required driving force for hydrate formation. Experimental evidence also suggests that methane-propane mixtures may simultaneously have s-I and s-II structures (Menezes et al., 2019). Another example is methane-ethane mixtures, which may have s-II structure for low concentrations of ethane (Ballard and Sloan, 2000; Subramanian et al., 2000; Ke et al., 2019).

Experimental evidence has also suggested that, if methane is the predominant component in a gas mixture, initial hydrate formation seems to have structure s-I, with only methane molecules being consumed to form the cages 5^{12} , and the other types of gas molecules being incorporated later, with hydrates gradually changing to structure s-II (Schicks and Luzi-Helbing, 2013). As one can notice, cavity formation and gas occupancy during hydrate formation are not sufficiently known. Understanding the structures of the hydrates in oil and gas pipelines is important because it directly affects the equilibrium pressure and temperature for hydrate formation.

Hydrate formation consists of two consecutive mechanisms: nucleation and growth of hydrate particles. They are followed by agglomeration, which may change the size of these particles. The next three subsections contain discussions about each one of these mechanisms.

2.1.1. Nucleation

Hydrate nucleation is commonly explained in the literature by means of the Classical Nucleation Theory. In this sense, the nucleation process can be divided in *primary nucleation* and *secondary nucleation*, as summarized in Figure 4. Primary nucleation refers to a nucleation processes that occur in a previously crystal-free solution, while secondary nucleation is the generation of new crystals by crystals already present in the suspension (Nienow, 1992). Primary and secondary nucleation have in common the fact that a free-energy barrier must be passed in order to form clusters of a critical size, beyond which the new phase grows spontaneously.



The primary nucleation can be further classified as *homogeneous* (perfect clean solution) or *heterogeneous* (presence of inert foreign particles). During the primary homogeneous nucleation, water molecules cluster around gas molecules to form crystal embryos. A sustainable growth of a hydrate from nuclei is possible only if the nuclei reaches a critical size, so it can overcome the free energy barrier required for growth. The process of reaching the critical or minimum size is considered a random process, based exclusively on local density fluctuations.

The primary homogeneous nucleation has three stages, as illustrated in Figure 5. The first stage, represented in Figure 5(a), consists in a continuous reaction between ions or molecules, resulting the formation of clusters. For a new phase to appear, an interface must be formed, which occurs by small embryos in the new phase being formed within the bulk metastable phase. The spontaneous density or composition fluctuations may lead to a formation or a destruction of embryos. In the second stage, represented in Figure 5(b), aggregation forces, acting to form larger aggregates, influence the clusters stability. The creation of nuclei can be described by a successive addition of units A according to the formation scheme $A_n + A = A_{n+1}$. Finally, in the third stage, represented in Figure 5(c), clusters will grow until a critical size.



Figure 5. Clusters formation by the Classical Nucleation Theory. Adapted from Mersmann (2001).

The reversible work necessary to form such a cluster is given by a balance of the *volume free energy* (ΔG_V) that is gained and the *free-surface energy* (ΔG_S) that is needed to build the new surface. The nucleus is thermodynamically stable when the *total free energy* (ΔG) does not change when elementary units are added or removed. The stability exists if the nucleus reach a *critical size* (r_c), correspondent to a *critical free energy* (ΔG_c). Figure 6 shows a representation of the free energy as function of cluster size. Surface free energy, which is unfavorable to hydrate growth, is defined as positive, while the volume free energy, which is favorable to hydrate growth, is defined as negative.



Figure 6. Free energy diagram showing free energy versus cluster size.

The *driving force* for the formation of a new phase is the chemical potential difference between the old phase and the new one. For hydrate formation, it is the supersaturation of gas into the water phase. The supersaturation for hydrate formation can mathematically be expressed as (Kashchiev and Firoozabadi, 2002):

$$\Delta \mu = \mu_G + N_h \mu_W - \mu_H \tag{2}$$
where μ_G and μ_W are the chemical potentials of gas and water molecules in the aqueous solution, and μ_H represents the chemical potential of a building unit (one gas molecule and N_h water molecules) in the hydrate crystal.

It is important to notice that, using the primary homogeneous nucleation to explain gas hydrate formation is a simplified approach. Indeed, perfectly clean solutions are hardly found in industrial applications, especially in the context petroleum exploration. Primary heterogeneous and secondary nucleation involve complex mechanisms not well understood. Further information about primary heterogeneous and secondary nucleation can be found in the specialized literature (Nienow, 1997; Mersmann, 2001; among others).

2.1.2. Growth

Hydrate growth refers to the growth of stable hydrate nuclei as solid hydrates (Bishnoi and Nararajan, 1996). It occurs right after hydrate nucleation, and it is the process which leads to the evolution of crystal form of defined size and shape (Vedantam and Ranade, 2013). The growth occurs layer-by-layer, molecules from the solute will bond in a place at the forming crystal surface with the maximum of neighborhood surface (most energetically favorable site). At microscopic level, hydrates level can be considered a combination of three factors (Sloan and Koh, 2008; Yin et al., 2018): (i) mass transfer of water and gas molecules to the growing surface, (ii) the intrinsic kinetics of hydrate growth at the hydrate surface, and (iii) transport of the heat released by hydrate formation.

As explained by Mersmann (2001), in molecular terms, if the surface is rough and has many kink sites, the growth continues, as long the system continues inside the hydrate formation thermodynamic domain. Each growth unit reaching the surface in a supersaturated solution is integrated into the crystal lattice. However, if the crystal surface becomes smoother, on a molecular scale, growth becomes considerably more difficult, as energetically favorable sites are limited.

2.1.3. Agglomeration and Deposition

Agglomeration occurs when two particles collide and adhere each other due to the attractive forces between them, thus it directly affects the size of the dispersed particles. The larger the particles flowing in the pipeline, the higher is the risk of plugging. Settling of particles at the pipeline wall takes place when the flow velocity is not enough to carry the particles. Settling of particles may cause deposition or sloughing. When deposition occurs, the cross-

sectional area reduces, affecting the flow rate and the pressure drop, which increases the risk of plugging. In this section, the mechanisms observed in gas hydrates agglomeration are analyzed and the forces involved are identified for different flow conditions. Discussion will be made regarding the use of AAs and how they affect the flow and the interaction between hydrate particles.

The main forces involved during agglomeration are the Van der Waals, the capillary bridge, the solid bridge, the shear, the Brownian and the turbulent forces (Anklam et al., 2008; Wang et al., 2014; Brown et al., 2016). The liquid bridge and the shear forces are the most important agglomeration forces (Anklam et al., 2008; Wang et al., 2014). However, the turbulent force may be the dominant aggregation mechanism in flowing systems with a high enough Reynolds number and sufficient size of the particles (Brown et al., 2016). In addition, the gravitational force acting on the hydrate particles is commonly mentioned in the literature, which causes settling of particles in the pipe wall.

2.1.3.1. Liquid-bridge force

Figure 7 illustrates the liquid bridge between two particles in an oil continuous system, where θ is the contact angle between the particle and the water in the bridge, *h* is the distance between the two particles, r_1 is the curvature of the liquid-oil interface, and r_2 is the smallest internal radius of the liquid bridge.



Figure 7. Liquid bridge between two spherical particles.

2.1.3.2. Dispersion forces

The dispersion forces (London-van Der Waals) depend primarily on the particle size, the particle composition, the composition of the medium, and the distance between particles. The Van der Waals force between the particle 1 and the particle 2 (see Figure 7) is expressed as:

$$F_{vw} = \frac{A}{12h^2} \frac{d_1 d_2}{d_1 + d_2} \tag{3}$$

where A is the Hamaker constant, while d_1 and d_2 are the particles diameter.

2.1.3.3. Capillary forces

Capillary forces are present when a liquid bridge connects two particles. This cohesive force depends on the particles size, the interfacial tension between the bridging liquid (water), and the liquid (oil or water) in which the particles are dispersed, the contact angle at the particle surface, the distance between particles, and the volume of bridging liquid. The capillary bridge force can be expressed as follows:

$$F_{cap} = \pi d\sigma_{o-w} \cos\theta \tag{4}$$

where σ_{o-w} is the interface tension between oil and water.

2.1.3.4. Shear forces

The shear force is caused by the friction between the different phases, and it acts on the interfaces between the phases. The shear force is proportional to the velocity gradient around them, and it can be expressed as:

$$F_{shear} = \frac{3}{2}\pi\mu_0 d^2\gamma \tag{5}$$

where μ_0 is the viscosity of the oil phase and γ is the shear rate. For Newtonian fluids in a circular pipe, it is given by:

$$\gamma = \frac{32Q}{\pi d^3} \tag{6}$$

2.1.3.5. Brownian force

This force is due to the stochastic motion, causing collision between particles (Brown, 2016). It creates Brownian motion, whereby particles can encounter one another by random movements of each particle. However, the collision force between hydrate particles is attenuated by the liquid bridge. As explained by Crowe et al. (2012), when two spheres in a fluid are approaching one another, the fluid pressure between the spheres becomes larger to move the fluid outward and the resulting force acts to prevent contact.

2.1.3.6. Turbulent forces

For flowing systems with a high enough Reynolds number, turbulent agglomeration is likely to be a dominant aggregation mechanism (Brown, 2016). As well known in the literature, the Reynolds number is the ratio between inertial and viscous forces observed on the flow. The turbulent flow has a chaotic motion that can increase the chance for collision, which is very difficult to model. It may increase the agglomeration due to the collisions between particles, and increase the breakage as well, due to the collisions to the wall.

2.1.3.7. Electrostatic force

The electrostatic force is due to the particle-particle and particle-wall friction and collision, which creates attraction on the agglomerate surface. However, as explained by Wang et al. (2014), the presence of water diminishes the electrostatic force rapidly.

2.1.3.8. Solid bridge force

A solid bridge may be created when water is in contact with hydrate agglomerates, forming more hydrates. Currently, a calculation for the solid bridge force is not known, and further studies are necessary to allow a comparison between this force to the other ones.

2.1.3.9. Particles size distribution

The hydrate agglomeration is a complex phenomenon that depends not only on the forces involved on particle-particle interaction, but it depends on the type of dispersion as well. It depends on the size distribution and the number of particles per unit of volume, which is related to the total amount of hydrates in volume.

Assuming a flow with spherical particles with diameter *d* equally spaced of a distance *l* (see Figure 8), the ratio l/d can be calculated from the percentage of hydrates in volume, α_H . The following equation is obtained:

$$\frac{l}{d} = \left(\frac{\pi}{6\alpha_H}\right)^{1/3} \tag{7}$$



Figure 8. Inter-particle spacing. Adapted from Crowe et al. (2012).

Indeed, the particles will not have the same size or be equally spaced. There is a range of particles size with a distribution, that can be represented by a probability density function.

2.2. Basic notions of liquid-liquid flows

The flow of two immiscible liquids is easily encountered in nature and industrial processes. The petroleum industry often has systems with water and oil. For two-phase liquid-liquid flowing systems, there are different flow regimes reported in the literature. Brauner (2002) presented a few of these flow patterns observed in horizontal pipes, some of them are illustrated in Figure 9. The flow pattern depends on the liquids flow rates, tube diameter, wall-wetting properties of the liquids and surface tension forces. Due to the low discrepancies between the densities of the two liquids, the gravitational force does not play an important role for liquid-liquid flow patterns, except for the stratified regime (which is not possible in vertical or inclined upward flows). Several works have presented experimental results concerning the different flow patterns and the transitions between them (Tan et al., 2018), while mathematical models for the transition between different regimes are also available (Brauner and Maron, 1992; Brauner and Maron, 1993; Brauner, 2001, 2002; Ulmann et al., 2003). For gas hydrates formation, the importance of understanding the flow pattern is due to the fact that hydrates tend to nucleate at water-oil interfaces.



Figure 9. Some liquid-liquid (water-oil) flow patterns observed in horizontal flows of immiscible liquids: (a) stratified, (b) stratified with mixing at the interface, (c) layers of dispersion with w/o above o/w, (d) stratified with o/w above free water, (e) stratified with free oil above w/o, (f) o/w dispersion, (g) stratified with w/o dispersion above free water, (h) stratified with free oil above o/w dispersion, and (i) w/o dispersion.

Dispersion is defined as a heterogeneous system containing two immiscible liquids, where one of the phases is present in the form of droplets, the *dispersed phase*, and the other phase, which is in permanent contact with the pipe wall and surrounding the droplets, is called *continuous phase*. On this study, one of the phases is water and the other one is oil. Water continuous dispersions are called *oil-in-water* (o/w), while oil continuous dispersions are called *water-in-oil* (w/o). The dispersed phase often flows at different velocity from the continuous phase. The slippage can be negligible for fine o/w or w/o dispersions (Brauner, 2002), but it can be significant for relatively large droplets.

Special attention is given in the literature to well mixed (or uniform mixtures) of water and oil, also called *emulsions*. Emulsions normally present an average droplet size above 1 μ m, but, as explained by Sjoblom (2006), there are the nano-emulsions (droplets diameters inferior to 10⁻¹ μ m) and the mini-emulsions (droplets diameters between 10⁻¹ μ m and 1 μ m). Emulsions often involve the presence of surfactants that inhibit the coalescence of the dispersed droplets.

Another important parameter in emulsions and dispersions is the apparent viscosity. The apparent viscosity is dependent of several factors: volume fraction of the dispersed phase, viscosity of the continuous phase, shear rate (if non-Newtonian), temperature, average droplet size and size distribution, viscosity of the dispersed phase, nature and concentration of emulsifying agents, presence of solids in addition to dispersed liquid phase (Johnsen and

Rønningsen, 2003). Several correlations have been proposed in the literature (Richardson, 1933; Rønningsen, H.P., 1995; Pau, 2000; among many others).

The most well-known correlation for apparent viscosity, the Einstein's equation, is given by (Schramm, 2005):

$$\eta = \eta_C (1 + 2.5\alpha_D) \tag{8}$$

where η_C is the continuous phase viscosity and α_D is the fraction of the dispersed phase. The correlation is valid for $\alpha_D < 0.02$ or for $0.05 < \alpha_D < 0.1$, for Newtonian fluids.

Another well-known equation is given by the Mills model, valid for $\alpha_D < 0.62$:

$$\eta = \eta_C \left[\frac{1 - \alpha_D}{\left(1 - \frac{\alpha_D}{\alpha_{max}} \right)^2} \right]$$
(9)

where α_{max} is the maximum compact fraction. Through an empirical approach, Pal and Rhodes (1985) correlated viscosity data of both Newtonian and non-Newtonian crude oil emulsions. The correlation is given by:

$$\eta = \eta_C \left[1 + \frac{\alpha_D / \alpha^*}{1.1884 - \alpha_D / \alpha^*} \right]^{2.5}$$
(10)

where α^* is the dispersed phase volume fraction from which the relative viscosity (η/η_c) becomes 100.

Considering all the mentioned works about apparent viscosity for emulsions and dispersions, two relevant conclusions follow:

- The apparent viscosity is strongly affected by the viscosity of the continuous phase, but it increases with increasing fraction of the dispersed phase.
- As the dispersion becomes thinner (small droplets), the viscosity increases, because there is more contact between the phases and collisions to the wall, which increases the friction.

Phase inversion is another important concept for oil-water dispersions. It corresponds to the transitional boundary between o/w and w/o. Phase inversion is associated to a sudden change on the rheological properties of the flow, causing abrupt changes on the pressure drop. When hydrates are forming in oil-in-water systems, the water cut is continuously being reduced, which may cause a phase inversion to water-in-oil. The phase inversion process can be classified into two types: a *sudden inversion*, which occurs at a specific dispersed phase volume fraction, or a *transitional phase inversion* occurring in a water content range (Tan et al., 2020).

2.3. Basic notions of solid-liquid flows

Solid-liquid flows consist of flows in which solid particles are carried by the liquid (Crowe et al., 2012). It is referred as *slurry flow*, and it can be found in several industrial applications. Especially in oil and gas pipelines with hydrate formation, the multiphase flowing systems contain hydrate particles dispersed in the liquid phases.

As explained by Crowe et al. (2012), slurries are classified as *homogeneous*, *heterogeneous*, *moving bed* or *stationary bed*. Homogeneous slurries consist of small particles which are kept in suspension by the turbulence of the carrier fluid, while heterogeneous slurries are composed of coarse particles which tend to settle on the bottom of the pipe. The moving bed regime occurs when the particles settle on the pipe but continue moving along. Finally, the stationary bed occurs when particles fill the duct, and no further motion is possible.

Important definitions that help characterizing the slurry flow are *dilute flow* and *dense flow*, as presented by Crowe et al. (2012), represented in Figure 10. In a dilute dispersed phase flow, the particle motion is caused by the liquid forces, drag and lift. In a dense flow, particle motion is caused by collisions and/or continuous contact between the solid particles.



Figure 10. Flow regimes for dilute and dense flows. Adapted from Crowe et al. (2012).

Crowe et al. (2012) proposed a qualitative estimate of the flow regime, solute or dense. For that, the author defined the *average time between particle-particle collisions*, τ_c , and the *momentum response time*, τ_V . The momentum response time concerns the time required for a particle to respond to a change in velocity, and it can be calculated by the equation:

$$\tau_V = \frac{\rho_s d^2}{18\eta_c} \tag{11}$$

Then, Crowe et al. (2012) considered the flow to be *dilute* if:

$$\frac{\tau_V}{\tau_C} < 1 \tag{12}$$

because the particles have sufficient time to respond to the local fluid dynamic forces before the next collision. But the flow is said *dense* if:

$$\frac{\tau_V}{\tau_C} > 1 \tag{13}$$

because the particle has no time to accelerate due to the fluid forces. It is possible to estimate the time between collisions, in a very simplified way, by considering a group of particles with a uniform diameter d, as represented in Figure 11. Assuming that one particle has a velocity v_r relative to the other particles, in a time δt , the particle will intercept all the particles in the tube with radius 2d and length $V_r \delta t$, the number of particles in this tube is:

$$\delta N_p = n_p \pi d^2 V_r \delta t \tag{14}$$

where n_p is the number density of particles. The collision frequency is:

$$f_c = n_p \pi d^2 V_r \tag{15}$$

and the time between collisions is:

$$\tau_c = \frac{1}{f_c} = \frac{1}{n_p \pi d^2 V_r}$$
(16)



Figure 11. Particle-particle collisions. Adapted from Crowe et al. (2012).

Despite the model presented by Crowe et al. (2012) is simplified and cannot be used at this moment for a quantitative analysis, it is observed in Figure 12 that, fixing a particle diameter, the transition from dilute to dense becomes easier (at a lower hydrates fraction or water conversion) as the velocity increases.



Figure 12. Ranges for dilute and dense dispersion for methane spherical hydrates in water with fluctuation velocities magnitude of 0.25 m/s and 1.0 m/s.

2.4. Gas hydrate formation and plugging in oil-water systems

Gas hydrate formation in petroleum pipelines involves a number of phenomena, such as agglomeration, film growth/deposition, local viscosification, bedding, sloughing and jamming. The manifestation of these mechanisms (and intensity) depends on several variables, such as water-cut, supply of gas, flow rate, pipeline geometry (diameter, inclination, length, and roughness), pressure and temperature distributions along the pipeline, fluid properties, among others. There are several studies in the literature concerning the conceptual mechanisms of plugging formation at different conditions. This work focuses on oil-water systems.

It is well known that hydrate formation consumes water and gas and, therefore, the crystallization is likely to begin at water-oil interfaces. There are two approaches to explain how hydrates form and grow on a droplet surface, the *shell approach* and the *sponge approach*.

According to the shell approach (Sloan et al., 2011), when crystallization begins on a droplet surface, it forms a hydrate shell that may trap the dispersed phase (whether oil or water), as illustrated in Figure 13. It is important to remark that, due to the consumption of gas and water to form hydrates, there is an inward growth for water-in-oil dispersions and an outward growth for oil-in-water dispersions.

High water-cut systems are not well studied in the literature as low water cut systems. For emulsified systems with oil and water, some authors propose that there is w/o and o/w simultaneously. Hydrate plugging mechanisms at high water cuts are supposedly similar as those presented for oil continuous systems, with hydrates forming at oil-water interfaces, as illustrated in Figure 13(b). In the presence of free gas, there is also crystallization on water-gas interfaces.



Figure 13. Illustration of the "shell approach" for hydrate formation around (a) a water droplet and (b) an oil droplet.

Alternatively, there is the sponge approach, shown in Figure 14, where gas hydrates are assumed to be porous crystals, as proposed by Bassani et al. (2019). Hydrates have affinity with the water phase, and growth occurs mostly in the water trapped inside the capillaries.



Figure 14. Illustration of the "sponge approach", showing that for oil and water continuous, water trap only water, which can cause phase separation or total phase inversion. Adapted from Bassani et al. (2019).

The hydrate plugging mechanisms presented in the literature for water-oil systems contain, in general, the five steps represented in the diagram of Figure 15. The first step is the formation of a dispersion or partial-dispersion. The second step is the beginning of hydrate formation around droplets. The next two steps, agglomeration and deposition, may occur simultaneously, and they occurs due to capillary attractive forces between the particles. The final step is plugging formation that may occurs depending on the quantity of hydrates and on the particle size distribution. The differences between o/w and w/o will be discussed in the next two sections.



Figure 15. Summary of the mechanisms of hydrate formation for water-oil systems described in the literature.

2.4.1. Oil-dominated systems

For oil-dominated systems, the literature often divides the hydrate plugging mechanisms in steps: emulsification/liquid-liquid dispersion, hydrate nucleation and growth, agglomeration and plugging. Turner (2005) proposed that hydrates form rapidly on the water droplet surfaces as soon as the flowing mixture enters a region in which pressure and temperature allow hydrate formation. Since hydrates can be wet or have free water within them, the particles attract each other by capillary forces. Agglomeration may cause the plugging of the pipeline. Regarding the morphology of the particles, Sloan et al. (2011) proposed that the hydrate shell around a water droplet, as illustrated in Figure 13(a), can continue grow in a way that the entire droplet can be converted into hydrate. For the sponge approach proposed by Bassani et al. (2020), the attraction between the particles are also due to capillary forces, with the water phase forming a bridge between particles, causing agglomeration or deposition in the pipe wall.



Figure 16. Low water cut dispersions. Adapted from Sloan et al. (2011) and Turner (2005).

Melchuna et al. (2016) presented results from flow loop tests for several water-cuts. For oil-dominated systems, an inward growth was proposed, with some water droplets being completely converted into hydrates. Experiments at low water-cuts were identified as the most critical for hydrate plug formation.



Figure 17. Topological model proposed by Melchuna et al. (2016) for oil-water dispersion before and after hydrate formation.

While most works propose mechanisms for emulsified systems, Akhfash et al. (2016) presented results of hydrate formation in partially dispersed water-oil systems using an autoclave apparatus. The authors observed that hydrate formation disrupts the stratified water-oil interfaces, following a rapid hydrate growth.



Figure 18. Conceptual mechanism for hydrate plug formation in partially-dispersing oil-water systems proposed by Akhfash et al. (2016).

Another work was presented by Ding et al. (2019) with w/o emulsions, and it aimed to investigate the effect of hydrate agglomeration and deposition on slurry flow viscosity following the five steps presented in Figure 19. After hydrate formation, a sharp increase on apparent viscosity and immediate pressure loss is observed, due the formation of large hydrate-water structures. However, the system experiences later a decrease on the viscosity and on pressure drop because large agglomerates tear up due to the shear; hydrates have a stable growth. The pressure drop may eventually increase in case there is deposition.



Figure 19. Steps of the evolution of viscosity and pressure drop in a slurry flow in o/w emulsions proposed by Ding et al. (2019).

2.4.2. Water-dominated systems

As the wells fields become mature, the water-cut increases due to the injection of water to maintain the system pressurized and exploitable. Sloan et al. (2011) initially proposed that water is not totally entrained in the oil phase, and a separate water phase may exist, accompanied by some oil droplets dispersed in the water phase. Hydrates will form on wateroil interfaces. Agglomeration between hydrates can occur, causing a viscosification, which may eventually lead to hydrate plug formation. In recent years, some experimental tests have been reported, bringing more insights for high water-cuts systems.

Melchuna et al. (2016) proposed mechanisms for two scenarios where water is the continuous phase. First, for very high water cuts, shown in Figure 20(a), oil droplets are well-distributed in the water phase. Hydrate grow outward from oil droplet surfaces. Hydrates can detach from the droplets and flow in the water continuous phase. The second case is for intermediate water cuts, shown in Figure 20(b), where large packages of oil (free oil phase) can be present, with a higher formation kinetic of hydrates.



Figure 20. Topological model proposed by Melchuna et al. (2016) for oil-water emulsion before and after hydrate formation.

An experimental work with water and methane as the gas hydrate former, without oil, was conducted for Joshi et al. (2013). The flow loop tests have shown that, during hydrate formation, there were three distinct regimes of suspensions in the system. These regimes were identified due to a change in viscosity. First, for relatively low fractions of hydrates, the suspension of hydrates in the water phase is homogeneous, which did not cause much change on the apparent viscosity. However, after a "critical" hydrate fraction, the apparent viscosity starts increasing, presenting what the authors called a heterogeneous behavior, without bedding. Finally, as the amount of hydrates increases, it was observed another change on the apparent viscosity, characterized by an increase on the oscillation along time, with bedding formation.



Figure 21. Conceptual model of hydrate plug formation mechanism in 100 % water cut systems according to Joshi et al. (2013).

2.5. Hydrate plugging avoidance strategies

There are several techniques used to avoid hydrate blockage in pipelines. In general, they can be classified in *thermal*, *chemical* or *process* methods. Thermal methods include

insulation of the pipeline and electrical heating, among others, to maintain the fluid warm. Thermal methods are economically unfavorable, especially for long pipelines. Chemical methods involve the use of hydrate inhibitors (THIs, KHI and AAs) and salt. Finally, there are the process solutions, which involve techniques of gas dehydration and water cut reduction. In this section, it is discussed some results concerning the use of hydrate inhibitors and process techniques to avoid or manage hydrates.

2.5.1. Hydrate avoidance using THIs

THIs are used to change the equilibrium pressure and temperature of gas hydrate formation, to prevent the mixture flowing in the pipe to enter the region where hydrates are stable. Common THIs are methanol, ethylene glycol and ethanol. Several laboratory tests to study pressure and temperature conditions for hydrate formation have been done. Because of the relatively large amount of data available, the use of THIs is predictable and well understood. The disadvantage of THIs is that they are expensive and environmental unfriendly, due to their toxicity (especially methanol and ethylene glycol) and large amounts required for hydrate inhibition (between 20 and 60% vs water fraction).

2.5.2. Hydrate management using KHIs and AAs

Low dosage hydrate inhibitors have gained especial attention due to their potential in reducing the costs of hydrate inhibition. There are demonstrations that they can be effective at fractions from 0.25 to 3% wt. vs water. They include KHIs and AAs. These additives have different functions. While KHIs are leading to delay or block hydrate formation, AAs are leading to limit the size of hydrate particles and prevent plugging. The disadvantage of LDHIs is that they are still not completely understood, leading to limited operating conditions, meaning that they are for some scenarios unpredictable or apparently not very effective from some literature data.

KHIs are polymers with low molecular weight that appear to delay or block hydrate growth for a given time, with effectiveness limited to low or mild subcooling (up to 14 °C from some literature data, but it depends on the pressure, temperature, gas composition, KHI dose and time inside the hydrate domain). Recent works have shown the unpredictability of KIs, with experimental evidence that some additives delay hydrate formation, but hydrate growth is catastrophic and hydrate dissociation takes longer (Shariphi et al., 2014). If the flowing system

remains for a longer period in the non-protected hydrate formation zone, hydrates will form and grow anyway. It limits the applicability of KHIs to non-harsh conditions.

AAs has been the focus of relatively recent work for hydrate management and they are gaining especial attention from the industry. This type of additive was initially defined as an agent that prevents agglomeration of hydrate particles. However, considering several works reported in the literature, it appears that it is still not clear how AAs work. Different AAs may have different ways of act. Therefore, an alternative definition of AA could be an agent that prevents plugging by producing a flow with dispersed fine hydrate particles. Several works in the literature have reported a good effectiveness of AAs for several scenarios, except, in some cases, at high water cuts.

Melchuna et al (2016) performed tests with very low doses of a commercial AA (0.005 and 0.01% wt.) in tests with water and oil with methane and reported that the experiments still plug at high water-cuts. Sun and Firoozabadi (2013) presented results of rocking cell tests with a surfactant and claimed success in avoiding plugging at high water-cuts with 0.2 wt.% of their additive. The limitation of their results is that the tests were conducted in a way that the maximum hydrate fraction was kept at under 24%. Some works have attempted to study if the addition of salt improves the effectiveness of AAs, and found promising results for high-water cuts (Dong et al., 2017).

2.5.3. Process Methods for Hydrate Management

This group of methods consist in limiting the contact between water and gas, which, in theory, could limit the amount of hydrates in the system. Straume et al. (2019) presented a few process methods from literature known as *cold flow* hydrate management strategies. The definition presented for cold flow is the transport of hydrate particles without unconverted water. The idea is that if the hydrate particles are "dry", they do not agglomerate.

One method was patented by the research institute SINTEF (Lund et al., 2004). It consists in seeding hydrate crystals to initiate a controlled growth of hydrate particle in the bulk. It is expected that all the hydrate formation occurs due to the growth of injected particles without forming new particles in the system. By mixing gas, water with hydrates in the oil continuous phase, hydrate particles absorb water. Tests in real field are still necessary to validate this method.

The institute SINTEF has also proposed a gas dehydration process to limit hydrate formation (Lund et al., 2011). It consists in: (i) separation of phases (water, oil and natural gas) while they are still warm; (ii) cool the gas phase after the separation in order to form hydrates

(water that is initially vapor is then consumed for hydrate formation); and (iii) separation of gas and hydrates phases, with the hydrates being reinjected into a region with warm fluid (before the separation described in (i)). This method has never been tested in laboratory or field.

Another method, named "Hydraflow", was patented by the Centre for Gas Hydrate Research at Heriot-Watt University (Tohidi, 2006). It consists in converting all the gas into hydrates, which can be done in a loop where hydrates are constantly separated from the liquid phases (oil, water and AAs) and transported to a production facility, while the liquid phases are recycled in order to increase the transportability of the system (Azarinezhad et al., 2008).

These process techniques could substantially reduce the costs of hydrate plugging avoidance. However, besides the very few tests reported, these methods lack of validation and they are apparently not in use by the industry, where they are considered unrealistic. The unclear effectiveness of these methods and the intrusive (and probably costly) modifications that would be required in the production facilities are the reasons for not testing and implementing them on field.

2.6. Numerical predictive tools for hydrate plugging risk

Taking into account all the findings and data from experimental tests with hydrate formation, one important question that arises is how to use this knowledge in real field management and dimensioning. Predicting the plugging mechanisms, plugging risk, which additive or how much of it to be used for each specific scenario in petroleum extraction seems to be a difficult task. It is uncertain how to extrapolate the results from laboratory tests to field. One approach is the development of *mathematical models*, this one already being explored for more than three decades. Another approach that has the potential to be used in the near future is *machine learning*. In both solutions, the coupling between the different domains (crystallization, multiphase flow and data science) is essential to be modeled together and not apart like in the past.

2.6.1. Mathematical Models

The development of mathematical models is one approach to predict hydrate formation and plugging under flowing conditions. Hydrate formation and multiphase flow are commonly studied separately. There are models for hydrate formation (Chen and Guo, 1998; Ballard and Sloan, 2004; Bouillot and Herri, 2016; Mohebbi et al., 2017; among others), several models for hydrate growth (Englezos et al., 1987; Skovborg and Rasmussen, 1994; Herri et al., 1999; Talatori et al., 2012; Turner et al. 2009; Shi et al., 2011; among others) and hydrate agglomeration (Pauchard et al., 2007; Colombel et al., 2009; among others). Recent works have attempt to couple multiphase flow with hydrate formation. For example, models for slurry viscosification in oil-water systems (Fidel-Dufour et al., 2005; Moradpour et al., 2011; among others), and hydrate formation and growth under slug flow ("pseudo" w/o liquid and methane free gas) with hydrate growth (Bassani et al., 2017; Bassani et al., 2018; Bassani et al., 2020). The growth and agglomeration models currently available are limited to water-in-oil emulsions, while nowadays petroleum exploration experiences higher and higher water-cuts.

The high complexities of all the mechanisms involved in hydrate formation and plugging in pipelines represent a challenge for researchers, who have to impose several limiting simplification hypotheses to their models. Due to these important simplifications, there are uncertainties concerning potential application on field. These models also depend on experimental data for closure relationships, which adds, once more, questions about the uncertainty on how to extrapolate the fitted correlations from data obtained in specific designed experiments to other conditions. However, the development of these models in recent years has brought important advancements in our understanding about the mechanisms of hydrate formation in pipelines and in the mathematical description of these mechanisms, which creates perspectives for the future on the evolution of predictive physical-based simulators that could be used by engineers on field.

2.6.2. Machine Learning

Another predictive tool that has some potential to be used in hydrate management is machine learning. As explained by Simeone (2018), machine learning consists in the collection of large *data sets* to train general-purpose learning machines. Machine learning requires the following inputs: an *objective*, a *model* to be trained, an *optimization technique*, and a data set used for the training algorithms. Oil and gas companies have access to massive amount of data (Perrons and Jensen, 2015), and machine learning is already gaining some space on this sector, with special attention to *production, anomaly detection* and *price prediction* (Hanga and Kovalchuk, 2019).

So far, very limited studies have been reported in the literature evaluating plugging risk in flowing systems with hydrates using machine learning. Qin et al. (2019) used data from several laboratory tests and from field, showing the potential of this technique for development of hydrate risk predictive tools. Despite its possible application in hydrate management, it is very important to notice that machine learning does not take into account the physics of the problem, it is based on data. Therefore, the implementation of this technique requires a careful definition of the four inputs used in machine learning. A good collaboration between data scientists and domain experts is also a requirement for implementation on field (Hajizadeh, 2019). Nevertheless, due to the lack of a completely understanding about all the mechanisms involved in hydrate plug formation and an advanced mathematical description of the phenomena, combined to an increasing amount of data from laboratory and field tests, machine learning may gain more and more the attention of hydrate specialists and flow assurance engineers in the coming years.

2.7. The contributions of this work

From the literature, the mechanisms involved in plug formation in water dominated systems are not well understood. With AAs, hydrate formation is accepted, but risk of plugging must be limited, which is apparently not easy to achieve at high water-cuts. The mechanisms involved in plug formation under flow require a better understanding of the flow regime. With the experiments performed in this work, new insights for the description of the different steps from the onset of hydrate formation until blockage will be given. A connection between multiphase flow and hydrate formation is expected from this work, describing some of the mechanisms of hydrate plug formation because of the flow regime and how the solid phase interacts with the liquid phases. For tests with AA, the observed results may enable industrials to consider its use in harsh conditions, and, in this sense, numerical tools may help to dimension and manage AA injection in pipelines.

Extracting meaningful information from experiments with large data sets is also a challenge. Therefore, the other important contribution of this work is the development of a methodology for data processing to isolate the different mechanisms involved in the experiments of hydrate formation. Concerning the new instruments installed in the Archimedes flow loop, this work shows the application of permittivity, acoustic energy measurements and high-speed imaging for laboratory tests of this kind.

The modelling, the data sets and the calculation methodologies obtained from this work can serve as a base for the future preparation of advanced treatments combining mathematical models, statistics, and machine learning techniques. A multidisciplinary approach involving experiments, mathematics and modern data processing techniques could lead to the development of predictive tools that provide quantitative results for industrials, in pipelines dimensioning and management, supporting them with the difficult decisions that they face on this sector.

2.8. Summary of the Chapter

In this chapter, it was presented the basic definition of gas hydrates, the different types of cages, and how crystallization occurs. It was presented a basic review on liquid-liquid and solid-liquid flows. Then it was discussed hydrate formation under flow, with some of the recent research from literature being discussed. The focus was on liquid dominated systems (gas dominated systems are outside of the scope of this thesis). Then, additional strategies other than the use of chemicals, which are called process methods, were discussed. The use of mathematical models and a possible application of machine learning techniques in data from tests with hydrate formation were briefly discussed.

2.9. Highlights in French - Résume du Chapitre 2 en Français

Dans ce chapitre, il a été présenté la définition de base des hydrates de gaz, les différents types de cages et comment se produit la cristallisation. Il existe trois structures hydratées trouvées dans la nature : structure I, structure II et structure H. Les structures diffèrent les unes des autres par la manière dont les cages sont formées, le nombre de molécules d'eau, la taille et la manière dont elles sont connectées. La compréhension des structures des hydrates dans les oléoducs et les gazoducs est importante car elle affecte directement la pression et la température d'équilibre pour la formation d'hydrates.

Il a été présenté un examen de base sur les écoulement liquide-liquide et solide-liquide. Le régime d'écoulement dépend des débits de liquides, du diamètre du tube, des propriétés de mouillage des parois des liquides et des forces de tension superficielle. L'écoulement avec des solides disperses dans le liquide (slurries) sont classées comme homogène, hétérogène, lit mobile et lit stationnaire. Les slurries homogènes sont constituées de petites particules qui sont maintenues en suspension par la turbulence du fluide porteur, tandis que les boues hétérogènes sont composées de particules grossières qui ont tendance à se déposer sur le fond du tuyau. Le régime du lit mobile se produit lorsque les particules se déposent sur le tuyau, mais continuent à se déplacer. Enfin, le lit stationnaire se produit lorsque des particules remplissent le conduit et qu'aucun mouvement supplémentaire n'est possible. Les définitions importantes qui aident à caractériser l'écoulement de lisier sont l'écoulement del particules est causé par les forces du liquide, la traînée et la portance. Dans un écoulement dense, le mouvement des particules est provoqué par des collisions et / ou un contact continu entre les particules solides.

Ensuite, il a été discuté de la formation d'hydrates sous écoulement, certaines des recherches récentes issues de la littérature étant discutées. La formation d'hydrates de gaz dans les pipelines de pétrole implique un certain nombre de phénomènes, tels que l'agglomération, la croissance / dépôt de film, la viscosification locale, la litière, la mue et le coincement. La manifestation de ces mécanismes (et intensité) pour chaque scénario dépend de plusieurs variables, telles que la coupure d'eau, l'approvisionnement en gaz, le débit, la géométrie du pipeline (diamètre, inclinaison, longueur, rugosité), les distributions de pression et de température le long du pipeline, le fluide propriétés, et quelques autres. Il existe plusieurs études dans la littérature concernant les mécanismes conceptuels de la formation de bouchage dans différentes conditions. Ce travail se concentre sur les systèmes huile-eau (les systèmes dominés par le gaz sortent du cadre de cette thèse).

Il est bien connu que la formation d'hydrates consomme de l'eau et du gaz et, par conséquent, la cristallisation est susceptible de commencer sur les interfaces eau-huile. Il existe deux approches pour expliquer la formation et la croissance de l'hydrate sur une surface de gouttelettes, l'approche de la coquille et l'approche de l'éponge. Ensuite, des stratégies supplémentaires autres que l'utilisation de produits chimiques, appelées méthodes de traitement, ont été discutées. L'utilisation de modèles mathématiques et une application possible de techniques d'apprentissage automatique dans les données d'essais avec formation d'hydrates ont été brièvement discutées.

CHAPTER 3 – METHODOLOGY FOR HYDRATE FORMATION EXPERIMENTS IN A FLOW LOOP APPARATUS

In this chapter, the experimental methodology used in this work is described. The experimental apparatus, the installed instruments and the experimental protocol are presented. The models used in this work to calculate the dissolution of gas (and oil density) and hydrate fraction are presented.

3.1. Archimedes flow loop

The tests were carried out in the Archimedes flow loop, illustrated in Figure 22. It is installed at the SPIN Centre at École des Mines de Saint-Étienne. The apparatus has a pipeline of approximately 56 meters, divided into three section. It contains a vertical downward section of approximately 9.5 meters, a slightly downward section (inclination of approximately -3.6°) of approximately 36 meters and a vertical upward section of approximately 10.5 meters. The vertical sections have a pipe diameter of 15.7 mm, while the slightly inclined section has a pipe diameter of 10.2 mm. The slightly inclined section will often be referred on this thesis as "horizontal section", because there is a negligible gravitation effect (approximately 90 cm is the difference between the highest and lowest point).

The apparatus has a total of ten temperature probes (one measures the room temperature), two absolute pressures probes (one for the separator and another one for the gas injection system), four differential pressure drop probes, a gas compensation system and a Coriolis that measures density and flow rate.

The system has also a FBRM installed in the downward section and a PVM in the horizontal section. These two instruments give information of the flow at microscopic scale. In addition, the flow loop has been upgraded (after the theses of Melchuna (2016) and Pham (2018)) with the installation of six acoustic emission sensors, a permittivity probe and a high-speed camera. These three instruments give information at macroscale.



Figure 22. Schematic illustration of the Archimedes flow loop at Mines Saint-Etienne.

3.1.1. Separator

The separator is illustrated in Figure 23. It was designed to allow contact between the liquid mixture and the gas. The pressurization of the flow loop is done by injecting gas in the separator. Even though the mixture flowing in the pipeline is composed mostly by water and oil, there are gas bubbles that are entrained in the flow. The flow enters the separator by means of the internal pipe on the left side of the separator. Once the liquid reaches the top part of this internal (vertical) pipe, the liquid will fall in the direction of the bottom of the separator, using a channel between the internal and external pipes on the left side of the separator. The shock between the falling liquid with the stagnant liquid will cause the entrainment of gas bubbles in the flow.



Figure 23. Illustration of the separator of the Archimedes flow loop and its dimensions.

3.1.2. Moineau pump

The flow loop has a Moineau pump type MR 6120 S, provided by PCM® pumps. It is a progressive pump, consisting of a helical rotor that generates an axial displacement without breaking the hydrate particles. The pump provides a flowrate in a range 100 - 520 L/h. The working pressure is 0 - 20 °C, maximum pressure of 105 bars, and maximum differential pressure of 10 bar. It is installed at the bottom of the Archimedes flow loop (see Figure 22).

3.1.3. Flowmeter and Densimeter

A flowmeter with densimeter is installed in the downward section of the apparatus. It is based on the Coriolis principle, and, because of that, this instrument is referred in this thesis as Coriolis. It is provided by Micro Motion® (model F025S). The uncertainty is $\pm 0.2\%$ for liquid flow rate, $\pm 0.5\%$ for gas flow rate, while uncertainty in density measurement for liquid is ± 2.0 kg/m³ (Micro Motion, 2004).

3.1.4. Pressure Drop Probes

The flow loop is equipped with four differential pressure drop probes. They are sensortransmitter piezo-resistive, provided by Keller®. Those pressure drops are: Δp_1 (differential pressure in the downward section), Δp_h (differential pressure in the horizontal/slightly inclined section), Δp_2 (differential pressure in the upward section), and Δp_4 (separator). See Figure 22 for a visualization on where these pressure drops are measured.

		1	1 1
Probe	Range	Uncertainty	Minimum span
Δp_1	0-20 bar	$\pm (120 \text{ Pa} + 2.5 \times 10^{-4} \text{ p})$	0.001 bar
Δp_h	0 – 10 bar	$\pm (120 \text{ Pa} + 2.5 \times 10^{-4} \text{ p})$	0.001 bar
Δp_2	0-20 bar	$\pm (120 \text{ Pa} + 2.5 \times 10^{-4} \text{ p})$	0.001 bar
Δp_4	0 – 622 mbar	$\pm (10 \text{ Pa} + 2.5 \times 10^{-4} \text{ p})$	1 mbar

Table 2. Characteristics of the pressure drop probes.

The differential pressure in each section is a combination of gravitational and frictional effects. The differential pressure in the downward section, Δp_1 , has a positive contribution of the gravity force and a negative contribution of the friction to the wall. It means that an increase on the apparent viscosity (presence of hydrates) causes a decrease on this pressure drop, which can be represented by the following equation:

$$\Delta p_1 \approx \rho g L_1 - \frac{2L_1}{D_1} f_1 \rho U_1^2 \tag{17}$$

where L_1 is the equivalent length, D_1 is the pipe diameter, f_1 is the friction factor, and U_1 is the liquid average velocity in the downward section. The "approximately" is used in the equation because the flow loop apparatus may have some obstacles or changes in the geometry that may affect the pressure drop measurement, and deposition or settling of particles. The differential pressure in the horizontal/slightly inclined section, Δp_h , can be expressed by the following equation:

$$\Delta p_h \approx \frac{2L_h}{D_h} f_h \rho U_h^2 \tag{18}$$

where L_h is the equivalent length, D_h is the pipe diameter, f_h is the friction factor, and U_h is the liquid average velocity in the horizontal section. The differential pressure in the upward section has positive contribution of the gravity force and friction, and it can mathematically be expressed by:

$$\Delta p_2 \approx \rho g L_2 + \frac{2L_2}{D_2} f_2 \rho U_2^2$$
 (19)

where L_2 is the equivalent length, D_2 is the pipe diameter, f_2 is the friction factor, and U_2 is the liquid average velocity in the upward section. Finally, the pressure drop in the separator has basically the contribution of the gravity, and can be used to estimate the liquid level in the separator:

$$\Delta p_4 \approx \rho g L_4 \tag{20}$$

where L_4 is the liquid column measured by the probe. It is important to notice that the probe measures the liquid column starting from a point that is approximately 37 cm above the bottom of the separator, meaning that the actual liquid column in the separator is 37 cm longer than L_4 .

3.1.5. Gas injection system

The gas used in all the tests is a natural gas whose composition and corresponding hydrate curve in given in Appendix B. The working pressure (75 bars) and working temperature (4 $^{\circ}$ C) correspond to a subcooling of 10.3 $^{\circ}$ C (the conditions and the protocol for the experiments are detailed in section 3.2, page 48).

An automatic gas compensation system is installed in the apparatus to maintain the absolute pressure constant. During the experiments, the pressure can change due to a variation in the temperature, dissolution of gas into the liquid phases, or hydrate formation. The injection of gas is done through a line that connects the bottle of gas to the flow loop apparatus. The gas is injected in the upper right side of the separator (see Figure 23). The pressure controller installed was provided by Brooks® Instrument (model 5866). The system can inject gas in a range 0 - 20 ln/min (normal liters per minute), with a minimum span of 0.01 ln/min. It has an accuracy of $\pm 1.00\%$ and a repeatability of $\pm 0.1\%$ (Brooks, 2008).

3.1.6. Focused Beam Reflectance Measurement system

The Focused Beam Reflectance Measurement (FBRM) is an in-situ particle analyzer for real-time (on-line) monitoring the particle size in the process, by measuring the chord length distribution (CLD) of the droplets or formed particles, shall they exist in the system. A FBRM

probe is used in the Archimedes flow loop to monitor the crystallization process, for a range 1-1000 μ m. The FBRM, illustrated in Figure 24, is provided by Mettler-Toledo Lasentec® (Mettler-Toledo Lasentec, 2001). It consists in an infrared laser with wavelength of 785 nm, which is transmitted through an optical fiber to the probe tip and emitted from a rotating optical lens into emulsion or suspension. The emitted laser is reflected when it encounters the particle surface. The chord length determination is obtained by the product of the reflectance time (measured by the probe) and the laser scan speed (which is 2 m/s). The FBRM measures chord lengths instead of particles sizes. An important limitation of this instrument is its range, not being able to measure chord lengths above 1000 μ m.



Figure 24. FBRM probe description. Adapted from Melchuna (2016).

An example of measurement of CLD over time for an experiment with hydrate formation in shown in Figure 25. The number of chord counts is measured in an interval of 5.0 seconds, which is then converted to counts per second.



Figure 25. Chord length distribution along time for an experiment at 30% water cut, 200 L/h, without AA (#11).

3.1.7. Particle Vision Microscope system

The Particle Vision Microscope probe (PVM) is an in-situ particle analyzer that provides real-time, in-process images of particle and droplet systems. It is provided by Mettler-Toledo Lasentec® (Mettler-Toledo Lasentec, 2011). Six independent lasers illuminate a fixed area in front of the probe face, as illustrated in Figure 26. Digital images have size of $1075 \times 825 \,\mu$ m, recorded each 5.0 s.



Figure 26. PVM instrument. Adapted from Mettler Toledo Lasentec (2011).

The PVM probe allows observing the beginning of crystallization, as it can be seen in Figure 27. Oil or water droplets present a well-rounded shape with clear surface on which it is possible to see the six laser beams reflections. During hydrate formation, the texture of droplets surface changes and their shapes become irregular (this was previously explained by Melchuna, 2016), as shown in Figure 27(a). It is possible to obtain the grayscale of the images, which gives 0 for a complete black image or 255 for a complete white image, as shown in Figure 27(b).

(a) PVM images



Figure 27. PVM data for an experiment at 50% water cut, 200 L/h, without AA, showing (a) some images before and after hydrate formation, and (b) the grayscale of the images.

3.1.8. Acoustic emission testing

Acoustic emission (AE) is the appearance of transient acoustic waves due to a change in the system that is being analyzed. For the experiments carried out in the Archimedes flow loop, it measures the noises produced by the flow inside the pipe (Cameirao et al; 2018). The appearance of hydrates is expected to produce more noise, due to the collision of particles. Some changes in the viscosity, which are related to the friction of the mixture with the pipe wall may also be detected. Each sensor is fixed outside of the pipe, meaning it is non-intrusive, as illustrated in Figure 28. For the system currently installed in the Archimedes flow loop apparatus, two types of data are obtained: *time driven data* (TDD) and *hit driven data* (HDD). For TDD, the parameters are registered every specific step of time (here, 0.5 s). For HDD, the registration of the parameters occurs when the amplitude reaches a minimum defined by the user. The acoustic waves captured by a sensor can be converted into absolute energy, amplitude, counts and many other parameters. For this work, it is analyzed only the absolute energy, using TDD. Others parameters using the TDD and HDD methods are available and might be used in future works.



Figure 28. Acoustic emission sensor installed in the Archimedes flow loop.

The position where the acoustic emission sensors are installed in the system are indicated in blue or red, Figure 22. For some experiments, four sensor were used (1A, 2B, 3C and 4A), and for others, six sensor were used (1B, 2A, 3C, 4C, 5A and 6B), with the installation of two addition sensor at the inlet and at the outlet of the separator. The experiments from #11 to #20 were conducted with fours sensors, while the experiments from #21 to #34 were conducted with six sensors.

The numbers indicate the position in the system (starting from the point where the flow exits the separator and goes to the loop, until the point where the flow finishes the loop and enters the separator), while the letters represent the nominal frequency of acoustic wave that, among all the frequencies captured by the sensors, represents the highest values in a distribution.

The acoustic emission system installed in the Archimedes apparatus is provided by Mistras®. The sensor defined here as type A has a nominal frequency of 150 kHz, the sensor B has nominal frequency of 300 kHz, and the sensor type C has a nominal frequency of 350 kHz.

3.1.9. Permittivity probe

Permittivity is the electric polarization of a material when it is subjected to an electrical field. Conductivity is its capacity to transport ions, or to conduct electricity. Each medium has a permittivity and a conductivity when an electric field is applied. Since each fluid (water and Kerdane) has a specific conductivity and dielectric, measuring these properties of the mixture in a flow loop has the potential to help identifying the continuous phase and the flow regime.

A permittivity probe has been installed in the Archimedes flow loop, in the horizontal section of the pipe. The device was provided by Norce®. As explained by Haukalid (2014), an open-ended coaxial probe, illustrated in Figure 29, consists basically of a coaxial transmission line that is cut off at one end. A signal transmitted to the probe is almost totally reflected at the

probe end, because of a severe impedance mismatch. The amplitude and phase of the reflected signal are dependent on the dielectric properties of the constituents in front of the probe, making the probe suitable for permittivity measurements. The probe is sensitive to permittivity changes in a small and roughly hemispherical-shaped volume in front of the probe (yellow volume in Figure 29).



The probe measures the permittivity for frequencies from 10^6 to 6×10^9 Hz. For practical purposes, in this thesis only data starting from 10^7 Hz will be analyzed, as indicated in Figure 30. The data shown refers to the calibration that was performed using the Archimedes apparatus, with saline water (30 g/L of NaCl added to deionized water) and Kerdane.



Figure 30. Dielectric of saline water (30 g/L of NaCl) and Kerdane at 4°C, obtained with the permittivity probe provided by Norce and installed in the Archimedes flow loop.

3.1.10. High speed camera

A monochromatic camera with an acquisition system for high-speed direct-to-disk recording was installed in the Archimedes flow loop. The system is shown in Figure 31. It is possible to record at 1 Gb/s of data, with a maximum resolution of 2560 x 2048 pixels. Because the recording is saved directly in a computer with a solid disk memory, the capacity of the recording for each experiment is limited to the computer storage capacity (currently 2 Tb). The maximum recording is 211 fps at maximum resolution. The camera was tested for some of the

experiments carried out for this thesis (tests at 50 and 80% water-cut, without LDHI-AA). At 30% water-cut, tests without hydrate formation were carried out. For the experiments presented in the work, acquisitions from 2 to 100 fps have been tested.

A visualization transparent window with size 52×11.5 mm is used for the visualization. Behind the window, there is a led that provides a constant luminosity to visualize the flow.



Figure 31. Camera installed in front of a visualization window in the Archimedes flow loop.

Hydrate particles are solid crystalline structures. Once they form, they can block the light from the LED crossing the visualization window and being captured by the lens of the camera (see the arrangement of the LED and the camera in Figure 31). With hydrates, it can be difficult to visualize the flow through the window. An increase of the contrast is a possible treatment with the image that can be used the better visualize the flow. A code in Python has been developed to increase the contrast of the images. An example of application of this procedure is shown in Figure 32.

(a) Original image



(b) Modified image



Figure 32. Comparison between (a) an original image from the camera with (b) the same image with an increased contrast.

3.2. Experimental conditions and protocol

The experiments were conducted at 4 °C and 75 bars (absolute pressure), using oil Kerdane, saline water (concentration of 30 g/L) and natural gas¹, which corresponds to a subcooling of 10.3 °C. The volume of the liquid (oil and water) injected is 10.0 liters at room pressure and temperature. The tests with LDHI-AA were conducted with only one type of additive², using 75 g of mass for all the experiments (which represents 1.50 wt.% vs water for a test at 50% water cut, and 0.94 wt.% vs water for the tests at 80% water cut). A series of 23 experiments were conducted at 30, 50 and 80% water cuts, with and without AA. Those experiments are listed in Table 3.

¹ The composition of the natural gas is shown in Table 6 (page 171).

² The name of the manufacturer and composition of the additive are not informed due to confidentiality.

E 4	Water	Flow rate	AA fraction	Water	Plug	Time with
Experiment	cut		(wt.% vs water)	conversion		hydrates
#11		200 L/h	-	18.70%	Yes	13.4 min
#12	30%		-	11.14%	Yes	6.1 min
#14	3070	400 L/h	-	13.21%	Yes	3.2 min
#15			-	9.65%	Yes	3.8 min
#16		200 L/h	-	3.73%	Yes	6.6 min
#17			-	2.25%	Yes	3.9 min
#18			-	2.91%	Yes	4.7 min
#19			-	4.58%	Yes	5.8 min
#27			1.5 wt.%	44.03%	No	322.7 min
#28	50%		1.5 wt.%	45.45%	No	287.1 min
#24		400 L/h	-	10.61%	Yes	7.3 min
#25			-	18.46%	Yes	13.7 min
#26			-	14.57%	Yes	9.3 min
#29			1.5 wt.%	67.50%	No	321.2 min
#30			1.5 wt.%	67.31%	No	307.0 min
#20		200 L/h	-	7.83%	Yes	92.1 min
#21			-	10.27%	Yes	120.1 min
#31			0.9375 wt.%	38.91%	No	309.2 min
#32	80%		0.9375 wt.%	35.89%	No	303.3 min
#22	0070	400 L/h	-	11.70%	Yes	26.9 min
#23			_	16.29%	Yes	37.3 min
#33			0.9375 wt.%	55.16%	No	359.3 min
#34			0.9375 wt.%	56.69%	Yes	244.4 min

Table 3. List of hydrate formation experiments conducted in the Archimedes flow loop for this thesis.

The protocol, illustrated in Figure 33, has the following steps:

- i. Controlling the temperature until 8°C at 100 L/h.
- ii. Setting the flow rate to the desirable value (200 or 400 L/h).
- iii. Pressurizing slowly until 8 bars using the gas compensation system.
- iv. Reducing the temperature until 4°C.
- v. Pressurizing rapidly (manual) until 75 bars with natural gas.
vi. Turning on the gas compensation system and setting it to 75 bars.



Figure 33. Experimental protocol.

3.3. Data processing

The experiments performed for this thesis involved several measurements, as discussed in the previous sections. There is the main acquisition system, the FBRM, the PVM, the acoustic emission, the permittivity measurements and the high-speed camera. The acquisition station of each instrument is individual (separate computer). Table 4 shows the instruments installed in the apparatus and their outputs.

Table 4. List of instruments installed in the Archimedes flow loop, with the type of	of data,
acquisition, and type of file.	

Instrument	Data	Step of time for acquisition	Type of file
Main acquisition system	$p(\times 2), T(\times 10), Q, \rho, Q_G, \Delta p(\times 4)$	1.0 s	CSV
FBRM	CLD for 1-1000 µm, divided in 90 intervals (log ₉₀ scale)	5.0 s	xlsx
PVM	Images	5.0 s	bmp
Acoustic Emission	TDD (absolute energy and ASL) and HDT (18 parameters) for each sensor	0.5 s	txt
Permittivity	Permittivity and conductivity	3-8 sec	txt
Camera	Images	Up to 211 fps	binary

Once the experiment is over, the data from all the instruments are collected, and then processed using a software for data treatment that was specifically designed for the Archimedes flow loop. The software was written in Python, and it was developed during this thesis. The main acquisition system is taken as a reference, and the initial time (t = 0) is the instant when the flow loop starts to be pressurized to 75 bars. The time sets from the other instruments are then calculated relatively to this instant of time that the system was pressurized. A screenshot of the main screen of the software with some plots is shown in Figure 34. A detailed presentation of the software is given in Appendix A.

In addition to the measurements, several models and calculations have been proposed and integrated to the software for data treatment. It is possible to obtain the hydrates fraction, the water conversion and the gas dissolution, as it is presented in section 3.4. In addition, it is possible to calculate the Reynolds number, the apparent viscosity and the water cut (before hydrate formation), as it is be presented in Chapter 4. Finally, with the density measured from the Coriolis and the water conversion, it is possible to estimate the apparent hydrate fraction flowing in the system, as presented in Chapter 6.





3.4. Gas dissolution and hydrate volume calculation

The natural gas is consumed due to the dissolution into the liquid phases and due to hydrate formation, as illustrated in Figure 35. An important information to be evaluated in the experiments is the amount (or the fraction) of hydrates in the system. The calculation of the hydrates volume is based on the consumption of gas to form hydrates. The experiments

performed for this thesis are at constant pressure. Due to gas dissolution and hydrate formation, gas must be constantly injected to maintain the pressure.



Figure 35. Consumption of gas during the experiment.

It is assumed in this thesis that, before hydrate formation, the natural gas is dissolved in the oil phase. A balance between the amount of gas injected (by the gas compensation system) and the volume of free gas (pressure and temperature dependent) is taken into account to obtain the dissolution of gas. Gas dissolution in the oil phase changes the density of the oil. It was observed in experiments of solubility for some of the component of the natural gas into the Kerdane) using a batch reactor. These results briefly explained in Appendix C.

After the onset of hydrate formation, it is assumed that the amount of gas dissolved in the oil phase remains constant. Then, a balance between the injected gas and the volume of free gas allows calculating how much hydrates formed.

The calculation procedures for gas dissolution and hydrate formation are presented in the next two subsections.

3.4.1. Calculation procedure to obtain the amount of gas dissolved in the oil phase and the oil density

When gas dissolves in the liquid phase, the pressure reduces if the system is at constant volume. Furthermore, the liquid phase suffers a volume expansion and a reduction on its density. In this work, the experiments were carried out with a mixture of natural gases. It is assumed that only three of the gas components are dissolved in the oil phase. These gases components are methane, ethane, and carbon dioxide, which represent 98.4% of the gas molar fraction (see Appendix B for the natural gas composition). The reason for this assumption is that only data for these three types of gas are available for solubility in Kerdane. Correlations for the solubility of methane, ethane and carbon dioxide in Kerdane and correlations for the oil

density (saturation point), as function of pressure, temperature, and as function of pressure and temperature are presented in Appendix C.

At the initial state, when the absolute pressure is 8 bars, just before the manual pressurization to 75 bars (see the experimental protocol represented in Figure 33), the amount of dissolved and free gas must be calculated. For that, it is assumed that the oil is saturated with the gas components. The fraction of each component is defined as:

$$f_i = \frac{n_{d,i} + n_{f,i}}{\sum (n_{d,i} + n_{f,i})}$$
(21)

where $n_{d,i}$ is the number of moles of a gas component *i* that are dissolved in the oil phase, while $n_{f,i}$ is the number of moles of free gas. The fraction *f* is the nominal composition (in molar fraction) of the natural gas used in the experiments, and it is given in Table 6 (page 171). The fraction of gas in terms of dissolution is defined as:

$$f_{d,i} = \frac{n_{d,i}}{\sum n_{d,i}} \tag{22}$$

while the fraction of each component present as free gas is defined as:

$$f_{f,i} = \frac{n_{f,i}}{\sum n_{f,i}}$$
(23)

Finding the solution for the equilibrium in the saturation point requires three inputs: the natural gas composition (f), the average temperature and the absolute pressure. The solution $n_d(0) = (n_{d,1}; ...; n_{d,7})$ and $n_f(0) = (n_{f,1}; ...; n_{f,7})$ is obtained by simultaneously solving equation (18), equation (82) (which gives the partial pressure that is used to calculate the concentration), and equation (86).

Once the initial state at t = 0 is known, the next step consists in obtaining the states during the pressurization. This pressurization is fast, it takes around 15 seconds (between 10 and 20 seconds), and it is not possible to know how much gas is being injected. It is assumed that all the gas being injected is pressurizing the system (without any dissolution of gas). This assumption is necessary; otherwise, the solution would be underdetermined. If all the gas being injected is added as free gas, the number of moles of dissolved gas for all components (n_d) remain constant. The solution $n_f(t) = (n_{d,1}; ...; n_{d,7})$ that is obtained for each step of time is obtained solving the equation (21), equation (88), and considering that the increase on the number of moles of free gas injected in the system obeys the nominal composition of the natural gas:

$$f_{i} = \frac{n_{f,i}(t) - n_{f,i}(0)}{\sum (n_{f,i}(t) - n_{f,i}(0))}$$
(24)

Once the system is pressurized and the gas compensation system is turned on, the dissolution of gas begins. The system of equation proposed contains four equations, based on mass conservation, constant volume of the system, gas density based on real gas model, and oil density as function of the amount of gas dissolved. The mass conservation is given by:

$$m_{Gf}^{0} + m_{G}^{inj,t_{d}} + m_{Gd}^{0} + m_{O} + m_{W} = m_{Gf}^{t_{d}} + m_{Gd}^{t_{d}} + m_{O} + m_{W}$$
(25)

where m_{Gf} is the mass of free gas in the system, m_G^{inj,t_d} is the accumulated mass of gas injected by the gas compensation system after the pressurization, m_{Gd} is the mass of dissolved gas, m_O is the mass of injected oil (without dissolved gas), m_W is the mass of injected water. One should notice that the left side of equation (25) is the initial state ($t_d = 0$), while the right side represents the state in any further step of time ($t_d > 0$). The total volume of the flow loop is constant, so, the following equation can be written:

$$\mathcal{V}_{G}^{0} + \mathcal{V}_{O}^{0} + \mathcal{V}_{W} = \mathcal{V}_{G}^{t_{d}} + \mathcal{V}_{O}^{t_{d}} + \mathcal{V}_{W}$$
(26)

where \forall is the volume. The gas density is the relation between mass and volume, and, for the gas phase, it can be calculated using the SRK model (see Appendix B), which depends on the pressure and average temperature:

$$\rho_G(p^{t_d}, T^{t_d}) = \frac{m_G^{t_d}}{\mathcal{V}_G^{t_d}} \tag{27}$$

The mass of oil is constant. However, due to the dissolution of gas, the mass, density and volume of the oil with dissolved gas changes. The total mass of oil is the mass of oil initially injected plus the total mass of dissolved gas. It can be mathematically expressed as:

$$\rho_0^{t_d} \mathcal{V}_0^{t_d} = m_0 + m_{Gd}^{t_d} \tag{28}$$

Substituting the equations (27) and (28) into the equation (25), it is obtained:

$$m_{Gf}^{0} + m_{G}^{inj,t_{d}} + m_{Gd}^{0} + m_{O} = \rho_{G}^{t_{d}} \Psi_{G}^{t_{d}} + \rho_{O}^{t_{d}} \Psi_{O}^{t_{d}}$$
(29)

From equations (26) and (29), the following system of equations is derived:

$$\begin{bmatrix} \rho_G^{t_d} & \rho_O^{t_d} \\ 1 & 1 \end{bmatrix} \begin{bmatrix} \Psi_G^{t_d} \\ \Psi_O^{t_d} \end{bmatrix} = \begin{bmatrix} m_G^0 + m_G^{inj} + m_{Gd}^0 + m_O \\ \Psi_G^0 + \Psi_O^0 \end{bmatrix}$$
(30)

The system of equation (30) requires an implicit solution, because the coefficient $\rho_G^{t_d}$ is dependent on the solution at the same step of time (t_d) . It is proposed for this work that the density of the oil phase changes according to the following equation:

$$\frac{\rho(t_d) - \rho_{sat}(T, n_f, n_d, f)}{\rho_{sat}(T, n_f, n_d, f)} = \frac{C(t_d, f_f) - C_{sat}(T, n_f, n_d, f)}{C_{sat}(T, n_f, n_d, f)}$$
(31)

where *C* is the concentration of gas at the saturation point, and ρ_{sat} is the oil density at the saturation point. The equations for density and gas concentration (dissolved gas) in the saturation point were obtained for each gas separately (Appendix C). For a composition of natural gas, it is proposed in this work that the total expansion of the oil phase is the sum of the relative expansions caused by each gas, based on partial pressure and temperature. This assumption can mathematically be expressed by:

$$\frac{\Delta \mathcal{V}_{o}}{\mathcal{V}_{o}} = \sum \left(\frac{\Delta \mathcal{V}_{o}}{\mathcal{V}_{o}}\right)_{i} \tag{32}$$

where each subscript *i* represents a gas type. In order to calculate the relative expansion on the oil caused by each gas component, $\left(\frac{\Delta V_0}{V_0}\right)_i$, it is necessary to obtain the relation between density and oil volume. The first step comes from the equation for oil density:

$$\rho_0^{sat} V_0^{sat} = m_0 (1 + M_i C_{sat}) \tag{33}$$

Then the difference between the final and initial oil volumes is given by:

$$\Psi_{O}^{sat} - \Psi_{O}^{0} = \frac{m_{O}(1 + M_{i}C_{sat})}{\rho_{O}^{sat}} - \Psi_{O}^{0}$$
(34)

And finally, dividing both sides of equation (34) by \mathcal{V}_{O}^{0} , it is obtained:

$$\left(\frac{\Delta \mathcal{V}_0}{\mathcal{V}_0}\right)_i = \frac{\rho_0^0}{\rho_0^{sat}} (1 + M_i C_{sat}) - 1 \tag{35}$$

The equation (35) is the relative expansion of oil for each gas. The total expansion of the oil phase is given by:

$$\frac{\Delta \Psi_{O}}{\Psi_{O}} = \sum_{i} \left[\frac{\rho_{O}^{0}}{\rho_{O,i}^{sat}} M_{i} C_{sat,i} + \frac{\rho_{O}^{0} - \rho_{O,i}^{sat}}{\rho_{O,i}^{sat}} \right]$$
(36)

The density of the saturated oil is then given by:

$$\rho_{O}^{sat} = \rho_{O}^{0} \frac{\left(1 + \sum_{i} M_{i} C_{sat,i}\right)}{\left(1 + \sum_{i} \left[\frac{\rho_{O}^{0}}{\rho_{O,i}^{sat}} M_{i} C_{sat,i} + \frac{\rho_{O}^{0} - \rho_{O,i}^{sat}}{\rho_{O,i}^{sat}}\right]\right)}$$
(37)

At this point, is possible to calculate the total mass of dissolved gas, which is given by:

$$\rho_{O}^{t_{d}} V_{O}^{t_{d}} - m_{O} = \sum n_{d,i}^{t_{d}} M_{i}$$
(38)

where all the terms of the left side of the equation (38) are known, but the terms on the right side must yet be calculated.

In this work, it is assumed that, at each step of time, the relative change of gas concentration for each gas type is proportional to the ratio between the solubility of the gas and the sum of all solubilities. This assumption can be expressed by:

$$\frac{C_i^{t_d} - C_i^0}{C_i^{sat} - C_i^0} \propto \frac{C_i^{sat}}{\sum C_i^{sat}}$$
(39)

It is also assumed that the relative change on concentration is proportional to the molar fraction of the gas. It can be expressed by:

$$\frac{C_i^{t_d} - C_i^0}{C_i^{sat} - C_i^0} \propto f_i \tag{40}$$

Combining equations (36) and (37), it is obtained:

$$n_i^{t_d} - n_i^0 = k f_i C_i^{sat} (m_0 C_i^{sat} - n_i^0)$$
(41)

The right side of equation (41) is then defined as:

$$k_{i} = k f_{i} C_{i}^{sat} (m_{0} C_{i}^{sat} - n_{i}^{0})$$
(42)

where the constant k is the same for all gas components. Using the equation (38) with the definition of k_i given by the equation (42), and writing the number of moles for each gas component as a function of the number of moles of one of the gas components (here, i = 1 it was chosen as a reference), it is obtained:

$$n_{d,i}^{t_d} = n_{d,i}^{t_d-1} + \left(n_{d,1}^{t_d} - n_{d,1}^{t_d-1}\right) \frac{k_i}{k_1}$$
(43)

Substituting the equation (43) into equation (38), it is obtained:

$$\rho_0^{t_d} \mathcal{V}_0^{t_d} - m_0 = \sum \left[n_{d,i}^{t_d-1} + \frac{k_i}{k_1} \left(n_{d,1}^{t_d} - n_{d,1}^{t_d-1} \right) \right] M_i \tag{44}$$

One can notice that all the terms into equation (44) are known, except $n_{d,1}^{t_d}$, which can therefore be calculated by:

$$n_{d,1}^{t_d} = \frac{\rho_0^{t_d} \Psi_0^{t_d} - m_0 - \sum \left[n_{d,i}^{t_d-1} - \frac{k_i}{k_1} n_{d,1}^{t_d-1} \right] M_i}{\sum \frac{k_i}{k_1} n_{d,1}^{t_d} M_i}$$
(45)

Once the term $n_{d,1}^{t_d}$ is calculated from equation (45), all the other values $n_{d,i}^{t_d}$ can be updated using the equation (42). The number of moles of each gas component that are present as free gas must be updates by means of a balance of gas moles:

$$n_{f,i}^{t_d} = n_{f,i}^{t_d-1} + \left(n_{f,i}^{t_d-1} - n_{f,i}^{t_d}\right) + \dot{n}_{inj,i}^{t_d}$$
(46)

where $\dot{n}_{inj,i}^{t_d}$ is the number of moles of a gas component that was injected by the gas compensation system during the step of time t_d . Finally, the fraction of the free gas present must also be updated:

$$f_{f,i}(t_d) = \frac{n_{f,i}^{t_d}}{\sum n_{f,i}^{t_d}}$$
(47)

Table 5 shows a summary of the model for gas dissolution presented in this subsection.

Table 5. Summary of the model to obtain the dissolution of gas in the oil phase.



Step 1: Obtaining the initial state

Objective: obtain the fractions of each gas component, free and dissolved, just before the pressurization to 75 bars, correspondent to the instant t = 0.

- Simultaneous solution of equations (21), (85) and (88).
- It gives $n_d(0)$ and $n_f(0)$.

Step 2: Obtaining the states during the manual pressurization to 75 bars

Objective: obtain the fractions of each gas component, free and dissolved, during all the instants while the system is being manually pressurized (which may take between 10 and 20 seconds), from t > 0 until $t_d = 0$. Since it is not possible to know the amount of gas being injected, dissolution of gas is neglected (all the gas injected is assumed to be pressuring the system).

- Simultaneous solution of equations (21), (24) and (88).
- It gives $n_d(t)$ and $n_f(t)$.

Step 3: Obtaining the states after the pressurization

Objective: obtain the fractions of dissolved and free gas from $t_d = 0$ until the onset of hydrate formation (at $t_H = 0$). Once hydrate formation begins, it is assumed that there is no more gas dissolution.

- Simultaneous solution of equations (28), (30) and (31) for each step of time $t_d > 0$ until he onset of hydrate formation.
- Update the number of moles $n_{d,1}^{t_d}$ using equation (45).
- Update each $n_{d,i}^{t_d}$ (i > 1) using equation (43).
- Update each $n_{f,i}^{t_d}$ using equation (46).

An example of the application of the model presented on this section is shown in Figure

36.



Figure 36. Gas dissolution calculation using the model proposed on this section, for the experiment #34 (80% water cut, 400 L/h, with AA at 0.94 % wt. vs water).

3.4.2. Calculation procedure for the amount of hydrate formation in the system

Calculating the total fraction of hydrates in the system, or the water conversion, is an important information. It can be calculated from pressure, temperature, injected gas, mass balance, volume conservation, density and hydration number. The following hypotheses are proposed for the model:

- The mass of dissolved gas in the oil phase is constant after the onset of hydrate formation;
- The fraction of each gas component being consumed for hydrate formation is proportional to the molar fraction of the free gas;

- The density of hydrate is constant and it is equal to 910 g/L (density of methane hydrates);
- The hydration number is constant and equal to 6.0.

The mass balance, considering the free gas, the free water and the hydrate phases, is given by the following equation:

$$m_G^0 + m_G^{inj,t_H} + m_W^0 = m_G^{t_H} + m_W^{t_H} + m_H^{t_H}$$
(48)

where t_H indicates the time since the onset of hydrate formation, and the superscript 0 corresponds to the instant of onset of hydrate formation ($t_H = 0$). The term m_g^{inj,t_H} is the mass of gas injected since the onset of hydrate formation.

The volume of the flow loop is constant, and therefore, the following equation can be written:

$$\mathcal{V}_{G}^{0} + \mathcal{V}_{W}^{0} = \mathcal{V}_{G}^{t_{H}} + \mathcal{V}_{W}^{t_{H}} + \mathcal{V}_{H}^{t_{H}}$$
(49)

where, once again, the superscript 0 corresponds to the exactly time of the onset of hydrate formation. One should notice that the oil phase and the dissolved gas were not taken into account in the equations (48) and (49), because the amount of dissolved gas is assumed to be constant after the onset of hydrate formation. The gas density, which can be calculated from the pressure, temperature and composition of the gas (see Appendix C for a complete description of the model implemented on this work to calculate the density of real gas), is given by the equation:

$$\rho_{G}^{t_{H}}(p,T) = \frac{m_{G}^{t_{H}}}{V_{G}^{t_{H}}}$$
(50)

The hydrate density is assumed to be constant and equal to 910 g/L (methane hydrates), and it is the ratio between mass and volume:

$$\rho_H = \frac{m_H^{t_H}}{V_H^{t_H}} \tag{51}$$

The water density is also constant (1023.8 g/L for saline water with 30g/L of NaCl):

$$\rho_W = \frac{m_W^{t_H}}{V_W^{t_H}} \tag{52}$$

Finally, the hydration number is assumed to be 6.0, and it is the ratio between the number of water molecules and gas molecules consumed for hydrate formation:

$$N_{h} = \frac{n_{W}^{crys}}{n_{G}^{crys}} = \frac{\frac{(m_{W}^{0} - m_{W}^{t_{H}})}{M_{W}}}{(m_{G}^{0} + m_{G}^{inj} - m_{G}^{t_{H}})}$$
(53)

Substituting the equations (50)-(53) into equation (48), it is obtained:

$$\begin{bmatrix} \rho_{W} & \rho_{g}^{t_{H}} & \rho_{h} \\ 1 & 1 & 1 \\ \frac{\rho_{W}}{M_{W}} & -\frac{N_{h}\rho_{G}^{t_{H}}}{M_{G}} & 0 \end{bmatrix} \begin{bmatrix} \Psi_{W}^{t_{H}} \\ \Psi_{G}^{t_{H}} \\ \Psi_{H}^{t_{H}} \end{bmatrix} = \begin{bmatrix} m_{G}^{0} + m_{G}^{\text{inj},t_{H}} + m_{W}^{0} \\ \Psi_{G}^{0} + \Psi_{W}^{0} \\ \Psi_{O}^{0} \end{bmatrix}$$
(54)

For simplification, it is assumed that the amount of dissolved gas into the oil phase is constant after the onset of hydrate formation. Then, any variation in pressure or gas injection is due to the consumption of gas for hydrate formation. Concerning the number of moles of a gas component *i* for hydrate formation in an instant $t > t_H$ (accumulated), defined as $n_{c,i}^{t_h}$, a simplified approach is used: it is assumed that the number of gas moles for each gas that is consumed for hydrate formation is proportional to the fraction of free gas:

$$n_{c,i}^{t_H} - n_{c,i}^{t_H-1} \propto f_{f,i} \tag{55}$$

Taking i = 1 as a reference, it can be deduced from equation (55) that:

$$n_{c,i}^{t_d} - n_{c,i}^{t_d-1} = \frac{f_{f,i}}{f_{f,1}} \left(n_{c,1}^{t_H} - n_{c,1}^{t_H-1} \right)$$
(56)

A simple moles balance for the gas, which consists is balancing the initial amount of gas and the injected gas with a final state consisting in free gas and gas consumed for hydrate formation, leads to the following expression:

$$\frac{m_G^0 - m_G^{t_H} + m_G^{\text{inj}, t_H}}{\sum f_{f,i}} = \sum n_{c,i}^{t_H} M_{G,i} + \sum n_{c,i}^{t_H-1} M_{G,i}$$
(57)

Finally, isolating the term $n_{c,1}^{t_h}$ from the equation (57), it is obtained:

$$n_{c,1}^{t_H} = n_{c,1}^{t_H-1} + \frac{m_G^0 - m_G^{t_H} + m_G^{\text{inj},t_H} - \sum n_{c,i}^{t_H-1} M_{G,i}}{\sum f_{f,i} M_{G,i}}$$
(58)

Once $n_{c,1}^{t_H}$ is known, all the terms $n_{c,i(i>1)}^{t_H}$ can be calculated using the equation (56). An example of application of this model for the experiments presented in this thesis is shown in Figure 37.



Figure 37. Hydrate fraction calculation using the model proposed on this section, for the experiment #34 (80% water cut, 400 L/h, with AA at 0.94 % wt. vs water).

3.5. Summary of the chapter

On this Chapter, it was presented the materials and methods used on this thesis. The experimental apparatus (Archimedes flow loop) was described. It is installed at Mines de Saint-Etienne, and it is used for tests with hydrate formation using oil, water and gas at high pressures (up to 75 bars) and low temperatures (4°C is the working temperature). Each one of the instruments used in the experiments was described as well, including the classical measurements (pressures, pressure drops, temperatures, density, flow rate and gas injection), the FBRM, the PVM, the permittivity probe, the acoustic emission and the high-speed camera. The experimental protocol was described in detail, which includes the emulsification outside

of the hydrate domain (control of temperature at low pressure) and flow inside the hydrate domain (manual pressurization and use of the gas compensation system). The models to calculate gas dissolution and water conversion (or hydrate fraction) were presented. The principle of data treatment used to analyze the results was briefly explained as well.

3.6. Highlights in French - Résume du Chapitre 3 en Français

L'objective de ce chapitre est de présenter la méthodologie pour les expériences de cristallisation, les modèles mathématiques pour calculer la dissolution de gaz et la conversion d'eau, et le principe de traitement de donnés.

Le dispositif expérimental est nommé « boucle Archimède », installé au SPIN Centre à l'Ecole des Mines de Saint-Etienne. Le système est utilisé pour des essais de formation d'hydrates de gaz utilisant de l'huile Kerdane, de l'eau salée (avec 30 g de NaCl per litre d'eau) et du gaz naturel à hautes pressions (jusqu'à 75 bars) et basses températures (4 °C est la température de fonctionnement). Un pompe moineau donne la puissance pour l'écoulement jusqu'à 520 L/h. Pour les essais de cette thèse, les débits de 200 ou 400 L/h ont été utilisés. Un séparateur est installé en haut de l'appareil et permet le contact entre le liquide et le gaz naturel. La pressurisation du système est possible avec l'injection de gaz naturel dans le séparateur, manuellement ou en utilisant un système d'injection automatique de gaz que mesure aussi le débit de gaz injecté. La boucle est équipée avec un Coriolis pour mesurer le débit et la densité, dix capteurs de température, quatre capteurs de perte de charge, et deux capteurs de pression. Le système de mesures classiques enregistre les données touts les 1 seconde.

En plus des mesures classiques, la boucle Archimède est équipée avec un FBRM, un PVM, une sonde de permittivité, six capteurs d'émission acoustique et une caméra de haute vitesse. Le FBRM donne la distribution de longueur de corde dans une gamme entre 1 et 1000 micromètres toutes les 5 secondes. Le PVM prendre des photos (1075 x 825 micromètres) toutes les 5 secondes aussi. La sonde de permissivité donne le diélectrique et la conductivité toutes les 2-7 secondes. L'émission acoustique donne plusieurs donnes, et c'est l'énergie absolue (mesure toutes les 0.5 second) qu'est utilisé dans cette thèse.

Le protocole expérimental a été présenté en détail, qui comprend l'émulsification hors du domaine des hydrates (contrôle de la température à basse pression) et le débit à l'intérieur du domaine des hydrates (pressurisation manuelle et utilisation du système de compensation des gaz).

Des modèles mathématiques ont été développés pour calculer la dissolution des gaz et la conversion de l'eau (ou fraction d'hydrates) à partir des mesures de pression, température et d'injection de gaz naturel. Les modèles prennent en compte la conservation de la masse dans un système à volume constant et des équations de gaz real.

Finalement, le principe du traitement des données utilisé pour analyser les résultats a été brièvement expliqué. Un logiciel en Python a été développé pour la synchronisation de toutes les données. Une explication complète de tous les outils de ce logiciel sont disponibles dans l'Appendix A.

CHAPTER 4 – ANALYSIS OF THE OIL-WATER FLOW REGIME BEFORE HYDRATE CRYSTALLIZATION FROM PERMITTIVITY AND DENSITY MEASUREMENTS AND APPARENT VISCOSITY CALCULATION

The objective on this chapter is to discuss about the flow pattern before hydrate formation. An analysis combining dielectric measurement, apparent viscosity (obtained from the pressure drop in the horizontal section), and instant water cut (calculated using the density measured in the Coriolis) is presented.

4.1. Detection of the continuous phase and characterization of the flow regime using permittivity measurements

The definition of dielectric used in this work is the relative permittivity at 10^8 Hz, as explained in subsection 3.1.9. However, a range of frequencies from 10^7 to 6×10^9 Hz is available. For experiments without AA, Figure 38 shows the relative permittivity for all frequencies during the dispersion of oil and water before hydrate formation at low, intermediate and high water-cut. This gives the ranges where the relative permittivity at all frequencies is located most of the time. Comparing the experiments at 200 and 400 L/h, one can notice that the ranges of values for the permittivity (at all frequencies) reduce when the flow rate increases. This can be explained by the size of the droplets because an increased flow rate reduces the sizes of the droplets.

At 30% water cut and 200 L/h (Figure 38(a)), the permittivity presents values that are intermediate between the permittivity of Kerdane and saline water, but closer to the water permittivity than to the oil permittivity. Since it is unlikely that water is the continuous phase for 30% water-cut, the presence of large water droplets may be affecting the measurements (see image of the flow pattern in Figure 44(a)). At 400 L/h (see Figure 38(b)), the relative permittivity seems to converge in the direction of the oil permittivity. At 50% water cut, the permittivity is a lot closer to the water permittivity when the flow rate is 200 L/h (Figure 38(c)), with all the measurements being detected in the upper half close to the saline water permittivity. At 50% water-cut and 400 L/h (Figure 38(d)), the permittivity also concentrates in the upper half of the graph, an indication that water is the continuous phase, but in a reduced range, because the higher shear causes better homogenization of the droplets (see Figure 44(d)). At 80% water cut, the system is homogeneous, with the permittivity bordering the permittivity of water at 200 L/h (Figure 38(e)) and slightly moving down in the graph as the system is even more dispersed at 400 L/h (Figure 38(f)).

On this first analysis, the relative permittivity at all frequencies were monitored. The conclusion is that there are similarities between the tests at 50 and 80% water cut, with the values of permittivity closer to the salted water permittivity than to the oil permittivity, which suggests that those are water continuous systems, while the tests at 30% water cut seem to be in oil continuous systems. The range of the values of permittivity are dependent on the flow rate, depending on the shear forces that will control the size of the droplets and the particles size distribution.



Figure 38. Permittivity at all frequencies added over the time before hydrate formation, for experiments without AA.

For the experiments with AA, the graphs are shown in Figure 39. The tests at 50% watercut, whether at 200 or 400 L/h (Figure 39a-b) give a thin range of values for permittivity, which are intermediate between the salted water and oil permittivity. At 80% water-cut, the thin range is also observed, with values closer to the permittivity of salted water. These results indicate that the additive causes a formation of fine dispersions. The permittivity at frequencies lesser than 10^8 Hz are large and following the water permittivity for the four cases analyzed, which suggests that salted water is the continuous phase for the tests with AA.



Figure 39. Permittivity at all frequencies added over the time before hydrate formation, for the experiments with AA (doses: 1.50 % wt. vs water at 50% water cut, and 0.94 % wt. vs water at 80% water cut).

For the tests at 50% water-cut with AA, the confirmation that they are water-continuous is possible by looking to the permittivity data after the onset of hydrate formation, as shown in Figure 40. For both experiments, the relative permittivity converges to values near the oil after the onset of hydrate formation, indicating an inversion of phase. At 200 L/h, the inversion of phase, when it occurred, was instantly, switching from the intermediate values between salted water and oil directly to values near the dielectric of oil. At 400 L/h, the inversion of phase presented some intermediate steps, with a small gradual reduction, and then an immediate change to oil continuous.



Figure 40. Permittivity at all frequencies after the onset of hydrate formation, for the tests at 50% water-cut, with LDHI-AA (dose 1.5 % wt. vs water).

The analysis presented in this section gives important indications on how to obtain the continuous phase using the relative permittivity. The next section presents additional methods using the permittivity with the density measured by the Coriolis and the apparent viscosity obtained from the horizontal pressure drop that can be used to detect the continuous phase and characterize the flow regime.

4.2. Detecting the continuous phase with dielectric, density and viscosity

In the previous section, it was shown that the continuous phase can be deduced from the permittivity measurements. From the measurements there are homogeneous and heterogeneous dispersions. The definition of homogeneous dispersions presented in the literature is a flow with a constant distribution of droplets characterized by a constant pressure drop (Pham et al., 2020). For the permittivity measurements obtained in this work, the response is a thin range of dielectric values. In this section, a method is proposed to find a correspondence between the dielectric (relative permittivity at 10⁸ Hz) and the instant flowing water cut, that will be called apparent water cut. It is calculated using the density measured by the Coriolis. In fact, it has been observed in the experiments that the flow is often not completely dispersed, especially for experiments at 200 L/h without LDHI-AA. The non-homogenous distribution of droplets (of the dispersed phase) is the reason for these variations. Therefore, the water cut distribution along space is not constant, corresponding to a non-homogenous dispersion. In the second part of this section, the apparent viscosity is calculated over time and correlated to the water-cut.

4.2.1. Methodology to relate dielectric and water cut

The density measured by the Coriolis has the contributions of the oil and the water phases. The amount of free gas flowing in the system is relatively low, and therefore, it will be neglected. The density, as function of the water and oil densities, can be expressed by the following equation:

$$\rho = \rho_W \alpha_W + \rho_0 (1 - \alpha_W) \tag{59}$$

Rearranging the equation (59), the water cut can be calculated using the following equation:

$$\alpha_{\rm W} = \frac{\rho - \rho_0}{\rho_{\rm W} - \rho_0} \tag{60}$$

The water density is assumed to be constant over time, but the oil density must be corrected beforehand using the methodology proposed in subsection 3.4.1 to take into account the amount of dissolved gas. The apparent water cut over time is calculated before hydrate formation, that is, from the instant of pressurization to 75 bars until the instant of the onset of hydrate crystallization. Once this calculation is done, the apparent water cut is compared the dielectric. For that, it is necessary a synchronization in time and space between the data from the two instruments, because the Coriolis and the permittivity probes are installed in different positions in the flowloop (see Figure 22). The volume between the instruments and the flow rate are used to obtain the time it takes for the mixture to flow from one instrument to another.

Once the data form the two instruments are synchronized, the method to find a correspondence between dielectric and water cut, represented in Figure 41, consists in identifying, at each 30 seconds, the maximum, the minimum, and the average values of dielectric and water cut. The next step consists in linking the minimum water cut to the minimum dielectric obtained in that 30 seconds interval, and then linking the average and maximum values. The interval of 30 seconds was chosen to have a minimum of five measurements for the dielectric, and at the same time, detect the variations in the signals over time (these variations may not be detected for longer intervals of measurement).



Figure 41. Schematic of the method to link apparent water cut and dielectric.

Figure 42 shows an example after using the proposed method for an experiment at 50% water cut, 200 L/h, without AA. While the water cut ranges between 30% and 70%, the dielectric ranges between 40 and 87. Figure 42(a) shows the water cut over time, while Figure 42(b) shows the water cut for the selected point (average, maximum and minimum). The same procedure is used to the dielectric measurements, where the continuous measurements are shown in Figure 42(c) and the selected points in Figure 42(d). The dielectric of the oil is around 2.7 and dielectric of the water is around 87.9 (at 4°C), as presented in the subsection 3.1.9. One should notice that, for the selected point in Figure 42(b) and Figure 42(d), the green points correspond to the minimum, the blue points correspond to the average, and the red points correspond to the maximum values in a 30 seconds interval.



Figure 42. Selecting the minimum, maximum and average values for dielectric and water cut for an experiment at 50% water cut, 200 L/h, without LDHI-AA (#19).

Figure 43 shows the correspondence between dielectric and water cut. Indeed, it seem to exist a linear relationship between dielectric and water cut for the experiment analyzed.



Figure 43. Correspondence between dielectric and water cut for an experiment at 50% water cut, 200 L/h, without LDHI-AA.

Figure 44 shows some images obtained with high-speed imaging and the relation between dielectric and water cut for experiments at 30, 50 and 80% water cut, 200 L/h, without AA. The first thing that can be observed, especially for the experiments at 30 and 50% water cut, is that there is a large range of variation of apparent water cut. At 30% water cut, the water cut distributed along space may vary from 16 to 58% (Figure 44(a)). At 50% water cut, it ranges from 22% to 81% (Figure 44(b)). By its turn, the experiment at 80% water cut show a low variation, ranging from 69 to 88% (Figure 44(c)). In that sense, at 30 and 50% water cut, the dispersions appear to be a lot more heterogeneous than for the dispersion at 80% water cut.

Yet in Figure 44, while the dielectric values for 30% water cut range from low values (near the oil dielectric) to high values (near the salted water dielectric), the dielectric for the experiments at 50 and 80% water cut appear to range in the upper half part of the graph, closer to the salted water dielectric. This enable to conclude that oil is the continuous phase for 30% water-cut, while water is the continuous phase for 50 and 80% water cut. In the images, droplets with size up to 4 mm are dispersed in the continuous phase at 30% water-cut and 200 L/h (Figure 44(a)). Due to the high brightness of the droplets, it appears again that the droplets are of water, which are flowing in the oil continuous phase. At 50% water cut, one can notice that droplets are larger than at 30% water cut (Figure 44(c)). A partial stratification of the water phase appears in the window, with droplets flowing preferably in the upper part, due to gravity. It confirms that the droplets are of oil, due to the difference in density (oil is lighter than water). Finally, at 80% water cut, it is clear that there is a fine dispersion of oil droplets in the water continuous phase, with most of the droplets at the top of the pipe when flowing in front of the window (installed in the horizontal part).



Figure 44. Analyses of the flow patterns comparing the correspondence between dielectric and water cut with the images obtained with high-speed imaging.

The tests with AA limit the visualization using the PVM and the camera, because it causes a completely dispersion between the two phases, which induces a high dispersion of the light, as shown in Figure 45.





A correspondence between dielectric and water-cut for all the experiments (listed in Table 3) is shown in Figure 46. The experiments ware separated in four groups, depending on the flow rate (200 or 400 L/h) and the use or not of LDHI-AA. For the tests without LDHI-AA, shown in Figure 46(a)-(b), despite the large variation of the values (from the minimum to the maximum) of water-cut and dielectric, it appear that there is a curve that relates them. As expected, when the dielectric increases, the water cut also increases. The shape of the curve is not exactly linear, and it seems that there is a slightly difference between the curves for 200 and 400 L/h. In fact, the dielectric measured is not the dielectric of the mixture in the entire cross-section where the probe is installed, but rather the dielectric of the mixture that touches or passes near the sensor. Therefore, the size of the droplets and how they are distributed in the cross-section may affect the measurements, and that is why the results in Figure 46 were split in four groups, depending on the flow rate and the use of LDHI-AA.

For the tests with LDHI-AA, shown in Figure 46(c)-(d), the repeatability of the tests can be noticed. At 200 L/h, the dispersion is homogeneous, because there is not difference between the minimum and maximum points of water-cut and dielectric. The tests at 400 L/h with LDHI-AA are also completely dispersed, but the presence of gas bubbles may affect the calculated water cut and cause the difference between the maximum and minimum points. Since the use of LDHI-AA completely disperse the system, the amount of free gas (flowing as dispersed bubbles) can be estimated taking into account the density measured. Each experiment with LDHI-AA was repeated once, and the fractions of free gas ware estimated to be around 2.60% and 2.98% for the tests at 50% water-cut and 400 L/h (against 0.54% and 0% at 200 L/h). For

80% water-cut, it was estimated around 4.59% and 4.82% for the tests at 400 L/h (against 0.67% and 0.95% for 200 L/h).



Figure 46. Correspondence between dielectric and water-cut.

4.2.2. Methodology to relate viscosity and water-cut

The viscosity of the flowing mixture is another indicator of the flow regime and the homogeneous or heterogeneous behavior of the dispersion. The apparent viscosity for a two-phase oil-water flow is greater than the water or the oil phase viscosities. There are some models for apparent viscosity in the literature, indicating that the apparent viscosity is not equal to the viscosity of the continuous phase, rather increasing as the fraction of the dispersed phase increases. The apparent viscosity can be calculated as a function of the frictional pressure drop:

$$\frac{\Delta p_{\rm h}}{L_{\rm h}} = \frac{2}{D} f \rho U_{\rm h}^2 \tag{61}$$

where the Fanning friction factor is a function of the Reynolds number:

$$f = C \cdot Re^{-n} = C \left(\frac{\rho UD}{\eta}\right)^{-n}$$
(62)

The coefficients *C* and *n* in are dependent of the laminar-turbulent transition. It is assumed C = 16 and n = 1 if $Re \le 2300$ (laminar), or C = 0.079 and n = -0.25 if Re > 2300 (turbulent). Finally, from equation (62), the apparent viscosity can be calculated as:

$$\eta = \rho U_{\rm h} D \left(\frac{C}{f}\right)^{-n} \tag{63}$$

The method to relate the apparent water-cut and the apparent viscosity, before hydrate formation, consists in synchronizing the pressure drop in the horizontal section and the watercut calculated from the density. However, the horizontal pressure drop is a measurement that depends on two points. Therefore, the apparent water-cut for this case must be the average water fraction present in the horizontal part, between the two exactly positions where the pressure drop is measured. In order to obtain this average water fraction, it is necessary to record the water cut over time, during the interval that it takes for the flow to pass the horizontal section. Then, these values are used to calculate the average water-cut.

Figure 47 shows an example of the calculation procedures to obtain the Reynolds number, the apparent viscosity and the relation between viscosity and water cut and dielectric and water cut, for an experiment at 30% water cut, at 200 L/h, without LDHI-AA. The Reynolds number is lower than 2300 all the time, as shown in Figure 47(a), which indicates a laminar flow. Laminar flow appears to be the general case for all the experiments of this work (see Appendix C). The viscosities of water and Kerdane indicated in the graphs were obtained with the Archimedes flowloop. When hydrates from, after around 17 minutes, the Reynolds number reduces even more, due to the increasing viscosity forces.



Figure 47. Experiment #11 (30% water cut, 200 L/h, without AA).

As discussed in section 2.2, the apparent viscosity of the flow is highly dependent on the viscosity of the continuous phase, and it increases as the fraction of the dispersed phase increases. Then, the apparent viscosity as function of water cut can be used to deduce the continuous phase.

Figure 48 shows the relation between apparent viscosity and water cut for the tests without LDHI-AA. One can see that, at 30% water-cut and 200 L/h, the viscosity increases as the water cut increases (Figure 48(a)). This observation is more obvious for the test at 400 L/h, where there is a clear linear relation between water cut and viscosity (Figure 48(b)). On the other hand, the tests at 50% water cut have an opposite behavior. The viscosity reduces as the water cut increases (see (Figure 48(c)-(d)), which indicates that oil is the dispersed phase. At any water cut, the apparent viscosity increases if the flow rate increases, because the shear creates more interfaces.



Figure 48. Relation between apparent viscosity and water cut for experiments without AA.4.3. Flow regimes as function of water-cut, flow rate, and use of additive

Based on the previous discussions, the depictions of the identified flow regimes are illustrated in Figure 49. The tests at 30 and 50% water-cut without AA are not well dispersed, with large droplets (a few milliliters of size) of the dispersed phase. The experiments at 80% water-cut are, overall, well mixed. As the flow rate increases, the dispersion becomes finer for

any water-cut. It was observed that tests with AA are completely well dispersed, being no possible to distinguish droplets from the dispersed phase.



Figure 49. Depiction of the flow regimes identified in the experiments, before hydrate formation.

4.4. Summary of the Chapter

In this chapter, the oil – water dispersion before hydrate formation was analyzed. The objective was to use dielectric measurements, apparent water cut and apparent viscosity to detect the continuous phase and understand better the flow regime. It was observed that experiments at 200 L/h (30 and 50% water-cut) are heterogeneous, or not completely dispersed, with large droplets. As a response, the water-cut, dielectric and viscosity present a large range

of oscillations. From the dielectric measurement, it is was possible to identify the continuous phase, noticing that the values remain rather in the upper (for water continuous) or lower (for oil continuous) half of the range of the possible dielectric measurements. For tests at 400 L/h, it was easier to detect the continuous phase, not only with the dielectric measurements, but also with the apparent viscosity, because the dispersion is composed of small droplets. This is in agreement with the literature the observation that the viscosity increases when the fraction of the dispersed phase increases. The understanding achieved in this Chapter for the dispersed systems before hydrate formation will help understanding how is the dispersion behaves after hydrate formation, as it will be discussed in the Chapter 5.

4.5. Highlights in French - Résume du Chapitre 4 en Français

Dans ce chapitre, l'émulsion huile-eau avant la formation d'hydrates a été analysée. L'objectif était d'utiliser des mesures diélectriques, de densité et de viscosité apparente pour détecter la phase continue et mieux comprendre le régime/géométrie d'écoulement. Des méthodes pour synchroniser le diélectrique, la fraction d'eau local (à partir de la densité du Coriolis) et la viscosité apparent (a partir de la perte de charge horizontal) ont été présenté.

Il a été observé que les régimes à 200 L/h (30 et 50% de *water cut*) sont hétérogènes, ou pas complètement dispersés. En réponse, la fraction d'eau local, le diélectrique et la viscosité présentent une large gamme d'oscillations. A partir de las mesures du diélectrique, il a été possible d'identifier la phase continue. Quand les valeurs restent plutôt dans la moitié supérieure, l'eau est la phase continue. Ou, quand les valeurs restent plutôt dans la moitié inferieur, l'huile est la phase continue.

Pour les tests à 400 L/h, il était plus facile de détecter la phase continue, non seulement à partir des mesures diélectriques, mais aussi du calcul de la viscosité apparente, car la dispersion est fine. Comme prévu dans la littérature, l'augmentation de la fraction de phase dispersée augmente la viscosité apparente. Avec les calculs de viscosité apparent, il a été observé que, à 50% *water cut*, la viscosité augmente avec la fraction d'eau (donc l'eau est la phase dispersé). A 80% water cut, la viscosité réduisent avec le *water cut* (donc l'huile est la phase dispersé).

La compréhension obtenue dans ce chapitre pour le système dispersé avant la formation d'hydrates aidera à comprendre comment la dispersion se comporte après la formation d'hydrates, comme cela sera discuté dans le Chapitre 5.

CHAPTER 5 – HYDRATE FORMATION AND PLUGGING MECHANISMS FOR OIL AND WATER DOMINATED SYSTEMS

This chapter presents the results and discuss the mechanisms of hydrate formation and plugging. While the Chapter 4 was focused in the analysis of the data of the experiments before hydrate formation, this chapter will resume and analyze the data after the onset of hydrate formation. The objective is to discuss how hydrates are formed and in which manner they affect the flow pattern, in order to propose new insights into the mechanisms of hydrate plug formation and prevention. In the first section of this chapter are presented the results for the experiments without LDHI-AA, while in the second section are presented the results with LDHI-AA.

5.1. Hydrate formation for oil-water system without AA

In this section, it is presented and discussed the results for the experiments without LDHI-AA. The first three subsections show the results at low (30%), intermediate (50%) and high (80%) water-cut. The last subsection proposes the hydrate plugging formation mechanisms for oil and water continuous systems from the results of the experiments without LDHI-AA.

5.1.1. Experiments at 30% water-cut

Hydrate formation is an exothermal process that causes an increase on the temperature of the surrounds where they are forming. Therefore, in the experiments, hydrate formation can often be detected by an increase of the temperature. There are nine temperature probes distributed in the flowloop apparatus, so if the volume of hydrates formed is enough to increase the temperature, it is possible to detect when and where hydrates are initially formed. However, since the heat generated by crystallization warms the fluid around it, it is not possible to track where hydrate particles are located only from the temperature measurements. The acoustic emission probes were installed with the objective to track the particles in time and space by capturing the absolute energy.

For the first experiment analyzed, at 200 L/h (#11³), Figure 50(a) shows that, around 16.8 minutes, the temperature measured by the probe T_8 , which is installed right after the pump, increases. Less than a minute later, around 17.6 minutes, Figure 50(b) shows that the AE sensor 1A has a sudden increase on the absolute energy, and then one by one of the sensors used in that experiment also react, in sequence, with an increase of absolute energy. Finally, the last

³ The list of experiments is shown in Table 3 (page 49).

temperature probe to detect an increase of the temperature is the sensor T_7 , around 18.5 minutes, as shown in Figure 50(c). The probe T_7 is installed just before the pump.



Figure 50. Detecting the onset of hydrate formation with temperature and absolute energy measurements for a test at 30% water cut, 200 L/h, without AA (#11).

The data shown in Figure 50 indicates that the onset of hydrate formation occurred between the temperature probes T_7 and T_8 , where the pump is located. Indeed, for most of the experiments, this is the location where hydrates form. Hydrate formation may have started after the pump⁴, because this is the point with the highest absolute pressure in the apparatus. Another

⁴ Another location where hydrates may form is the downward section, because there is gas being dissolved in the liquid phase after the separator.

possible explanation is that the energy provided may facilitate the free energy fluctuations that cause clusters to reach a critical size. The data shown in Figure 50 also shows that the absolute energy increases once hydrates start passing in front of the acoustic emission sensors. The measured absolute energy increases up to three orders of magnitude when hydrates are formed.

Figure 51 shows the data of PVM, FBRM and absolute energy when hydrates are initially detected. The data is synchronized in such way that the time that it takes for the flow to move between the instruments is taken into account. As indicated in the x-axes, the instrument used as reference is the Coriolis. The first PVM image to show hydrates is the image 3 (see Figure 51(a)). These particles seem to be flowing dispersed in the liquid phase (dark background), while images 4-8 indicate that there are relatively large porous agglomerates passing in front of the PVM. Since the images 5-7 are very similar, there was deposition on the instrument. The passage of the first particles (image 3) was not detected by the FBRM (Figure 51(b)), but it could be detected with the absolute energies (Figure 51(c)), which have a first peak when the particles seen in image 3 pass near the sensors.

The second peak observed on the absolute energy coincides with the arrival of the large amount of hydrates seen in the PVM (images 4-8). It is likely that there was also deposition on the FBRM instrument, since the number of counts remains approximately constant after the detection of hydrates (between 19.5 and 20.5 minutes), and it slightly decreases beyond 20.5 minutes.

The results indicate that immediately after hydrate formation, the phases started separating. There are regions with hydrates (peaks in absolute energy) and regions with mostly liquid (absolute energy with the same values as before hydrate formation). One reason for this phase separation is the tendency of hydrates to flow with the water phase (as it will be explained later, deduced from the Figure 53). Another reason is the drift velocity between hydrate particles and liquid (the hydrates are slower than the liquid phase). Moreover, another reason can be the loss of kinetic energy of particles due to collision to the walls, or collision between particles; the loss is intensified due to the capillary forces, which slow the particles during collisions and cause temporary accumulation, this mechanism is called sloughing. A combination of these three mechanisms are likely to be the reasons for the separation of phases identified after hydrate formation, which forms a heterogeneous suspension, where some regions have more hydrates and other regions have liquid single-phase flow.



Figure 51. Onset of hydrate formation for the experiment at 30% water cut, 200 L/h, without AA (#11), comparing (a) the PVM images, (b) chord counts and PVM-brightness, and (c) absolutes energies.

Figure 52 shows the results (absolute energy, temperature, pressure drop and flow rate), for the experiment at 200 L/h (#11), from the onset of hydrate formation until the end of the experiment, when the system is plugged. Again, the data from the different instruments are synchronized in time, with the Coriolis as a reference, as indicated in the x-axis. One can notice that all the measurements, around 17.5 minutes, present an immediately change, due to the onset of hydrate formation. The absolutes energies (Figure 52(a)) from all the sensors, as discussed

previously, increase up to three orders of magnitude after the onset of hydrate formation, and remain at high values for almost three minutes, which is approximately the time it takes for a turn around the loop at 200 L/h. However, the absolute energies from all sensors start presenting a heterogeneous behavior after the first turn (near the instant 20.5 minutes), between high values (which increase over time) and low values corresponding to the same level as before hydrate formation. This means that hydrates are not homogeneously distributed in the continuous phase and that there are certain volumes of the fluids with hydrates (peaks in absolute energies) and others without (or a low amount of dispersed) hydrates (low levels of absolute energies), due to the separation of phases, as previously discussed. This separation of phases seems to intensify during hydrates crystallization and flow with values of absolute energy increasing during short times intervals.

The pressure drops are shown in Figure 52(c). The horizontal pressure drop (Δp_h) increases nearly five times when hydrates form, staying at such level during the first turn around the loop (the first three minutes) after hydrate formation. At the same time, there is an oscillation of the flow rate (Figure 52(d)). After the first three minutes since the onset of hydrate formation, there is a reduction on the horizontal pressure drop, while all the pressure drops and flow rate start to present a heterogeneous behavior, the same observed for the absolute energy. The pressure drops are sensitive to the friction to the wall (except the static differential pressure in the separator (Δp_4)), as discussed in subsection 3.1.4, and so to the viscosity⁵. In fact, the apparent viscosity increases after hydrate formation (Figure 47, pg. 77), presenting the maximum values during the first three minutes since the onset of hydrate formation. An explanation for the reduction of apparent viscosity after a few minutes is that the first hydrate particles are relatively large and contain liquid inside (with hydrates trapping water), and at the same time there is a continuous disruption of hydrates from the surfaces of the water droplets where these hydrates initially formed. After a continuous breakage and disruption during the growth period, hydrates will reduce in size (average size of hydrate particles), explaining why there is a reduction of the apparent viscosity. In addition, hydrates may be accumulating (settling and/or depositing) in some parts of the loop, which could be another reason for the reduction of the apparent viscosity of the flowing mixture (the pressure drop will reduce in regions where the hydrates are not accumulating).

Concerning the exactly location (and reason) of plugging, these informations are given by the pressure drops in the downward pipe (Δp_1), upward pipe (Δp_2) and liquid level in the

⁵ Calculation of apparent viscosity is presented in Appendix D.
separator (Δp_4). When the pressure drop in the downward pipe (green line in Figure 52(c)) decreases after hydrate formation, it means that there is an increase of apparent viscosity or accumulation of hydrates that competes with the differential static pressure (see equation (17), subsection 3.1.4). The pressure drop in the upward flow (red line in Figure 52(c)) increases, but not as much as observed for the horizontal pressure drop. It is the pressure drop in the separator that gives the information about where the plug occurred. The static pressure Δp_4 (cyan line in Figure 52(c)) reduces when hydrates are passing in the separator, which means that hydrates temporarily block the flow in the bottom horizontal pipe of the separator (see Figure 23). Over the time, the value for this differential pressure reduces more and more when hydrates are passing in the separator and reaches zero just before the flow rate indicates the value zero. In order to protect the pump and for safety concerns, the experiment is shut down when the flow rate indicates zero and the pressure drop Δp_1 or Δp_4 also shows zero, and it is considered that the system "plugged".

Figure 53 shows a comparison between dielectric, density, and absolute energy (sensor 1A) for the experiment at 200 L/h (#11). The comparison between dielectric and density, in Figure 53(a), shows that the two curves have peaks in the same regions, indicating that regions of the flow with more water are the regions with the peaks in dielectric and density, while low levels of dielectric and density correspond to the regions of the flow with more oil. From Figure 53(b), it is possible to see that the peaks in absolute energy, which indicates the regions with hydrates, correspond to the regions with more water from the dielectric values. Therefore, a few minutes after the onset of hydrate formation, hydrates are flowing mostly with the water phase, while there are regions with oil flowing as single-phase almost free of hydrates and water. The region with oil is apparently a single phase because the density is constant and near 800 kg/m³, which is close to the expected Kerdane oil density at those conditions of pressure and temperature with dissolved natural gas. A separation of phases has been previously observed by Palermo and Sinquin (1997), with the water with hydrates immediately separating from the oil.

The grayscale of the PVM images increase after hydrate formation, as indicated in Figure 53(c), with most images showing hydrates in the system. Finally, the chord counts shown in Figure 53(d) indicate that is class between 100-1000 μ m (red line) which changes more due to the passage of hydrates. When hydrates are passing near the sensor, particles may attach to the sensor, which is "cleaned" when oil is passing near it. The main cause of the plug was therefore heterogeneous dispersion of hydrates in the liquid, with regions at higher hydrate fractions then others.



Figure 52. Experiment at 30% water-cut, 200 L/h, without AA (#11), showing the: (a) absolute energies, (b) temperatures (T₈ and T₉), (c) pressure drops and (d) flow rate.



Figure 53. Experiment at 30% water-cut, 200 L/h, without AA (#11), showing a comparison between: (a) dielectric and density, (b) dielectric and absolute energy, (c) dielectric and PVM images grayscale and (d) dielectric and chord counts.

Figure 54 shows the results for an experiment at 400 L/h (#15). At a higher flow rate, the increase of absolute energy, temperature and horizontal pressure drop is higher than at 200 L/h, meaning that hydrates form faster at 400 L/h. In fact, comparing two tests at 30% watercut, one at 200 L/h (#11) and the other at 400 L/h (#15), the water conversion was 3.4% for the test at 200 L/h and 8.2% for the test at 400 L/h three minutes after the onset of hydrate formation. The onset of hydrate formation occurred between the downward and the horizontal section, because they were detected by the AE probes and the horizontal pressure drop and no increase of temperatures in the sensor T₉ (installed after the separator) or T₈ (installed after the pump) was detected.



Figure 54. Experiment at 30% water-cut, 400 L/h, without AA (#15), showing the: (a) absolute energies, (b) temperatures (T₈ and T₉), (c) pressure drops and (d) flow rate.

Figure 55 shows the comparison between dielectric, density, absolute energy, PVM images grayscale and chord counts, for the test at 400 L/h (#15). There is not much change on the dielectric measurements, except during a short period, around 16 minutes. It means that the phase in contact with the wall is the oil phase, and that hydrates might be better dispersed than at 200 L/h. In fact, the dielectric slightly increased after the onset of hydrate formation, and remained approximately constant most of the time. This indicates that there was some deposition in the horizontal section, which is in agreement with the horizontal pressure drop (Δp_h) , that also slightly increases after the onset of hydrate formation and then remained constant most of the time (see yellow line in Figure 54(c)). Hydrate blockage occurred due to accumulation of hydrates in the separator and in the downward section of the pipe, as indicated

by the pressure drops Δp_1 and Δp_4 (also shown in Figure 54(c)). The plug occurred around 17.5 minutes, with an amount of 3.62% of hydrates fraction. However, due to the separation of phases, the apparent hydrate fraction in the region where the blockage occurred is estimated to be near 8.8%, as obtained from the methodology presented in Chapter 6 (see Figure 85, page 135). Besides that, hydrates are porous and trap liquid (water, for this experiment). Which means that the volume of the mixture containing hydrates and water can be a lot more than 8.8%. The main cause of plug in this experiment was deposition.



Figure 55. Experiment at 30% water-cut, 400 L/h, without AA (#15), showing a comparison between: (a) dielectric and density, (b) dielectric and absolute energy, (c) dielectric and grayscale of PVM images, and (d) dielectric and chord counts.

As conclusions, for the tests at 30% water-cut without additive:

- The initial w/o dispersion completely disrupts into hydrates flowing preferred with the water phase while oil flows without hydrates;
- At 200 L/h the main cause of the plugs was the accumulation of hydrates in parts of the liquid volume, while at 400 L/h there was a combination between deposition and accumulation of hydrates in parts of the liquid volume;
- After hydrate formation, the oil phase apparently flows as a single phase;
- The higher the flow rate, the higher the hydrate formation rate, due to the increased contact between water and gas;
- Due to the accumulation of hydrates in some volumes of the fluid (caused by the separation of phases) the local hydrate fraction can be higher than the calculated hydrate fraction;
- The porosity of hydrates is another mechanism that may be causing plugging even at relatively low water conversions, since the apparent volume of hydrates might be higher than the calculated values (Bassani et al., 2019).

5.1.2. Experiments at 50% water-cut

For an experiment at 200 L/h (#19), a comparison between the PVM images, chord length counts and absolute energies is shown in Figure 56. When the first hydrates are visualized by the PVM (image 3 in Figure 56(a)) and pass near the AE sensors, there is a first peak on the absolute energies (Figure 56(c)). The absolute energies from all sensors decrease a few seconds after the first hydrates have passed, and then for a few seconds present levels of energies which are similar to the ones before hydrate formation. After that, once more, the absolute energies increase, indicating that again hydrates are passing in front of the AE sensors. Between 19.6 and 22.1 minutes, the absolute energies remain oscillating at levels between 10 and 10² times larger than before hydrate formation, indicating a constant passage of hydrates in a heterogeneous suspension. Beyond 22.1 minutes, after a turn around the loop, a separation of phases is observed in the acoustic emission, with "peaks" (regions with hydrates) and "valleys" (regions without hydrates, or with a fine dispersion of hydrates).

(a) PVM images (1075x825 μm)



Figure 56. Detection of hydrate formation by comparing the (a) PVM images, (b) chord length separated by groups with PVM images grayscale , and (c) absolute energies, for an experiment at 50% water-cut, 200 L/h, without AA (#19).

For the tests at 50% water-cut without additive, the camera was used. A comparison between the absolute energy from the AE sensor 3C (which is installed near the window) and some images for the test at 200 L/h (#19) is presented in Figure 57. The images are shown with an increased contrast. Before of hydrate formation (image 1), relatively large oil droplets (larger than 1 mm) are dispersed in the water phase. The droplets are concentrated in the top part of the pipe, which, once more, indicates that the droplets are of oil (oil is lighter than water, so due

to the gravity, it flows in the upper part of the pipe, when passing in the horizontal section). Once hydrates form, they also flow in the upper part (hydrates are lither than the water).



Figure 57. Comparison between the images from the camera and the absolute energy measured near the window for the test at 50% water-cut, 200 L/h, without AA (#19).

Hydrates apparently do not form around all the oil droplets immediately. Indeed, it seems that while hydrates form around some of the oil droplets, they break and disrupt from the droplets surfaces, forming particles that are smaller than the droplets. Comparing the images 2-4 (with hydrates) with the image 1 (before hydrate formation), the hydrates particles are larger

than the oil droplets. Images after the ones shown in Figure 57 are too dark, due to a deposition of hydrates in the surface of the window.

Yet for the test at 200 L/h (#19), a comparison between absolute energies, temperatures, pressure drops and flow rate is shown in Figure 58. Right after the onset of hydrate formation (around 19.5 minutes), there is an increase of the temperatures (Figure 58(b)), and an increase of the horizontal pressure drop (yellow line in Figure 58(c)). However, it seems that it is after the second turn around the loop that hydrates grow more, which results in another increase of the temperature around 22 minutes that is higher than the first one. Figure 58(c) shows that the horizontal pressure drop also increased around 22 minutes, while the pressure drops in the downward section and separator decreased, indicating an accumulation or deposition of hydrates on those sections.

Overall, it is possible to see that the hydrates are distributed everywhere in the flow, with some separation of phases starting around 22 minutes, when the absolute energy has, for a few seconds, values similar to the ones before hydrate formation. However, this distribution is not homogeneous, as one can see with the data for horizontal pressure drop. In some parts of the fluid, the apparent viscosity is higher, and these specific parts where the apparent hydrate fraction is higher can block the pipe. The calculated hydrate fraction at the end of this experiment, just before plug, was 2.88%. The maximum local hydrate fraction was estimated to be 2.7% (see Figure 86, pg. 136). There are two reasons why the systems plugs with such low hydrate fraction. The first one is the porosity of the particles, which can entrap liquid. The images obtained with the cameras become completely dark after the onset of hydrate formation, blocking the passage of light from one side to another, which would not be possible with only 2.88% of hydrates fraction without taking into account the porosity of the hydrates. Another reason is due to a local accumulation of hydrates somewhere in the system, especially in regions with a change in the geometry (separator) or in the downward section.

The comparison between dielectric, density, absolute energy, PVM images grayscale and chord counts, for the experiment at 200 L/h (#19), is shown in Figure 59. There is an immediate reduction of dielectric once hydrates form, indicating that the first hydrates to form, shown in Figure 57, are being carried by the oil phase. The highest values of dielectric are coincident with the highest values of density, while the dielectric reduces for a few seconds between 22 and 23 minutes when there is only liquid flowing (low values of absolute energy).



Figure 58. Experiment at 50% water-cut, 200 L/h, without AA (#19), showing the: (a) absolute energies, (b) temperatures (T₈ and T₉), (c) pressure drops and (d) flow rate.

As conclusion, a few minutes after hydrate formation, hydrates are flowing with the water phase. Therefore, even if the continuous phase is water, with hydrates forming on oil droplets, the flow regime is completely disrupted once hydrate form. Hydrate seem to have more affinity with the water phase, and because of that, hydrates will flow preferably with the water phase.



Figure 59. Experiment at 50% water-cut, 200 L/h, without AA (#19), showing a comparison between: (a) dielectric and density, (b) dielectric and absolute energy, (c) dielectric and grayscale of PVM images, and (d) dielectric and chord counts.

For an experiment at 400 L/h (#24), Figure 60 shows a few images once the first hydrates are detected compared to the absolute energy near the sensor. The droplets are well dispersed due to the shear, so the hydrate particles, once they form, they are apparently better dispersed than for the test at 200 L/h previously discussed. It is possible to see that also there is the formation of an intermittent regime. The regions with the highest values in absolute energy are dark and seems to carry more hydrates (image 3) than regions with low values of absolute energy, which are lighter and have no much hydrates flowing⁶ (image 4).

⁶ Part of the particles seem in image 4 are not flowing but attached to the window.



Figure 60. Comparison between the images from the camera and the absolute energy measured near the window for the test at 50% water-cut, 400 L/h, without AA (#24).

A comparison between the absolute energies from all sensors, temperatures (T_8 and T_9), pressure drops and flow rate for the experiment at 400 L/h (#24) is shown in Figure 61. It is worthy noticing that, for the absolute energy, there is a change on the intermittence between the volumes with hydrates and the volumes without hydrates. As the time passes, the region without hydrates expands because the absolute energies remain at the same level than before hydrate formation for longer and longer time at each turn around the loop). Since hydrate are forming

all the time, the conclusion is again that hydrates tend to agglomerate together over time. There is a continuous increase of the temperatures after the onset of hydrate formation (Figure 61(b)). Hydrate formation provokes a large increase on the frictional pressure drops as seen in Figure 61(c). The horizontal pressure drops increases when the volume of the flow with hydrates passes in that section, while the pressure drops in the separator and in the downward section reduces. Once hydrates block the cross section in the bottom horizontal section of the separator, free gas from the right vertical pipe of the separator (see Figure 23) may be sucking by the flow, which causes an oscillation on the flow rate (Figure 61(d)).



Figure 61. Experiment at 50% water-cut, 400 L/h, without AA (#24), showing the: (a) absolute energies, (b) temperatures (T_8 and T_9), (c) pressure drops and (d) flow rate.

Figure 62 shows the comparison between dielectric, density, absolute energy, PVM images grayscale. Once more, hydrates seem to be flowing mostly with the water phase, because the highest values of dielectric are coincident with the highest values of density and absolute energy.



Figure 62. Experiment at 50% water-cut, 400 L/h, without AA (#24), showing a comparison between: (a) dielectric and density, (b) dielectric and absolute energy, (c) dielectric and grayscale of PVM images, and (d) dielectric and chord counts.

As conclusions from the test at 50% water-cut, without AA:

- The initial o/w dispersions is completely disrupted after hydrate formation, because the hydrates initially formed on oil droplets surfaces have more affinity to the water phase, and therefore, they are detached and carried by the water phase;
- Separation of phases seems to cause local increases on viscosity;

- The main cause of plug was due to a blockage of hydrates in specific parts of the loop (downward section and separator);
- The tests at 50% water-cut were the most critical, causing strong oscillations on the frictional pressure drop and on the flow rate immediately after hydrate formation.

5.1.3. Experiments at 80% water cut

The data from the first 20 minutes of an experiment at 80% water, 200 L/h, without AA (#20), is shown in Figure 63. The first hydrates can be seen in the image 2, in the PVM-images shown in Figure 63(a). Once hydrates form, the absolute energy (Figure 63(c)) increases gradually, contrary to the tests at 30% and 50% water-cut previously presented (that had an immediately large increase of two or three orders of magnitude). The absolute energies from all the sensors present oscillations from around 3 minutes, which is the onset of hydrate formation, until around 11 minutes. This interval coincides with a fine particle dispersion seen in the PVMimages 2-4. In addition, between 3 and 11 minutes, there was no detectable increase on the temperature (Figure 63(d)). A change of the dispersion occurs near 11 minutes where larger hydrate particles can be seen with the PVM. The oscillations on the absolute energy reduce, and there is an increase on temperature. For this experiment, the initial hydrate formation, which occurred at microscopic level, was not detectable by an increase of the temperature, but it was observable from the PVM images and from the absolute energy. Hydrate growth was gradual, with hydrates forming until reaching a certain size. During this gradual growth, it is possible that there were some hydrates detaching from the droplets, as it can be seen in some of the images from the PVM.

(a) PVM images (1075x825 µm)



Figure 63. Detection of hydrate formation by comparing the (a) PVM images, (b) chord length separated by groups with PVM images grayscale , and (c) absolute energies, for an experiment at 80% water-cut, 200 L/h, without AA (#20).

Figure 64 shows some images from the camera compared to the absolute energy captured from the AE sensor installed near the visualization window. Based on both information, it is possible to separate in three the different steps the beginning of hydrate formation and growth. Once hydrates start forming, they form on oil surfaces. One can notice that because the droplets become darker once hydrate start forming (image 2, Figure 64(a)) compared to the image of the flow before hydrate formation (image 1). This beginning of hydrate formation causes a slightly increase on the absolute energy (before the instant 6.5 minutes, Figure 64(b)). As the flow continues circulating around the loop, small hydrate particles break and detach from the oil surfaces. One can notice that because the image 3 becomes darker, even in regions where it is not possible to see particles with a defined shape (bottom of the image). During this step observed in image 3, the absolute energy increases once again, and it starts oscillating more than during the previous step, which again indicates the continuous hydrate formation and breakage of particles. The last image (image 4, Figure 64(b)), shows the flow regime once the oscillations of absolute energy are over. The flow becomes more stable, with relatively large particles (several millimeters, that can be seen in the image) dispersed in the liquid.

For the experiment at 200 L/h (#20), it is shown in Figure 65 that the time with hydrates until the plug was much longer for this experiment than for the others (at 30 or 50% water-cut). After the intial hydrate formation, hydrates start arranging themselves in an intermittent behaviour that is periodic in time and space. The results of absolute energy (Figure 65(a)) show that hydrates are dispersed everywhere in the flow, because the absolute energy always stay higher than the levels before hydrate formation. However, the "valleys", or the regions of low absolute energies, seem to present lower and lower absolute energies over time. It indicates that hydrates are slower moving to the regions with more hydrates, so the regime is becoming more heterogeneous. The pressure drops (Figure 65(c)) indicate that there is an increase on the frictional pressure drops over time, due to the accumulation of hydrates. The peaks of absolute energy are coincident with the peaks of the horizontal pressure drop. Hydrate blockage occurred after 92 minutes from the onset of hydrates crystalization, when the flow rate indicates zero at the same time that differential pressure in the separator also indicates zero.



Figure 64. Comparison between the images from the camera and the absolute energy measured near the window for the test at 80% water-cut, 200 L/h, without AA (#20).



Figure 65. Experiment at 80% water-cut, 200 L/h, without AA (#20), showing the: (a) absolute energies, (b) temperatures (T_8 and T_9), (c) pressure drops, and (d) flow rate.

Figure 66 shows a comparison between dielectric, density, absolute energy, grayscale of PVM images and chord counts. Figure 66(a)-(b) shows that regions with more hydrates are located in regions with more oil, because the highest values of absolute energy are coincident with low values of density and dielectric. It means that most of the hydrate particles are flowing with the oil droplets, and therefore, hydrate are trapping the oil droplets after the crystallization around their surfaces. Figure 66(c) indicated that, until approximatelly 75 minutes, the brightest images from the PVM (images with more hydrates) are located in times between regions without and with hydrates. Therefore, the front part contains more hydrates, that are followed by a finer dispersion. After 75 minutes, the peaks in brightness move back, to the times between the region with and without hydrates. The chord counts, shown in Figure 66(d), also show that

more particles are being detected in the regions with more oil. The peaks before the instant 75 minutes are nearer the point where the dielectric is reducing, and, after the instant 75 minutes, the peak is nearer the time where the dielectric is increasing; the same change was observed with the PVM images.



Figure 66. Experiment at 80% water-cut, 200 L/h, without AA (#20), showing a comparison between: (a) dielectric and density, (b) dielectric and absolute energy, (c) dielectric and grayscale of PVM images, and (d) dielectric and chord counts.

In order to better understand the impact of this intermittent behavior and why the regions with the highest chord counts and brightest images seems to be moving, it is shown in Figure 67 a zoom at two different moments plotted in Figure 66. It is shown a plot between 21.3 and 24.3 minutes, and between 85.0 and 88.0 minutes (near the end of the experiment). There is a pattern that repeats at each turn of the dispersion around the flow loop. There are two regions

on this pattern: a front, which carries the largest hydrate particles in the system, and the back region, with dispersed hydrates that flow with the continuous phase.

Figure 68 shows some images during these two intervals, with visual confirmation of the intermittent behaviour captured by the signals. The images on the left are taken during the passage of large agglomerates, while images on the right are taken during the passage of dispersed hydrates with the continuous phase.



Figure 67. Two short intervals for the experiment at 80% water cut, 200 L/h, without AA (#20), showing the initial and finals distribution of particles in the system.



Figure 68. Images from the camera for the experiment at 80% water cut, 200 L/h, without AA (#20), showing that parts of the flow contain hydrates all the time (images on the left), while others have a reduction on the number of particles over time (images on the right).

Figure 69 shows the results for an experiment at 400 L/h (#23). Overall, the results are similar with the tests at 200 L/h, but the plugging was much earlier. The induction time was less than 2 minutes. Once hydrates formed, the absolute energy increased a bit, and remained oscillating during 1.5 minutes, which is the time for a lap around the loop (see Figure 69(b)). Then, after the 1.5 minutes, the absolute energy increased rapidly. It is possible to see with the dielectric that it decreases slowly over time, due to the consumption of water, but it remains as water continuous. In Figure 69(b), it is possible to see that hydrates are dispersed everywhere in the flow, because the absolute energy remains at values that are at least 100 times higher than before the onset of hydrate formation. But the dispersion is not homogeneous, and the hydrates are flowing preferably in regions with more oil (peaks of absolute energies coincide with the lowest values of dielectric). Again, with a higher shear, the rate of hydrate formation is also higher, as observed for tests at 30 and 50% water-cut. For the two tests at 200 L/h, water conversion was 7.8% in 92.2 minutes and 10.3% in 126.6 minutes. For the two tests at 400 L/h,



Figure 69. Experiment at 80% water-cut, 400 L/h, without AA (#23), showing a comparison between: (a) dielectric and density, (b) dielectric and absolute energy, (c) dielectric and grayscale of PVM images, and (d) dielectric and chord counts.

As conclusions, for the tests at 80% water-cut:

- Hydrate formation and plugging can be divided in three main steps: crystallization on oil droplet surfaces, growth with breakage and disruption, formation of an intermittent regime due to multiphase flow effects.
- The first two steps are relatively fast compared to the last one.
- The accumulation of hydrates in parts of the liquid volume was the cause of the plugging.
- Hydrate formation and growth is gradual, but it increases with higher shears.

- As the flow rate increases, the hydrate formation rate also increases, and the system becomes more critical for hydrate blockage formation.
- 5.1.4. Plug formation mechanisms for oil and water continuous systems without AA

It has been observed to low water-cuts systems which are oil continuous systems that, after hydrate formation, the oil phase separates from a mixture containing water and hydrates. The proposed mechanism for low water-cuts systems is represented in Figure 70. The water droplets are dispersed in the oil continuous phase before hydrate formation. Hydrates initially form on droplet surfaces, as illustrated in Figure 70(a). Parts of the hydrates will detach from the surfaces (the first particles detected), while the largest particles will decelerate, and will agglomerate, deposit or accumulate in the loop, as represented in Figure 70(b). A separation of phases will occur rapidly, between the oil continuous phase containing large agglomerates and regions with hydrates with a large amount of water. This wetted region is likely to be porous, with water phase being entrapped in the particles and agglomerates.

Water

Hydrate

Oil

Flow direction

Figure 70. Depiction of hydrate blockage formation mechanisms for oil continuous phase.

At intermediate water cuts, the proposed mechanism is illustrated in Figure 71. It was observed that the water is the continuous phase before hydrate formation (Figure 71(a)). Once hydrates form, they apparently detach from the interface, and the disruptions cause coalescences between the oil droplets (Figure 71(b)). As hydrate grow, the oil phase separates from the region containing water with hydrates (Figure 71(c)). The region with hydrates may eventually cause a plug.



Flow direction

Figure 71. Depiction of hydrate blockage formation mechanisms for experiments with an intermediate water cut.

At high water-cuts, hydrates form initially on oil droplet surfaces, as represented in Figure 72(a). Some hydrates may detach from the surfaces, but, overall, hydrates trap part of the oil phase, as represented in Figure 72(b). Hydrates flow dispersed in the water continuous phase. However, over time, particles will accumulate behind the region where the first hydrates formed. This is likely due to the difference in velocities between particles and agglomerates with different sizes, and due to the drift velocity between the solid particles and the liquid, as indicated in Figure 72(c).



Flow direction

Figure 72. Depiction of hydrate blockage formation mechanisms for high water cuts.

5.2. Hydrate formation for oil-water systems with AA

This section presents the results for the experiments with AA. The tests were conducted at 50 and 80% water-cut, at 200 and 400 L/h. Each experimental condition was tested twice, which add up eight experiments. The four tests at 50% water cut were conducted with an AA dose of 1.5 % wt. vs water, and none of them plugged. The four tests at 80% water cut were conducted with 0.94 % wt. vs water of AA, and only one of them plugged, at 400 L/h. All the experiments were carried out during working hours, which limited the time inside the hydrate formation domain to approximately 6 hours. The tests that did no plug until the end of the working day were shut down.

5.2.1. Experiments at 50% water-cut

Figure 73 shows the results for an experiment at 200 L/h (#27). Hydrate formation could not be detected by the absolute energy from the AE sensors, as shown in Figure 73(a). There were no important changes on the absolute energies during hydrate formation, and the gradual increases or decreases (depending of the sensor's type) on the absolute energies are due to the dissolution of gas into the oil phase. Hydrate formation was detected by an increase of the temperature, as shown in Figure 73(b), with an induction time of approximately 35 minutes. There were two noticeable moments detected with the temperature probes: an increase of the temperatures during the onset of hydrate formation (at 35 minutes), and a sudden increase of the temperatures around 160 minutes, indicating that, for some reason, more hydrates started forming around that time. One can notice that the horizontal pressure drop (yellow line in Figure 73(c)) did not change immediately after hydrate formation, maintaining constant values until around 160 minutes (or 125 minutes after the onset of hydrate formation). The only pressure drop that significantly changed was the differential pressure drop in the separator, Δp_4 , that increases because the liquid level in the separator increases. This is because the hydrate phase has a lower density than the water phase, then there is an expansion of the mixture containing liquid and hydrates as water is consumed for hydrate formation. Around the instant 160 minutes, there was a change on the flow regime, characterized by an instant increase on the horizontal pressure drop. This increase of the horizontal pressure drop at 160 minutes is coincident with the sudden increase of the temperatures. At the same time of these changes on pressures drops and temperatures, a slightly decrease of the flow rate occurs at 160 minutes, as shown in Figure 73(d).

The important change of the flow regime that occurred around 160 minutes for the experiment at 200 L/h (#27) can be better understood with the data shown in Figure 74, which shows the dielectric, density, PVM-images grayscale and chord counts. Around the instant 160 minutes, the dielectric changes from an intermediate value between the oil and water dielectrics to values that are closer to the oil dielectric. This is an indication that the continuous phase changed from water to oil. The transition observed in the flow pattern occurred with the hydrates fraction around 11.8% (which corresponds to 17.9% of water conversion). The grayscale of the PVM-images (Figure 74 (c)) and chord counts (Figure 74(d)) also show some change around 160 minutes. The PVM images become brighter, which is also a result of the inversion of phase from water to oil. In addition, the number of chord counts changes, with a reduction for chords between 1-100 μ m, and an increase of counts for the group 100-1000 μ m.

This adjustment in the number of chord counts is due to a change on the droplets size distribution.

Yet for the horizontal pressure drop for the test #27, shown in Figure 73(c), the fact that it remains approximately constant during oil-in-water emulsion and then continuously increases during water-in-oil emulsion indicates that hydrates are dispersed in the oil phase. The hydrates are dispersed inside the oil droplets before the instant 160 minutes and they do not increase the shear of the flow with the wall. However, once the hydrates are dispersed in the oil continuous phase, after the instant 160 minutes, they will be colliding directly to the wall and create more shear, which increases the apparent viscosity and, therefore, it increases the horizontal pressure drop. The hydrates are not detected by the FBRM, which responds for this experiment only to the change of the flow regime from o/w to w/o, but not to hydrate formation. The reason why hydrates are not detected by the FBRM for this case is that the particles are in a scale lesser than 1 micrometer, the minimum chord length detected by the instrument.



Figure 73. Experiments at 50% water cut, 200 L/h, with AA at 1.5 wt.% vs water (#27), showing (a) absolute energies, (b) temperatures, (c) pressure drops, and (d) flow rate.



Figure 74. Experiments at 50% water cut, 200 L/h, with AA at 1.5 wt.% vs water (#27), showing a comparison between dielectric constant and (a) density, (b) absolute energy, (c) grayscale of PVM-images, and (d) chord counts.

For a test at 400 L/h (#29), the absolute energy, the temperatures, the pressure drops and the flow rate are shown in Figure 75. The onset of hydrate formation was around 38 minutes, when an increase of the temperature was detected (Figure 75(b)). It has also been observed an inversion of phase, from water to oil. After the inversion to oil continuous phase, the horizontal pressure drop (yellow line in Figure 75(c)) gradually increased, the same as observed at 200 L/h. The horizontal pressure drop continued increasing until it reached a maximum value around 260 minutes, and then it started decreasing for a short time until it finally stabilizes. The reason why the horizontal pressure drop would decrease a bit after reaching the maximum is that there was settling or accumulation of hydrates somewhere else in the loop, so the amount

of flowing hydrates at the horizontal section would reduce. The pressure drop at the downward section (green line in Figure 75(c)) decreases continuously between 260 minutes and 300 minutes, indicating a possible settling of particles at the downward section. The absolute energy (Figure 75(a)) gradually increases (and oscillates in a high range) between 260 minutes and 300 minutes, and then continues oscillating without increasing more after 300 minutes. It indicates that the collision of particles increases, and that the system may be heterogeneous and dense (dense dispersion of solid particles in the liquid phase), where part of the motion of the particles might be collision-dominated rather than due to the liquid forces (see Figure 10, page 21).



Figure 75. Experiments at 50% water cut, 400 L/h, with AA at 1.5 wt.% vs water (#29), showing (a) absolute energies, (b) temperatures, (c) pressure drops, and (d) flow rate.

Figure 76 shows that the dielectric instantly decreases around 110 minutes, when there was the inversion of phase. Around 260 minutes, there was an increase on the absolute energy, dielectric and chord counts, especially for the group 100-1000 μ m. As explained before, the reason for that is that the dispersion experiences a transition to dense. Part of the particles transportation is dominated by contact with other particles, which may explain why there is some deposition or settling of particles in specific parts of the system. This behavior has been explained in the hydrate's literature as a change to a heterogeneous flow with a moving bed after the formation of a "critical" amount of hydrates (Joshi et al., 2013). The formation of a moving bed would increase the number of collisions between the particles, and that is why the absolute energy increases.



Figure 76. Experiments at 50% water cut, 400 L/h, with 1.5 wt.% vs water (#29), showing a comparison between dielectric constant and (a) density, (b) absolute energy, (c) grayscale of PVM-images, and (d) chord counts.

5.2.2. Experiments at 80% water-cut

Figure 77 shows the results for an experiment at 200 L/h (#31). Hydrate formation was detected by an increase of the temperature around 55 minutes, as shown in Figure 77(b), and changes on the pressure drops, as shown in Figure 77(c). The static differential pressure in the separator (Δp_4) rapidly increases after the onset of hydrate formation. After that, this differential pressure gradually increases until the end of the experiment (hydrate formation increases the volume of liquid with hydrates in the apparatus, which increases the level of liquid in the separator). The other pressure drops (Δp_1 , Δp_2 , and Δp_h) remain approximately constant or without a significant change that would endanger and plug the system, even after several hours

of experiment. The hydrate fraction at the end of the test was 36.49%, with 38.91% of water conversion. Despite there were no significant changes in the apparent viscosity during the experiment, some oscillations were detected in the system around 180 minutes (or approximately 125 minutes after the onset of hydrate formation). The AE sensors detect increases on the absolute energies (see Figure 77(a)), while the flow rate started oscillating around the same time (see Figure 77(d)). It indicates an increase on the number of collisions, which induces fluctuations on the flow rate. The cause of these oscillations is the formation of a heterogeneous system, which may be due to the high fraction of dispersed phase, where the dispersed phase is the oil with hydrates. This transition from homogeneous to heterogeneous regime occurred when the hydrate fraction was around 14% (64% of water and 22% of oil).

Figure 78 shows the comparison between the dielectric with density, absolute energy (sensor 2A), grayscale of PVM images and chord counts. The dielectric increases as hydrates form, meaning that the amount of oil detected by the permittivity probe reduces over time. This can be explained by the continuous formation of hydrates at the oil surfaces. Figure 78(a) shows that the density starts oscillating between 920 kg/m³ (a bit more than the hydrate density) and 1010 kg/m³ (a bit less than the saline water density). This indicated that the system contain regions with more and more free water (higher density) and regions containing more oil with hydrates (lower density). It means that the flow is becoming heterogeneous, despite it did not affect the apparent viscosity, Figure 78(b) shows that the oscillation of absolute energy 2A increases as the flow apparently becomes dense, which also caused a change on the chord counts of the group 100-1000 μ m, detected by the FBRM (Figure 78(d)).



Figure 77. Experiments at 80% water cut, 200 L/h, with AA at 0.94 wt.% vs water (#31), showing (a) absolute energies, (b) temperatures, (c) pressure drops, and (d) flow rate.


Figure 78. Experiments at 80% water cut, 200 L/h, with AA at 0.94 wt.% vs water (#31), showing a comparison between dielectric constant and (a) density, (b) absolute energy, (c) grayscale of PVM-images, and (d) chord counts.

Figure 79 shows absolute energies, temperatures, pressure drops and flow rate for a test at 80% water-cut and 400 L/h (#33). The onset of hydrate formation was around at 13 minutes, detected by an increase of the temperatures. The pressure drops did not change much during the first 130 minutes with hydrates (or until the instant 150 minutes), as shown in Figure 79(c), but it was noticed an important change after this time. The absolute energies (Figure 79(a)) and the pressure drops started gradually increasing, indicating an increase on the apparent viscosity and the number of collisions. The horizontal pressure drop continuously increased between 150 and 220 minutes, while the pressure drops in the downward section (Δp_1) and (Δp_2) diminished. Around 220 minutes, hydrate formation rate decreased, probably due to a limitation of contact between gas and water. In fact, as hydrates form, the volume of liquid in the separator increases, so the amount of gas entrained will reduce (entrainment caused the shock between the falling liquid and the stagnant liquid on the left right part of the separator).



Figure 79. Experiments at 80% water cut, 400 L/h, with AA at 0.94 wt.% vs water (#33), showing (a) absolute energies, (b) temperatures, (c) pressure drops, and (d) flow rate.

Yet for the experiment at 400 L/h (#33), it is possible to see that the dielectric increased after the onset of hydrate formation, until it reached values near the salted water dielectric. It was the same as observed for the test at 200 L/h. The explanation for that is that hydrates form at the surfaces of the oil droplets, changing their properties. Once the hydrate formation rate diminished, around 150 minutes, the dielectric started detecting the oil phase again, because

there is a continuous oscillation between the water dielectric and the dielectric that was observed before hydrate formation.



Figure 80. Experiments at 80% water cut, 400 L/h, with AA at 0.94 wt.% vs water (#33), showing a comparison between dielectric constant and (a) density, (b) absolute energy, (c) grayscale of PVM-images, and (d) chord counts.

5.2.3. Mechanisms of hydrate formation observed in the tests with AA

The experiments with AA performed for this thesis were identified as being water continuous phase before hydrate formation, as discussed in Chapter 4. For the tests at 50% water-cut, it was observed an inversion of the continuous phase, with the systems suddenly changing to oil continuous after an amount of water is converted to hydrates. The tests at 80% water-cut remained water continuous all the time. Another mechanism observed was a change

to what can be called dense flow, when the liquid can no longer transport all the particles. Bedding will form if the flow is dense.

Figure 81 shows the mechanisms of hydrate formation for tests at 50% water-cut, with AA. The use of AA causes the formation of a very fine dispersion. The hydrate particles are expected to initially form on oil droplet surfaces, as illustrated in Figure 81(a). The hydrates will immediately detach and disperse into the oil droplets, allowing a continuous hydrate formation, as illustrated in Figure 81(b). At some point, due to a reduction of the water-cut, the system will instantly reverses to oil continuous phase, as represented in Figure 81(c). As soon as the system becomes oil continuous, more hydrates will form, due to an increase of the interfacial area between oil and water. The collision of particles is significant at the end, along with an increase on the apparent viscosity. A moving bed may occur after a certain amount of hydrates is formed. Despite the formation of a dense flow, the presence of large amount of oil limits the hydrate fraction and, therefore, there is no indication that a plug can occur.



Figure 81. Depiction of the mechanisms of hydrate formation for the experiments at 50% water-cut with AA.

Figure 82 shows the mechanisms of hydrate formation observed for the experiments at 80% water-cut with additive. Hydrates initially form on oil droplet surfaces, as shown in Figure 82(a). As hydrates continue forming, part of them may detach, but they are entrapped by the oil phase (Figure 82(b)). At some point, the system changes to a dense flow, as illustrated in Figure 82(c), where the water cannot transport all the particles. Part of the transport of these hydrates occurs then due to contact with other particles, rather than fluid forces. If the hydrate fraction is too high, the system may eventually plug.



(a) Hydrates start forming on droplet surfaces



(b) Oil with hydrates increase in volume



(c) Droplets break and the flow becomes dense



Figure 82. Depiction of the mechanisms of hydrate formation for the experiments at 80% water-cut with AA.

5.3. Transportability of hydrates at different conditions

It was observed in the experiments that the time scale for hydrate plugging was affected by the water-cut and flow rate. Figure 83 shows for all the experiments what is the water conversion and the time with hydrates. The time with hydrates for the experiments that plugged is the time from the onset of hydrate formation until the instant of plug. For the experiments that did not plug, time with hydrates is the time from the onset of hydrate formation until the experiment is shut down due to the limitation of working hours.

Overall, all the tests with AA had much more water conversion and were flowable much longer than the tests without AA. While the tests with AA had between 40 and 70% of water conversion in 6 hours, the tests without AA had conversions up to 20%, remaining flowable for a maximum of 1.5 hour. All the tests at 400 L/h had a higher hydrate formation rate than at 200 L/h (if the other conditions were the same).

Among the tests without AA, the most critical cases were at 30 and 50% water cuts, while the tests at 30% water cut / 400 L/h and tests at 50% water-cut / 200 L/h were the most critical cases. For these two, there was a combination of significant deposition and accumulation of hydrates in parts of the liquid volume. At 50% water cut and 200 L/h, the tests plugged even with a low conversion of hydrates. It probably occurred due to the sufficient supply of water and gas (dissolved in the oil phase) in contact, and due to the presence of large droplets (that originated large hydrate particles). The tests at 80% water-cut were more flowable, because the water phase seems to transport better the hydrates. However, as the time passes, the accumulation of hydrates in part of the liquid causes a local viscosification that leads to hydrate blockage.



Figure 83. Water conversion as function of water-cut, flow rate and use of additive for all the 23 experiments performed for this thesis.

One of the eight tests with LDHI-AA plugged, with a dose of 0.94 %wt. vs water, at 80% water-cut, 400 L/h. It shows that, despite the use of AA that increases the transportability of hydrates, apparently there is a maximum limitation for the transportability of solid particles by the liquid phase.

5.4. Summary of the Chapter

In this Chapter, the results of the experiments were presented, focusing on the mechanisms of hydrates formation. The tests without AA were initially discussed, showing

three different scenarios: at low, intermediate and high water-cut. All the tests without AA plugged, where the tests at 30 and 50% water-cuts were the most critical. Hydrate formation completely changes the flow regime, partially separating the oil phase from a mixture containing water with hydrates. At 80% water cut, water is the continuous phase, and oil droplets may be entrapped by the hydrates. A local accumulation of hydrates causes a viscosification, and it eventually causes plugging.

The use of AA causes a complete dispersion of the liquid-liquid dispersion, allowing a high water conversion without causing a plug. The tests at high water-cut are water continuous, and hydrates trap part of the oil phase (with or without AA). The use of AA also forms a fine hydrates suspension, but the viscosification occurs once the high fraction of hydrates causes a dense flow and possibly a moving bed. The plug may still occur at high water-cut, despite the transportability of the system increases.

A combination of measurements allowed monitoring the different steps, from the onset of hydrate formation, until the formation of the plug. With four to six acoustic emission probes distributed along the loop, it was possible to track hydrate particles. With the permittivity probe (and density), it was possible to identify the regions with more water or more oil. By identifying the regions that were carrying the hydrates and the regions that had more water or oil, it was possible to deduce the morphology of the particles, which was confirmed from the images from in the camera (for the tests which the camera was used).

5.5. Highlights in French - Résume du Chapitre 5 en Français

Dans ce chapitre, les résultats des expériences ont été présentés, en se concentrant sur les mécanismes de formation des hydrates et leur transportabilité. Les tests sans antiagglomérant ont été initialement discutés, montrant trois scénarios différents : à basse, moyenne, et haut *water cut*. Tous les tests sans AA formée de bouchage ; les tests à 30 et 50% de *water cut* ont été les plus critiques.

Les essais à bas *water cut* (30%) sont en phase continue huile, tandis que les essais à *water cut* intermédiaire (50%) sont apparemment continus l'eau. La formation d'hydrates modifie complètement le régime d'écoulement, séparant partiellement la phase huile d'un mélange contenant de l'eau et des hydrates. À 80% de *water cut*, l'eau est la phase continue et des gouttelettes d'huile peuvent être étrapées par les hydrates. Une accumulation locale d'hydrates provoque une viscosification, et éventuellement un colmatage.

L'utilisation d'AA provoque une dispersion complète de l'émulsion liquide-liquide, permettant une conversion d'eau plus élevée et sans provoquer de bouchon. Les tests à haute *water cut* sont en phase continue eau où les piègent une partie de la phase huile (avec ou sans AA). L'utilisation d'AA forme une dispersion liquide-liquide avec des goutes très fines, et la viscosification se produit une fois que la fraction d'hydrates est élevée. Le bouchon peut toujours se produire à fort *water cut*, malgré l'augmentation de la transportabilité du système.

Une combinaison de mesures a permis de suivre les différentes étapes, depuis le début de la formation d'hydrates, jusqu'au bouchon. Avec quatre à six sondes d'émission acoustique réparties le long de la boucle, il était possible de suivre les particules d'hydrate. Avec la sonde de permittivité (et de densité), il était possible d'identifier les régions avec plus d'eau ou plus d'huile. En identifiant les régions qui transportaient les hydrates et les régions qui avaient plus d'eau ou d'huile, il a été possible de déduire la morphologie des particules, qui a été confirmée avec les images de la caméra (pour les tests où la caméra a été utilisée).

CHAPTER 6 - ADDITIONAL TREATMENTS USING THE PRESSURE DROP, DENSITY AND Absolute Energy

This Chapter presents some preliminary results on two additional treatments using the data from the experiments. In the first section of this Chapter, it is presented two models to calculate the apparent hydrate fraction from density measurements and water conversion calculation. In the second section, a comparison between absolute energy and frictional pressure drop is proposed.

6.1. Apparent hydrate fraction and the transportability of the system

In Chapter 5, it was identified for some of the experiments a separation of phases for the tests without LDHI-AA. For 30 and 50% water cut, the hydrates have the tendency to flow mostly with the water phase, and the oil flowing as single-phase. At 80% water cut, the hydrates seem to be forming around the oil droplets and trapping part of them.

Due to this heterogeneity of the systems without AA, the question that arises is if it is possible to calculate the amount of hydrates flowing in each volume of fluid of the system. In this section, two simplified models to calculate the apparent hydrate fraction over time are proposed. They are based on the density measured by the Coriolis and one the water conversion (which is calculated from gas injection, pressure and temperature, as explained in subsection 3.4.2). The first model assumes that hydrates flow with the water phase, while the second model assumes that they flow with the oil phase. Preliminary results are presented. In addition, the apparent hydrate fraction is compared to the absolute energy.

6.1.1. Apparent hydrate fraction – model I: hydrates flowing with the water phase

The density measured in an instant of time has the contribution of the oil, the water, and the hydrate phase. For this model, it is assumed that the ratio between the hydrate and water fraction is constant over space, which means that they are only time dependent, and based on the water conversion that must be calculated beforehand using the methodology presented in subsection 3.4.2. The mixture between hydrates and the water phase is considered a pseudo single-phase mixture, with density ρ_m and fraction α_m (in volume). The density (measured) is expressed as follows:

$$\rho = \rho_{\rm m}(t_{\rm H})\alpha_{\rm m}(t_{\rm H}) + \rho_{\rm 0}(1 - \alpha_{\rm m}(t_{\rm H})) \tag{64}$$

As a remind from Chapter 3^7 , t_H is the time since the onset of hydrate formation. The mixture density has the contributions of the hydrate and the water phases:

$$\rho_{\rm m}(t_{\rm h}) = \frac{m_{\rm W}(t_{\rm H}) + m_{\rm H}(t_{\rm H})}{\Psi_{\rm W}(t_{\rm H}) + \Psi_{\rm H}(t_{\rm H})} \tag{65}$$

The total water conversion in the system, k_W , is defined as:

$$k_{\rm W}(t_{\rm H}) = \frac{m_{\rm W}(0) - m_{\rm W}(t_{\rm H})}{m_{\rm W}(0)} \tag{66}$$

Based on the definition of hydration number, the mass of hydrates (m_H) is a function of the mass of converted water:

$$m_{\rm H}(t_{\rm H}) = \left(m_{\rm W}(0) - m_{\rm W}(t_{\rm H})\right) \left(1 + \frac{M_{\rm G}}{N_{\rm h}M_{\rm W}}\right) \tag{67}$$

Combining the equation (66) and (67), the hydrate mass is re-written as:

$$m_{\rm H}(t_{\rm H}) = k_{\rm W}(t_{\rm H})m_{\rm W}(0)\left(1 + \frac{M_{\rm G}}{N_{\rm h}M_{\rm W}}\right)$$
 (68)

Substituting the equation (68) into equation (65), it is obtained:

$$\rho_{\rm m} = \frac{m_{\rm W}(0)(1-k_{\rm W}) + k_{\rm W}m_{\rm W}(0)\left(1+\frac{M_{\rm G}}{N_{\rm h}M_{\rm W}}\right)}{\frac{m_{\rm W}(0)(1-k_{\rm W})}{\rho_{\rm W}} + \frac{k_{\rm W}m_{\rm W}(0)\left(1+\frac{M_{\rm G}}{N_{\rm h}M_{\rm W}}\right)}{\rho_{\rm H}}$$
(69)

which leads to:

$$\label{eq:rhom} \begin{split} \rho_m &= \rho_W \frac{\left(1-k_W\right)+k_W \left(1+\frac{M_G}{N_h M_W}\right)}{1-k_W+\frac{\rho_W k_W}{\rho_H} \left(1+\frac{M_G}{N_h M_W}\right)} \end{split} \tag{70}$$

One can notice in equation (70) that the mixture density is a function of water conversion (k_W) and molar mass (M_G) . These values are known beforehand based on the methodology explained in Chapter 3. From equation (64), the mixture fraction is calculated as:

$$\alpha_{\rm m} = \frac{\rho - \rho_0}{\rho_{\rm m} - \rho_0} \tag{71}$$

Once the mixture fraction is known, the flowing hydrate and water fractions can be determined. The mixture density can be expressed as:

⁷ The definitions of some variables used in this Chapter were previously defined in Chapter 3.

$$\rho_{\rm m} = \rho_{\rm H} \beta_{\rm H} + \rho_{\rm W} (1 - \beta_{\rm H}) \tag{72}$$

The term β_H is defined here as the fraction of hydrates relative to the water-hydrate mixture, and it can be determined from equation (72). Finally, the flowing hydrate and water fractions can be calculated as:

$$\alpha_{\rm H} = \beta_{\rm H} \alpha_{\rm m} \tag{73}$$

$$\alpha_{\rm W} = (1 - \beta_{\rm H})\alpha_{\rm m} \tag{74}$$

where α_H is the apparent hydrate fraction, and α_W is the apparent water fraction.

Figure 84 shows the application of the model for a test at 30% water cut, 200 L/h, without LDHI-AA (#11). The hydrate fraction and apparent hydrate fraction are shown in Figure 84(a), while the absolute energy from the sensor 1A is shown in Figure 84(b). The peaks observed in the apparent hydrate fraction are coincident with the peaks observed on the absolute energy. Despite the final hydrate fraction is nearly 7%, the apparent hydrate fraction might range between 0 and approximately 18%. It is also important to notice that, due to the porosity, water may be trapped inside the particles and, therefore, the actual fraction of these hydrate particles can be even higher than the calculated apparent hydrate fraction.



Figure 84. Apparent hydrate fraction and absolute energy for a test at 30% water-cut, 200 L/h, without LDHI-AA (#11).

Figure 85 shows the results for an experiment at 30% water-cut, 400 L/h, without LDHI-AA (#15). For this test, the hydrates detected in the Coriolis until 15.1 minutes are detected by the AE sensor 1A. Beyond the instant 15.1 minutes, hydrates detected in the Coriolis were not passing in the position where the sensor 1A is installed (except a peak around the instant 16 minutes), which indicates deposition between the two instruments. In fact, as discussed in Figure 54, the pressure drops indicate that hydrates might be depositing in the downward pipe, and this is why hydrates that pass in the downward part might not reach the horizontal part of the loop.



Figure 85. Apparent hydrate fraction and absolute energy for a test at 30% water-cut, 400 L/h, without LDHI-AA (#15).

Figure 86 shows the results for an experiment at 50% water-cut, 200 L/h, without LDHI-AA (#19). It shows again that higher values of absolute energy coincide with the peaks in calculated hydrate fraction. After 5.8 minutes since the onset of hydrate formation, the system plugs with a hydrate fraction of 2.9%.

Figure 87 shows the results for a test at 50% water cut, 400 L/h, without LDHI-AA (#24). The calculated hydrate fraction is 6.65%, but due to the heterogeneous suspension of hydrates and their accumulation in some parts of the liquid, the apparent hydrate fraction varies between 0 and 11.3%.



Figure 86. Apparent hydrate fraction and absolute energy for a test at 50% water-cut, 200 L/h, without LDHI-AA (#19).



Figure 87. Apparent hydrate fraction and absolute energy for a test at 50% water-cut, 400 L/h, without LDHI-AA (#24).

For a test a 80% water-cut, 200 L/h, without AA (#20), shown in Figure 88, the comparison between apparent hydrate fraction and absolute energy gives divergent results, with peaks in absolute energy coincident with low hydrates fractions. The model proposed does not

fit well for a system at a high water cut, where the hydrates form on oil droplet surfaces, trapping part of the oil phase. For this case, a different model must be proposed, taking into account that hydrates may flow with the oil phase. The model is presented in the next section.



Figure 88. Apparent hydrate fraction and absolute energy for a test at 80% water-cut, 200 L/h, without LDHI-AA (#20).

6.1.2. Apparent hydrate fraction – model II: hydrates flowing with the oil phase

The model introduced in the subsection 6.1.1 does not fit well the experiments at 80% water-cut without AA. The reason is that the ratio between converted and unconverted water is not constant over the liquid volume when hydrates are forming on oil droplets. Therefore, an alternative model is proposed. For this modified model, it is assumed that hydrates form around oil droplets.

The density has the contribution of the water phase and the oil-hydrates mixture, relation that can be expressed by:

$$\rho = \rho_{\rm m}(t_{\rm H})\alpha_{\rm m}(t_{\rm H}) + \rho_{\rm W}(1 - \alpha_{\rm m}(t_{\rm H})) \tag{75}$$

The density mixture is then defined as:

$$\rho_{\rm m}(t_{\rm H}) = \frac{m_0 + m_{\rm H}(t_{\rm H})}{\Psi_0 + \Psi_{\rm H}(t_{\rm H})} \tag{76}$$

It is assumed that the ratio between hydrate and oil fraction is constant over space (time dependent). This ratio is defined as:

$$\kappa = \frac{V_H}{V_0} \tag{77}$$

The variable κ depends on the fraction of converted water, k_w. This relation is given by:

$$\kappa(t_{\rm H}) = \frac{k_{\rm W}(t_{\rm H})m_{\rm W}(0)}{\rho_H \Psi_0} \left(1 + \frac{M_{\rm G}}{N_{\rm h}M_{\rm W}}\right) \tag{78}$$

The mixture density defined in the equation (76) can be expressed as function of the variable κ :

$$\rho_{\rm m}(t_{\rm H}) = \frac{\rho_0 + \kappa \rho_{\rm H}}{1 + \kappa} \tag{79}$$

Once the mixture density is known, the mixture fraction can be calculated using the following expression, derived from equation (75):

$$\alpha_{\rm m} = \frac{\rho_{\rm W} - \rho}{\rho_{\rm W} - \rho_{\rm m}} \tag{80}$$

The mixture density has the contributions of hydrate and oil phases. It can alternatively be expressed as:

$$\rho_{\rm m} = \rho_{\rm H} \beta_{\rm H} + \rho_0 (1 - \beta_{\rm H}) \tag{81}$$

The term β_H is the fraction of hydrates relative to the oil-hydrate mixture, and it can therefore be determined from equation (81). Finally, the flowing hydrate and oil fractions can be calculated as:

$$\alpha_{\rm H} = \beta_{\rm H} \alpha_{\rm m} \tag{82}$$

$$\alpha_0 = (1 - \beta_H) \alpha_m \tag{83}$$

Figure 89 shows a 10 minutes interval for a test at 80% water-cut, 200 L/h, without AA (#20). The regions with high hydrate fractions are coincident with the peaks on absolute energy. Figure 90 shows the same experiment, from the beginning until plug formation. The system flows well until around 90 minutes, with a variation in hydrate fraction between 2.3% and 13.3%. Suddenly, near the end of the experiment, some peaks with a hydrate fraction of more than 20% appears, and then the blockage occurs.



Figure 89. Apparent hydrate fraction and absolute energy for a test at 80% water-cut, 200 L/h, without LDHI-AA (#20).



Figure 90. Apparent hydrate fraction and absolute energy for a test at 80% water-cut, 200 L/h, without LDHI-AA (#20).

Figure 91 shows the results for an experiment at 80% water cut, 400 L/h, without AA (#23). The peaks in absolute energy are coincident with regions with high hydrate fraction. However, Figure 91(a) shows that the apparent hydrate fraction is higher than the actual hydrate

fraction flowing in the system. There are a few reasons that could be causing this unexpected result. The first one might be some liquid accumulation somewhere in the flowloop apparatus. For example, in the separator (see Figure 23), the liquid level on the left vertical pipe can increase, which may cause some liquid to be static. It is also possible that part of the hydrates formed around gas droplets, are present in a higher quantity than at 200 L/h. The presence of the gas phase is not taken into account in the model. The third possible reason is that due to the higher shear than at 200 L/h, hydrates break more and disperse in the water phase. It means that the current model that assumes the hydrates flow with the oil phase does not fit well the with conditions for this experiment.



Figure 91. Apparent hydrate fraction and absolute energy for a test at 80% water-cut, 400 L/h, without LDHI-AA (#23).

6.1.3. Conclusions from this section

Two simplified models were proposed to calculate the apparent hydrate fraction in the system. The first one applies to suspensions where hydrates flow with the water phase, assuming the ratio between hydrate and water constant over space. The second model assumes that the ratio between hydrate and oil is constant.

These simplifications impose important limitations, because it is not possible to know exactly the ratio between two phases, especially when hydrates entrap oil and part of the particles break from the droplets and disperse in the water phase. Future studies could lead to an improved calculation procedure for hydrate fraction considering all the conditions observed in the experiments, with part of the hydrates dispersed in the water continuous phase.

6.2. Additional treatment using AE: a comparison to the frictional pressure drop

It was observed in the experiments that the frictional pressure drops and the absolute energy increase once hydrates form. A question that arises is the possibility to relate absolute energy and the friction to the wall, or if a combination between the two data sets may help understanding the different steps of hydrate formation and flow. In this section, the comparison between absolute energy and the frictional pressure drop is presented.

In order to compare the horizontal pressure drop with the absolute energy, it is necessary to obtain the total absolute energy in the region where the probe measures the differential pressure. A parameter of interest is defined here as the average absolute energy in the horizontal section relative to a sensor s, $\overline{E}_{s,h}$. This energy is calculated in the same region where the horizontal pressure drop (Δp_h) is calculated. It is assumed that the absolute energy observed in a time t in a sensor s was the same energy in $t - \Delta t$ in a position of the loop that is $Q \times \Delta t$ (volume) behind the sensor s or the same energy in $t + \Delta t$ in a point that is $Q \times \Delta t$ after the sensor s. The average horizontal absolute energy is then defined as:

$$\bar{E}_{s,h}(t) = \frac{\sum_{t=\Delta t_2}^{t+\Delta t_1} E_{abs,s}(t)}{\Delta t_1 + \Delta t_2}$$
(84)

where Δt_1 is the number of steps of time it takes for the flow to move from the beginning of the measurement Δp_h to the probe *s*, and Δt_2 is the steps of time it takes for the flow to move from the probe *s* to the end of the measurement Δp_h .

The comparison between $\overline{E}_{s,h}$ and Δp_h is for an experiment at 30% water-cut, without AA, at 200 L/h (#11) and 400 L/h (#15) is shown in Figure 92. A good agreement between the shape of the curves for the two parameters can be observed for the test at 200 L/h (Figure 92(a)). It means that there are not important accumulations/deposition in the section of the measurement, which plugs due to formation of agglomerates or large local hydrate fraction that may plug the system. The test at 400 L/h (Figure 92(b)) also shows a similar behavior between the two parameters analyzed. It is important to notice that, for both cases, the average absolute energy increases relatively to the pressure drop, implying that the friction of the flow to the wall decreases after a few minutes of hydrate formation, but the noise produced increases. This means that hydrates are being dispersed in the system from the breakage of particles.





Figure 93 shows the results for experiments at 50% water-cut, without AA (#19 and #24). A similar behavior was observed for the test at 400 L/h, with peaks in average absolute energy coinciding with the peaks in pressure drop.



Figure 93. Comparison between the average absolute energy to the horizontal pressure drop for the experiments at 50% water-cut, without AA, at 200 and 400 L/h (#19 and #24).

Figure 94 shows the results for tests at 80% water-cut, without AA. A good agreement was found for the comparison between the horizontal pressure drop and the average absolute energy. In fact, the systems at high water cut are more flowable, because the water phase seems to have a higher affinity and transport better the hydrate particles than the oil phase. Because of that, not much deposition was detected in the horizontal section, and most of the increase on friction and apparent viscosity is due to a viscosification of the flow rather than due to a local deposition or accumulation of hydrates.



Figure 94. Comparison between the average absolute energy to the horizontal pressure drop for the experiments at 80% water-cut, without AA, at 200 and 400 L/h (#20 and #23).

The procedure proposed in this section can also be applied to systems with LDHI-AA. Figure 95 shows the results for tests at 50% water-cut, with AA. Once the inversion of phase occurred, from water to oil continuous phase, the pressure drop and the absolute energy increased. It was observed in Figure 95(b) that the absolute energy increases until 205 minutes, and then suffers a sudden decrease, with is not followed by the pressure drop, that continuous to increase. The reduction in the number of collisions is due to the formation of a moving bed. Since the suspension of hydrate become dense, around 250 minutes the absolute energy increases again, because part of the transport of the particles is due to particle-particle collisions rather than due to the liquid forces (drag and lift). Once this dense flow forms, the pressure drop in the horizontal section starts slowly decreasing, indicating that less hydrates are flowing in that section, and that part of the hydrates may be forming a static bed somewhere in the loop.



Figure 95. Comparison between the average absolute energy to the horizontal pressure drop for the experiments at 50% water-cut, with AA at 0.9375% wt. vs water, at 200 and 400 L/h (#27 and #29).

6.2.1. Conclusions from this section

It was presented in this section a comparison between the accumulated absolute energy in the horizontal section and the horizontal pressure drop. The reason for that is that particles also collide to the wall during flow, so friction and absolute energy are expected to follow the same behavior. This approach allows quickly identifying systems that present deposition, accumulation, or stationary bed, and could be used in laboratory or field test to monitor in real time significant changes on the flow that may endanger the operation.

6.3. Summary of the Chapter 6

This Chapter presented some additional treatments that can be applied to the data obtained in the experiments. Due to the separation of phases and local increase on hydrate fraction, models were proposed to estimate the apparent hydrate fraction using the density measured from the Coriolis. The models are preliminary, and they limit to applications where hydrates are flowing completely with the water phase or entrapping all the oil. Future improvements in these models may allow a more precise calculation of the apparent hydrate

fraction, which is an important information, and may help future developments of correlations for the apparent viscosity as function of apparent hydrates fraction.

An additional treatment with acoustic emission was also proposed, defining an average absolute energy in the same region where a frictional pressure drop is measured. This allow identifying the nature of the plug (local increase of hydrate fraction) or deposition/accumulation of hydrates.

6.4. Highlights in French – Résume du Chapitre 6 en Français

Ce chapitre présente quelques traitements supplémentaires qui peuvent être appliqués aux données obtenues dans les expériences. En raison de la séparation des phases et de l'augmentation locale de la fraction d'hydrates, des modèles ont été proposés pour estimer la fraction d'hydrates apparente en utilisant la masse volumique mesurée par le Coriolis et la conversion de l'eau. Le premier modèle suppose que les hydrates s'écoulent avec la phase aqueuse, tandis que le second modèle suppose qu'ils s'écoulent avec la phase huileuse. Les résultats préliminaires sont présentés. La fraction d'hydrates apparente est comparée à l'énergie absolue. Les modèles sont préliminaires et se limitent aux applications où les hydrates s'écoulent complètement avec la phase l'eau ou emprisonnent l'huile. Des améliorations futures de ces modèles peuvent permettre un calcul plus précis de la fraction d'hydrates apparente, qui est une information importante, et peuvent aider aux développements futurs des corrélations de la viscosité apparente en fonction de la fraction d'hydrates.

Un traitement supplémentaire avec émission acoustique a également été proposé, définissant une énergie absolue moyenne dans la même région où une perte de charge par frottement est mesurée. Cela permet d'identifier la nature du bouchon (augmentation locale de la fraction d'hydrates) ou le dépôt / accumulation d'hydrates.

CHAPTER 7 - CONCLUSIONS

This work aimed to understand gas hydrate formation from Kerdane-salted water (30 g/L water) systems and the transportability of the suspension of hydrates in systems without and with LDHI-AA (0.94 to 1.5 wt.%/water) in the Archimède flow loop with new instruments: permittivity, high-speed camera, and acoustic emission.

In this sense, a new software was developed to synchronize and treat the data obtained from the flow loop experiments. A total of 29 probes were used in the experiments and several methodologies were proposed in order to take qualitative but also quantitative conclusions about the formation of plugs and the efficiency of the tested AA.

Some new calculations, methodologies and treatments were developed in this work, namely to decrypt the emission acoustic, the images and the permittivity data combined with the classical instruments. The focus was to be able to follow the hydrates during their displacement in the pipeline, their accumulation, their deposition, agglomeration and plug and the impact of these on the flow pattern during time and space in the pipeline. It includes two simplified models to calculate the apparent hydrate fraction during flow and a procedure to combine pressure drop and absolute energy to determine deposition. The models to calculate the water conversion and the gas dissolution for tests with natural gas are also presented.

The permittivity measurements enabled to monitor the phase (oil or water) which transports the hydrates and the one that is entrapped. The use of acoustic energy enabled to track the particles in the system and follow the suspension of hydrates over time and space, to better define the different steps of the mechanisms of hydrates plug formation. The analysis proposed in this work is mostly qualitative with some preliminary models in order to have some quantitative calculations.

The accumulation of hydrates in the flow and the deposition in the pipeline are two precursors of plugging. They can be deduced from the acoustic emission and the pressure drop, which can contribute to an estimation of the amount of settled and deposited particles and deduce the risk of plugging.

In chapter 4 it was possible to identify the continuous phase as oil for tests at 30% watercut and water for tests at 50% and 80% water-cut. The flow rate affects the size of the droplets: the higher the shear forces, more small droplets are in the dispersion, which increases the apparent viscosity.

In chapter 5, hydrate formation and plugging mechanisms were analyzed and proposed. Experiments without AA were carried out at 30, 50 and 80% water-cuts. Despite the time scale difference, all these experiments "plugged", and therefore, were identified as critical for hydrate blockage risk.

The proposed mechanism of hydrate formation and blockage presents a separation of phases, forming an intermittent regime with the water phase carrying most of the hydrates that accumulate, while the oil phase flows as single phase. A few reasons for that are the tendency of hydrate to flow with the water phase, and the difference in velocities between hydrates and the liquid phase, will cause an accumulation of hydrates, which facilitates local viscosification, agglomeration and deposition. The experiments at 80% water-cut show that hydrates will form around oil droplets and trapping part of the oil. The particles are relatively small, and the transportability of hydrates are higher than for the experiments at lower water-cuts because the water phase seems to have a higher affinity and better transport the hydrate particles. However, a plug was formed because of a local viscosification from particles with different sizes and different flow velocities that finally flow together.

Experiments with a commercial LDHI-AA were carried out at 50 and 80% water-cuts. The systems before crystallization were completely emulsified and water continuous. At 50% water-cut, there was an inversion of phase during hydrates formation due to the water consumption. While water is the continuous phase, the transportability of the system is not affected, because there is an approximately constant horizontal pressure drop. Once the oil becomes the continuous phase, there is an immediate increase on the viscosity, which reduces the transportability of the system. As hydrate formation continues, the horizontal pressure drop increases linearly and the dispersion becomes dense, with part of the hydrates being settled in the pipe. There was no plug formation after several hours of experiment. At 80% water-cut, there was no inversion of phase, but the hydrate formation rate was higher than at 50%-water-cut. Due to the large formation of hydrates, the dispersion of hydrates became dense, until the remaining liquid could not transport anymore all the solid particles. The formation continues as long as there is contact between water and gas, but when the fraction of solid is too high, the motion of hydrates becomes what is called in the solid-liquid literature contact-dominated, and the system may eventually plug.

Despite the use of AA was successful in avoiding agglomeration or deposition (or any attachment due to the capillary forces) and form a fine dispersion, there is a critical hydrates fraction that can be transported by the liquid where the liquid forces are insufficient to induce the motion of the hydrate particles and settling occurs.

7.1. Perspectives and Future Works

An important question that arises from this work is how much hydrates (fraction) can safely be transported. Two important parameters are the apparent viscosity and the particles size. It was observed that the viscosity before hydrate formation is dependent on the water-cut and flow rate and the presence of AA. After hydrate formation, it is also affected by the amount of hydrates flowing in the system. The apparent volume of hydrates can also be much larger, since the particles trap the liquid phases and it is difficult to know how much liquid in entrapped in the hydrates.

In this sense, a better understanding on how the apparent viscosity is affected by the water-cut and the particles size are necessary, and by the hydrates fraction and apparent hydrates fraction. The following works are proposed:

- Fit the data obtained from experiments on liquid-liquid dispersions with literature models for viscosity as function of the dispersed phase
- (2) Estimate the flowing water-cut after hydrate formation from permittivity and water conversion and calculate the amount of liquid trapped inside the hydrate particles.
- (3) Estimate deposition from a balance between the hydrate fraction and the apparent flowing hydrate fraction. A simplified model and preliminary results for calculating the apparent hydrate fraction is presented in Chapter 6.
- (4) Viscosity model from literature as function of each phase fraction, hydrate fraction and the particle size distribution
- (5) Acquire some fundamental knowledge from model particles in order to understand the distribution of particles in the flow and it impact on viscosity

The use of a commercial LDHI-AA changed the dispersion and formed a fine dispersion. However, it is unclear how this AA acts at microscopic level, and how it avoids agglomeration and some physical-chemical data about the AA (viscosity, superficial tensions, effect on the properties of the water) could be important to understand their impact. More experiments at controlled gas input can also improve this knowledge.

Furthermore, to complete the model developed in this some more experiments ca be done:

(6) Study the formation of hydrates with bubbles (varying the liquid volume of the flow loop or using the gas lift)

- (7) Improve the natural gas solubility model with data to other components like propane, nitrogen, isobutane, and normal butane (data for methane, propane and carbon-dioxide are already available and presented in the Appendix B).
- (8) Deeper explore the data from the acoustic emission system like frequency, counts, amplitude, and many others
- (9) Improve the permittivity data treatment by including the effect of hydrates in the measurements
- (10) Use machine learning to identify which parameters mostly affect the risk of plugging and develop a model from to estimate the transportability of the system as function of the input data
- 7.2. Highlights in French Résume du Chapitre 7 en Français

Cette thèse présent un travail expérimental visant à étudier la formation d'hydrates de gaz dans les systèmes kerdane-eau salé à haute pression et basse température dans la boucle de circulation Archimède. L'application de ce travail est dans le maintien de l'écoulement pétrolier, pour les applications de prévention de la formation de bouchons d'hydrate dans l'exploitation pétrolière en eaux profondes. Actuellement, l'industrie utilise des additifs anti agglomérant chimiques pour éviter le blocage des conduites. Il y a un intérêt particulier pour les antiagglomérants, qui pourraient être efficaces à des fractions relativement faibles et réduire la quantité d'additif utilisé (ce qui peut réduire les dépenses en additif pour la prévention du bouchage des conduites et être moins agressif pour l'environnement). La littérature a identifié les systèmes à haut *water-cut* comme problématiques, les antiagglomérants étant signalés comme non efficaces pour les systèmes avec plus d'eau. Il y a un manque de compréhension sur les raisons pour lesquelles les antiagglomérants ne sont apparemment pas efficaces. L'influence de la formation d'hydrates sur l'écoulement polyphasique est mal connue. Cette lacune a été le principal objet d'étude de ce travail.

Pour améliorer les résultats obtenus par la boucle Archimède une sonde de permittivité et des capteurs d'émission acoustique ont été installés. Une meilleure compréhension de la façon de surveiller la phase continue et de la phase (huile ou eau) transportée ou emprisonnée par les hydrates est possible grâce aux mesures de permittivité. L'utilisation de l'énergie acoustique pour mesurer l'énergie absolue permet de suivre les particules dans le système, et, savoir comment la dispersion des hydrates se comporte dans le temps, permettant une meilleure confiance dans la définition des différentes étapes des mécanismes de formation des bouchons d'hydrates.

Dans la seconde partie, la formation d'hydrates et les mécanismes de colmatage ont été analysés. Des essais sans AA ont été réalisés à 30, 50 et 80% de water-cut. Malgré la différence d'échelle de temps, toutes ces expériences ont bouché la conduite et par conséquent, ont été identifiées comme critiques. Il a été observé que la formation d'hydrates provoque un changement complet du régime d'écoulement pour les essais à 30% (huile continue) et 50% (eau continue) water-cut. La formation d'un régime intermittent entre la phase aqueuse portant la plupart des hydrates, et la phase huile s'écoulant seule a été observé. Quelques raisons à cela sont la tendance de l'hydrate à s'écouler avec la phase aqueuse. La différence de vitesses entre les hydrates et la phase liquide, provoque une accumulation d'hydrates qui facilite la viscosification, l'agglomération et le dépôt. Les expériences à 80% water-cut étaient un peu différentes des autres. Les hydrates semblent se former autour des gouttelettes d'huile en emprisonnant une partie. Les particules sont de taille relativement petite et la transportabilité des hydrates est plus élevée que pour les expériences avec des coupes d'eau plus faibles. Outre la taille des particules, la phase aqueuse semble avoir une affinité plus élevée avec les particules d'hydrate et donc mieux la transporter. Cependant, il y a eu la formation de bouchons, car les particules de tailles différentes s'écoulent à vitesses différentes finissant par le cumuler et créer une viscosification locale du liquide.

Les expériences avec un AA commercial ont été réalisées à 50 et 80% de water-cut. Dans les deux cas, l'eau était la phase continue et une dispersion complète du système liquideliquide a été obtenu. À 50% de *water-cut*, il y a eu une inversion de phase, en raison de la consommation d'eau. Alors que l'eau est la phase continue, la transportabilité du système n'est pas affectée par la formation d'hydrates, avec une viscosité apparente approximativement constante. Lorsque l'huile est la phase continue, il y a une augmentation immédiate de la viscosité, ce qui réduit la transportabilité du système. Au fur et à mesure que la formation d'hydrates se poursuit, la viscosité apparente augmente linéairement puis la dispersion devient dense, et une partie des hydrates subit une sédimentation. Il n'y a pas eu de formation de bouchon après plusieurs heures d'expérience. À 80% de coupure d'eau, il n'y a pas eu d'inversion de phase, mais le taux de formation d'hydrates est plus élevé qu'à 50% de water-cut. En raison de la grande quantité d'hydrates, la dispersion d'hydrates devient dense, car le liquide restant ne peut pas transporter toutes les particules solides. Lorsque la fraction de solide est trop élevée, le mouvement des hydrates devient ce que l'on appelle dans la littérature solide-liquide dominé par le contact et le système peux éventuellement se boucher. Bien que l'utilisation de l'antiagglomérant ait réussi à éviter l'agglomération ou le dépôt chimique (ou toute fixation due

aux forces capillaires) et à former une fine dispersion sèche, il semble qu'il existe une limitante maximale de fraction d'hydrates pouvant être transportée par le liquide.

7.2.1. Perspectives et travaux futurs

Une question importante qui découle de ce travail est de savoir quelle quantité d'hydrates (fraction) peut être transportée en toute sécurité en fonction des paramètres intrants. Deux paramètres importants sont la viscosité apparente et la taille des particules. Il a été observé que la viscosité avant formation d'hydrates dépend du *water-cut* et du débit et de la présence d'AA. Après la formation d'hydrates, il est également affecté par la quantité d'hydrates s'écoulant dans le système. Le volume apparent d'hydrates peut également être beaucoup plus important, car les particules piègent les phases liquides et il est difficile de savoir combien de liquide est piégé dans la phase hydrates.

Dans ce sens, il est nécessaire de mieux comprendre comment la viscosité apparente est affectée par le *water-cut* et la taille des particules, ainsi que par la fraction d'hydrates et la fraction d'hydrates apparents. Les travaux suivants sont proposés :

(1) ajuster les données issues des expériences sur les dispersions liquide-liquide avec les modèles de la littérature pour la viscosité en fonction de la phase dispersée

(2) après la formation d'hydrate, estimer la coupe d'eau qui s'écoule à partir de la permittivité et de la conversion de l'eau et calculer la quantité de liquide piégé à l'intérieur des particules d'hydrate.

(3) estimer le dépôt à partir d'un équilibre entre la fraction d'hydrates et la fraction d'hydrates apparente en circulation. Un modèle simplifié et des résultats préliminaires pour le calcul de la fraction d'hydrates apparente sont dans le Chapitre 6.

(4) utiliser un modèle de viscosité de la littérature en fonction de chaque fraction de phase, de la fraction d'hydrate et de la distribution granulométrique

(5) acquérir des connaissances fondamentales à partir de particules modèles afin de comprendre la distribution des particules dans l'écoulement et son impact sur la viscosité

L'utilisation d'un LDHI-AA commercial a changé la dispersion et a formé une dispersion fine. Cependant, on ne sait pas comment cet AA agit au niveau microscopique, et comment il évite l'agglomération et certaines données physico-chimiques sur l'AA (viscosité, tensions superficielles, effet sur les propriétés de l'eau) pourraient être importantes pour comprendre leur impact. Davantage d'expériences avec un apport de gaz contrôlé peuvent également améliorer ces connaissances. En outre, pour compléter le modèle développé dans ce travail, d'autres expériences peuvent être faites :

(6) étudier la formation d'hydrates avec des bulles (en faisant varier le volume de liquide de la boucle d'écoulement ou en utilisant le *gas -lift*)

(7) améliorer le modèle de solubilité du gaz naturel avec des données expérimentales sur la solubilité d'autres composants comme le propane, l'azote, l'isobutane et le butane normal (les données pour le méthane, le propane et le dioxyde de carbone sont déjà disponibles et présentées à l'annexe D).

(8) Explorez plus en profondeur les données du système d'émission acoustique telles que la fréquence, le nombre, l'amplitude et bien d'autres

(9) Améliorer le traitement des données de permittivité en incluant l'effet des hydrates dans les mesures

(10) Utiliser l'apprentissage automatique pour identifier les paramètres qui affectent le plus le risque de bouchage et développer un modèle d'estimation de la transportabilité du système en fonction des données d'entrée

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APPENDIX A – ARCHIMEDE DATA PROCESSING AND VISUALIZATION SOFTWARE

An application software for data treatment and data visualization was developed for the synchronization of the data from all the instruments installed in the Archimedes flow loop, the apparatus used in the experiments of this work. A screenshot of the user's interface with some plots can be seen in Figure 96. The objective of this Appendix is to give a brief presentation about the software, how it is programmed, how it is organized, and what tools are currently implemented.



Figure 96. Screenshot of the Archimede Data Processing and Visualization App with some plots.

A.1. Programing language and organization of the software

The software was coded in Python 3 (see information in Python, 2020). The Archimede Data Processing and Visualization App was coded using resources of Tkinder, Matplotlib, Numpy, Csv, Pandas, among other libraries. This programming language was chosen for this work because of the following advantages: it is open source and free; it hosts thousands of third-party modules, which allows a fast implementation of many utilities; and it has a simple installation procedure, so it would be easy to extend the use of the software in other computers and pilot systems. Furthermore, Python is known as an extremely powerful language for Data Science and Artificial Intelligence, and it is currently being used by major companies from these sectors around the world. Taking into account that one of the perspectives for the

continuation of this work is the use of machine learning techniques and the development of predictive tools for hydrate management, the choice for Python is once more justified.

The software can be divided in four parts: Graphical interface, Management, Data Processing, and Data Manipulation. In the Graphical Interface, it is programmed the friendly interface that the user sees and interacts with, which includes all the windows and buttons. The Management is where the data circulates; here, commands are given for the operations, which include opening the files where the data is stored, sending the data for processing, and plotting the graphs. The Data Processing is where the raw data is received, synchronized in time, and stored in a way that will allow fast reading and visualization. The Data Manipulation is where all the math and scientific operations occur: the data (not yet meaningful data) is received and then transformed in data sets (converted in actual values); here, it is also where the calculations procedures and solution of equations take place. A representation on how the software works is shown in Figure 97.



Figure 97. Organization of the Archimède Data Processing and Visualization Software.

A.2. Data processing

There are six instruments currently installed in the Archimède flow loop: the main acquisition system, the FBRM, the acoustic emission sensor, the permittivity probe, the PVM, and the camera. The data treatment involves the two steps represented in Figure 97:

 Processing: this must be done only once after each experiment and consists in collecting the data from the different computers and synchronizing them in time with the software for data treatment. The data sets are converted to csv files and the images are stored in bpm (PVM) or tif (camera) files. This step is necessary to reduce the computer processing time during the data visualization and data analysis. Visualization: once the data is synchronized, it can rapidly be accessed and converted in meaningful data using the data manipulation and visualization tools of the software. In this section, a description on how the data from each one of these instruments are

treated in explained.

A.3. Main classical acquisition system data

The main acquisition system stores the data from 19 probes, which are: 10 temperature probes, 4 pressure drop probes, 2 pressure probes, density, flow rate and gas injection. The data from an experiment is stored in a single csv file, where measurements are recorded at each 1.0 second (minimum time step possible). Then, all the data sets can be plotted using the software for data treatment, as shown in Figure 98.

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10:36:06	2	0	4,7	207,26	885,144	0,313		T10
10:36:07	3	0	4,7	209,02	879,681	0,314		Δp1
10:36:08	4	0	4,7	221,93	871,441	0,35		Δp2
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Figure 98. Data stored in a csv file from the main acquisition system.

From temperature, pressure and gas injection is possible to calculate the amount o gas dissolved into the oil phase and the oil density, according to the model presented in Section 3.4.1. From the same data, one can obtain the water conversion, based on the model presented in Section 3.4.2. From the horizontal pressure drop and flow rate, it is possible to obtain the apparent viscosity and Reynolds number, as presented in Section 4.2.2.

A.4. FBRM data

The data from the FBRM instrument is stored in a single csv file, containing the chord counts in a range 1-1000 micrometers divided in 90 intervals spaced in a log90-scale. The CLD is recorded each 5.0 seconds. The software allows visualization in 2 or 3 dimensions, as shown in Figure 99.

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(a) FBRM data in a csv file

(b) Visualizing the FBRM data

Files Serv FBRM Permittivity Acoustic emission PVM Advanced Camera



Figure 99. Storage and visualization of the FBRM data.

A.5. Acoustic emission data

The acoustic data is stored in txt files, containing the measurements of absolute energy each 0.5 second. The number of files depends on the time of experiment. For the processing, it requires that these files are read one by one and transferred to a single csv file, where the time of each measurement is calculated relatively to the reference time (pressurization). A screenshot with the data of absolute energy from 4 AE sensors used in an experiment is shown in Figure 100.

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(b) Visualizing the Δ by Energy

(a) Abs. Energy data in a csv file

Figure 100. Storage and visualization of the absolute energy data.

A.6. Permittivity data

The treatment of the data from the permittivity probe requires a complex processing after the end of the experiment before being treated. The data is stored in txt files in a way that each file stores only one measurement, showing the permittivity and conductivity for 201 frequencies. Therefore, it is necessary to open all the files, get the exact time that it was recorded, calculate it relatively to the time of pressurization, and then get the permittivity and conductivity at 10⁸ [Hz] from all the files saved in a single csv (see an example in Figure 101). In addition, it is also recorded how many times a specific range of frequency recorded a permittivity; this is recorded in two separate csv files, for the data before and after hydrate formation.



Figure 101. Storage and visualization of the permittivity data.

A.7. PVM data

The PVM images are stored in bmp files. For the pre-processing, the images are open and the time they were recorded are registered with the calculated brightness in a csv file. An example of the generated csv file after the processing is shown in Figure 102. The name of the file is registered in the third column, so it allows a fast opening of the file during the data visualization step.



Figure 102. Storage and visualization of the PVM data.

A.8. High speed camera data

The recording of the images with the camera is a challenge in terms of storage and processing because of the required large memory. The images are recorded in binary files. The number of binary files depends on the number of images (duration of the experiment and frames

per second). The processing consists in opening one by one of the binary files and registering the exact time each one of them was recorded.



Figure 103. Storage and visualization of the images from the camera.

A.9. Perspectives

Experiments with large data sets are becoming common in industry and academy. Tools to extract information from these data are in high demand, and the software presented in this Appendix was an important tool for the analysis of results for this thesis. Despite the current version of this software is already running many utilities, much work is still possible, which includes, but is not limited to:

- The development of utilities that allow comparing data from different experiments
- The development of an interface that allows displaying the data as function of space (and not only time)
- The implementation of tools that will allow quantifying deposition
- The improvement of the automatization of the software, creating more options for displaying images with multiple plots, especially when comparing data from different instruments
- The implementation of algorithms that allow converting the CLD (from the FBRM) to particle size distribution
- The use of machine learning techniques to analyze the results, as a complement to the current analyzes based on the physics of the problem
- The extension of the use of this software in other pilots designed for applications in hydrate management

APPENDIX B – SOAVE-REDLICH-KWONG REAL GAS MODEL

The objective of this Appendix is to present the real gas model from literature that is used in this work. An application for the natural gas composition used in the experiments is shown, comparing with results from a commercial software.

B.1. Soave-Redlich-Kwong equation

The Soave-Redlich-Kwong (SRK) equation of state is used for calculating the number of mols for each gas component. It is expressed in terms of pressure (p), temperature (T) and molar volume (V_m) . The SRK model can be written as follows:

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m(V_m + b)}$$
(85)

where *R* is the gas constant (R = 8.3145 J/mol·K). The values of *a* and *b* are calculated as functions of the critical temperature (T_c), the critical pressure (p_c), and the Pitzer's acentric factor (ω):

$$a = 0.427480234 \frac{(RT_c)^2}{p_c} \left[1 + (0.480 + 1.574\omega - 0.176\omega^2) \left(1 - \sqrt{\frac{T}{T_c}} \right) \right]^2 \quad (86)$$

$$b = 0.08664035 \frac{RI_c}{p_c} \tag{87}$$

For a mixture of gases, the SRK model is written as follows:

$$p = \frac{RT}{V_m - b_m} - \frac{a_m}{V_m (V_m + b_m)}$$
(88)

The modified parameters a_m and b_m are calculated as:

$$a_{m} = \sum_{i} \sum_{j} f_{f,i} f_{f,j} \sqrt{a_{i} a_{j}} (1 - k_{ij})$$
(89)

$$b_m = \sum_i f_{f,i} \, b_i \tag{90}$$

B.2. Application of the model for the experimental conditions of this work

Table 6 shows the molar fraction (f), molar mass (M_G), critical temperature, critical pressure, and Pitzer's acentric factor for each gas component present in the natural gas used in the experiments of this work.

Gas type	f [%]	M_G [g/mol]	<i>T_c</i> [K]	p_c [bar]	ω [-]
Methane	91.7	16.04	190.56	45.99	0.01155
Ethane	5.9	30.07	305.32	48.72	0.09949
Propane	0.6	44.10	369.83	42.48	0.15229
Carbon dioxide	0.8	44.01	304.21	73.82	0.22362
Nitrogen	0.8	28.01	126.20	34.00	0.03772
i-Butane	0.1	58.12	408.14	36.48	0.18077
n-Butane	0.1	58.12	425.15	37.99	0.2013

Table 6. Properties of each gas component present in the natural gas.

Figure 104 shows the equilibrium for hydrate formation using the natural gas (with the composition shown in Table 6) and saline water with 30 g of NaCl per liter of water. Since the experiments of this work as carried out at 75 bars and 4°C, the subcooling is 10.37 °C.



Figure 104. Hydrate formation curve for the natural gas composition used in the tests and saline water (30 g/L of NaCl). Obtained from HWPVT (Heriot-Watt University Hydrate and Phase Equilibria Software).

Figure 105 show the density comparison between the SRK equation of state against data from the literature. The values for gas methane were evaluated at 1, 10, 20, 40, 60 and 80 bars. For the other gas components, they were evaluated at 1, 3, 5, 10, 15 and 20 bars.



Figure 105. Comparison of data for some gas components for SRK model against data from the literature.



Figure 106. Comparison of data for natural gas for SRK model against data from the literature.

APPENDIX C - CORRELATIONS OF GAS SOLUBILITY AND DENSITY OF KERDANE OIL SATURATED WITH METHANE, ETHANE AND CARBON DIOXIDE GAS

The gas used in the experiments is a composition of natural gases. During pressurization, part of the gas dissolves in the liquid phases. Since solubility in oil is normally much higher than in water, knowing the solubility each gas component into the Kerdane is a required information. Experiments were conducted at Ecole des Mines de Saint-Etienne to obtain the solubility of methane, ethane and carbon dioxide in Kerdane, and how the dissolution affects the oil density (Straume, 2019). The correlations obtained for gas solubility and Kerdane density are presented in this Appendix. The correlations are used for the calculation procedure of gas solubility and Kerdane density, presented in subsection 3.4.1.

C.1. Results from tests with methane in Kerdane

The correlations for solubility and density of methane in Kerdane, valid for 0-80 bars and 4-20°C, are:

$$C = (-0.0000002088802 \cdot T^{2} + 0.000002648858 \cdot T - 0.00004479552)$$

$$\cdot p^{2} + (0.000001227564 \cdot T^{2} - 0.0002785752 \cdot T$$
 (91)

$$+ 0.0325703) \cdot p + 0.0000050759 \cdot T - 0.00033501$$

where *C* is concentration in mol methane/kg filled Kerdane, *T* is temperature in $^{\circ}$ C, and *p* is pressure in bar.

$$\rho = (-0.000051603 \cdot T^2 + 0.0016213 \cdot T - 0.59938) \cdot p - 0.60709 \cdot T + 819.48$$
(92)

where ρ is density in kg/m³ Kerdane saturated with methane, *T* is temperature in °C, and *p* is pressure in bar.

C.2. Results from tests with ethane in Kerdane

The correlations for solubility and density of ethane in Kerdane, valid for 3-4 bars and 4-20°C, are:

$$C = (0.000054836 \cdot T^2 - 0.0051435 \cdot T + 0.23957) \cdot p \tag{93}$$

where C is concentration in mol ethane/kg filled Kerdane, T is temperature in $^{\circ}$ C, and p is pressure in bar.

$$\rho = (0.030072 \cdot T - 5.4114) \cdot p - 0.60709 \cdot T + 819.48 \tag{94}$$

where ρ is density in kg/m³ Kerdane saturated with ethane, *T* is temperature in °C, and *p* is pressure in bar.

C.3. Results from tests with carbon dioxide in Kerdane

The correlations for solubility and density of ethane in Kerdane, obtained for a pressure of 2 bars (and assuming that solubility is 0 mol/kg at 0 bar) and 4-20°C, are:

$$C = (-0.00092385 \cdot T + 0.08027) \cdot p \tag{95}$$

where *C* is concentration in mol carbon dioxide/kg filled Kerdane, *T* is temperature in $^{\circ}$ C, and *p* is pressure in bar.

$$\rho = (-0.023466 \cdot T - 1.8923) \cdot p - 0.60709 \cdot T + 819.48$$
(96)

where ρ is density in kg/m³ Kerdane saturated with carbon dioxide, *T* is temperature in °C, and *p* is pressure in bar.

C.4. Summary of this Appendix

- Correlations for gas concentration and Kerdane density have presented
- Experimental data and correlations from this study can be used for calculations of gas concentration in the oil phase and hydrate quantity in flow loop experiments with Kerdane as oil phase.

APPENDIX D – REYNOLDS AND APPARENT VISCOSITY

This Appendix presents the calculated Reynolds number and viscosity for the experiments analyzed in Chapter 4 to characterize the flow regime before hydrate formation. An important information for these results is that the flow regime is mostly laminar, for all the experiments. As the flow rate increases, the increase on the viscosity forces balances the increase on inertial forces, and therefore, the regime is still laminar.



Figure 107. Reynolds number and apparent viscosity for an experiment at 30% water-cut, 400 L/h, without AA (#15).



Figure 108. Reynolds number and apparent viscosity for an experiment at 50% water-cut, 200 L/h, without AA (#19).



Figure 109. Reynolds number and apparent viscosity for an experiment at 50% water-cut, 400 L/h, without AA (#24).



Figure 110. Reynolds number and apparent viscosity for an experiment at 80% water-cut, 200 L/h, without AA (#20).



Figure 111. Reynolds number and apparent viscosity for an experiment at 80% water-cut, 200 L/h, without AA (#23).

Appendix **E** - Additional hydrate formation experiments

This appendix presents the results for the experiments not shown in the Chapters 4-6, dedicated to the results. The tests for any of the conditions were repeated at least once to verify the repeatability of the experiments, hereby presented.



Figure 112. Experiment at 30% water-cut, 200 L/h, without AA (#12), showing the: (a) absolute energies, (b) temperatures (T_8 and T_9), (c) pressure drops and (d) flow rate.



Figure 113. Experiment at 30% water-cut, 200 L/h, without AA (#12), showing a comparison between: (a) dielectric and density, (b) dielectric and absolute energy, (c) dielectric and PVM images grayscale and (d) dielectric and chord counts.



Figure 114. Experiment at 30% water-cut, 400 L/h, without AA (#14), showing the: (a) absolute energies, (b) temperatures (T_8 and T_9), (c) pressure drops and (d) flow rate.



Figure 115. Experiment at 30% water-cut, 400 L/h, without AA (#14), showing a comparison between: (a) dielectric and density, (b) dielectric and absolute energy, (c) dielectric and PVM images grayscale and (d) dielectric and chord counts.



Figure 116. Experiment at 50% water-cut, 200 L/h, without AA (#16), showing the: (a) absolute energies, (b) temperatures (T_8 and T_9), (c) pressure drops and (d) flow rate.



Figure 117. Experiment at 50% water-cut, 200 L/h, without AA (#16), showing a comparison between: (a) dielectric and density, (b) dielectric and absolute energy, (c) dielectric and PVM images grayscale and (d) dielectric and chord counts.



Figure 118. Experiment at 50% water-cut, 400 L/h, without AA (#25), showing the: (a) absolute energies, (b) temperatures (T_8 and T_9), (c) pressure drops and (d) flow rate.



Figure 119. Experiment at 50% water-cut, 400 L/h, without AA (#25), showing a comparison between: (a) dielectric and density, (b) dielectric and absolute energy, (c) dielectric and PVM images grayscale and (d) dielectric and chord counts.



Figure 120. Experiment at 80% water-cut, 200 L/h, without AA (#21), showing the: (a) absolute energies, (b) temperatures (T_8 and T_9), (c) pressure drops and (d) flow rate.



Figure 121. Experiment at 80% water-cut, 200 L/h, without AA (#21), showing a comparison between: (a) dielectric and density, (b) dielectric and absolute energy, (c) dielectric and PVM images grayscale and (d) dielectric and chord counts.



Figure 122. Experiment at 80% water-cut, 400 L/h, without AA (#22), showing the: (a) absolute energies, (b) temperatures (T_8 and T_9), (c) pressure drops and (d) flow rate.



Figure 123. Experiment at 80% water-cut, 400 L/h, without AA (#22), showing a comparison between: (a) dielectric and density, (b) dielectric and absolute energy, (c) dielectric and PVM images grayscale and (d) dielectric and chord counts.



Figure 124. Experiment at 50% water-cut, 200 L/h, with AA at 1.5 % wt. vs water (#28), showing the: (a) absolute energies, (b) temperatures (T_8 and T_9), (c) pressure drops and (d) flow rate.



Figure 125 Experiment at 50% water-cut, 200 L/h, with AA at 1.5 % wt. vs water (#28), showing a comparison between: (a) dielectric and density, (b) dielectric and absolute energy, (c) dielectric and PVM images grayscale and (d) dielectric and chord counts.



Figure 126. Experiment at 50% water-cut, 400 L/h, with AA at 1.5 % wt. vs water (#30), showing the: (a) absolute energies, (b) temperatures (T_8 and T_9), (c) pressure drops and (d) flow rate.


Figure 127. Experiment at 50% water-cut, 400 L/h, with AA at 1. 5 % wt. vs water (#30), showing a comparison between: (a) dielectric and density, (b) dielectric and absolute energy, (c) dielectric and PVM images grayscale and (d) dielectric and chord counts.



Figure 128. Experiment at 80% water-cut, 200 L/h, with AA at 0.94 % wt. vs water (#32), showing the: (a) absolute energies, (b) temperatures (T_8 and T_9), (c) pressure drops and (d) flow rate.



Figure 129. Experiment at 80% water-cut, 200 L/h, with AA at 0.94 %wt. vs water (#32), showing a comparison between: (a) dielectric and density, (b) dielectric and absolute energy, (c) dielectric and PVM images grayscale and (d) dielectric and chord counts.



Figure 130. Experiment at 80% water-cut, 400 L/h, with AA at 0.94 %wt. vs water (#34), showing the: (a) absolute energies, (b) temperatures (T8 and T9), (c) pressure drops and (d) flow rate.



Figure 131. Experiment at 80% water-cut, 400 L/h, with AA at 0.94 %wt. vs water (#34), showing a comparison between: (a) dielectric and density, (b) dielectric and absolute energy, (c) dielectric and PVM images grayscale and (d) dielectric and chord counts.

Appendix F - Gas dissolution, hydrate fraction and apparent hydrate fraction for all the tests

In this Appendix, the calculate gas dissolution, oil density, water cut, water conversion, hydrate fraction and local hydrate fraction is shown for all the experiments with natural gas performed for this thesis.



Figure 132. Calculated gas dissolution and hydrate fraction for the test #11 (30% water cut, 200 L/h, without AA).



Figure 133. Calculated gas dissolution and hydrate fraction for the test #12 (30% water cut, 200 L/h, without AA).



Figure 134. Calculated gas dissolution and hydrate fraction for the test #14 (30% water cut, 400 L/h, without AA).



Figure 135. Calculated gas dissolution and hydrate fraction for the test #15 (30% water cut, 400 L/h, without AA).



Figure 136. Calculated gas dissolution and hydrate fraction for the test #16 (50% water cut, 500 L/h, without AA).



Figure 137. Calculated gas dissolution and hydrate fraction for the test #17 (50% water cut, 200 L/h, without AA).



Figure 138. Calculated gas dissolution and hydrate fraction for the test #18 (50% water cut, 200 L/h, without AA).



Figure 139. Calculated gas dissolution and hydrate fraction for the test #19 (50% water cut, 200 L/h, without AA).



Figure 140. Calculated gas dissolution and hydrate fraction for the test #20 (80% water cut, 200 L/h, without AA).



Figure 141. Calculated gas dissolution and hydrate fraction for the test #22 (80% water cut, 400 L/h, without AA).



Figure 142. Calculated gas dissolution and hydrate fraction for the test #23 (80% water cut, 400 L/h, without AA).



Figure 143. Calculated gas dissolution and hydrate fraction for the test #24 (50% water cut, 400 L/h, without AA).



Figure 144. Calculated gas dissolution and hydrate fraction for the test #25 (50% water cut, 400 L/h, without AA).



Figure 145. Calculated gas dissolution and hydrate fraction for the test #26 (50% water cut, 400 L/h, without AA).



Figure 146. Calculated gas dissolution and hydrate fraction for the test #27 (50% water cut, 400 L/h, with 1.5 wt.%/water AA).



Figure 147. Calculated gas dissolution and hydrate fraction for the test #28 (50% water cut, 400 L/h, with 1.5 wt.%/water AA).



Figure 148. Calculated gas dissolution and hydrate fraction for the test #29 (50% water cut, 400 L/h, with 1.5 wt.%/water AA).



Figure 149. Calculated gas dissolution and hydrate fraction for the test #30 (50% water cut, 400 L/h, with 1.5 wt.%/water AA).



Figure 150. Calculated gas dissolution and hydrate fraction for the test #31 (80% water cut, 200 L/h, with 0.94 wt.%/water AA).



Figure 151. Calculated gas dissolution and hydrate fraction for the test #32 (80% water cut, 200 L/h, with 0.94 wt.%/water AA).



Figure 152. Calculated gas dissolution and hydrate fraction for the test #33 (80% water cut, 400 L/h, with 0.94 wt.%/water AA).



Figure 153. Calculated gas dissolution and hydrate fraction for the test #34 (80% water cut, 400 L/h, with 0.94 wt.%/water AA).

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NNT : 2020LYSEM031

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MULTI-INSTRUMENTAL DATA PROCESSING AND NATURAL GAS HYDRATE CRYSTALLIZATION MODELLING UNDER FLOW

Speciality: Chemical and Process Engineering

Keywords: gas hydrates, flow assurance, multiphase flow, flow pattern, anti-agglomerants, flow loop experiments, data processing.

Abstract:

Gas hydrates may cause the blockage of pipelines in deep-sea petroleum exploitation, especially at intermediate and high water cuts. This study is to understand the action of a Low Dosage Hydrate Inhibitor Anti-Agglomerant (LDHI-AA) to limit agglomeration and deposition, and to prevent the formation of plugs in the pipeline. In this work, experiments were conducted using the Archimède flow loop (56 m of length and diameters of 10.2 and 15.7 mm) to study natural gas hydrate formation in Kerdane-salted water (30 g/L of NaCl) dispersions without and with LDHI-AA (0.94 and 1.50 wt.%/water) to monitor the flow conditions and track hydrate particles in time and space. New insights for the mechanisms of hydrate formation and blockage for the conditions tested are presented. They were deduced from three new measurements: a permittivity probe, acoustic emission probes, a high-speed camera. In this sense, a new software was developed to treat and synchronize the data obtained from the total 29 probes and instruments present in the flow loop. Some quantitative models were developed to deduce the continuous phase from permittivity and quantify the apparent instantaneous hydrate fraction in the flow from the density. Furthermore, the acoustic emission enabled to detect the accumulation of hydrates in parts of the flow and the deposition in the pipeline. Further works will enable to quantify these two mechanisms responsible for plugging.

École Nationale Supérieure des Mines de Saint-Étienne

NNT : 2020LYSEM031

Vinicius RODRIGUES DE ALMEIDA

TRAITEMENT DE DONNEES DE MULTI-INSTRUMENTS ET MODELISATION DE LA CRISTALLISATION DES HYDRATES DE GAZ NATUREL DANS UN ECOULEMENT

Spécialité : Génie des Procèdes

Mots clefs : hydrates de gaz, maintiens de l'écoulement, écoulement polyphasique, géométrie d'écoulement, bouchage d'hydrates, antiagglomérants, traitement de données.

Résumé :

Les hydrates de gaz peuvent provoquer le blocage des pipelines en exploitation pétrolière en eaux profondes, en particulier à fort et intermédiaire water-cut. Cette étude vise à comprendre le comportement des additifs Low Dosage Hydrate Inhibitors Anti-Agglomerant (LDHI-AA) pour éviter l'agglomération et la formation de bouchons dans la conduite. Les expériences de formation d'hydrates de gaz et de transport de la dispersion ont été réalisées dans la boucle Archimède (56 m de longueur et diamètres de 10,2 et 15,7 mm) dans des dispersions de kerdane et d'eau salée (30 g/L de NaCl) sans et avec LDHI-AA (0,94 % et 1,50% poids / eau) de façon à suivre les conditions d'écoulement et les particules d'hydrate dans le temps et dans l'espace. Un modèle de comportement a été développé à partir de trois nouvelles mesures : une sonde de permittivité, des sondes d'émission acoustique, une caméra à grande vitesse. Dans ce sens, un nouveau logiciel a été développé pour traiter et synchroniser les données obtenues à partir des 29 sondes et instruments présents dans la boucle. Deux modèles quantitatifs ont été développés pour déduire la phase continue à partir de la permittivité et quantifier la fraction d'hydrates instantanée apparente dans l'écoulement à partir de la densité. De plus, l'émission acoustique a permis de détecter l'accumulation d'hydrates dans certaines parties de l'écoulement et le dépôt dans la conduite. D'autres travaux permettront de quantifier ces deux mécanismes responsables du blocage de la conduite.