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A Multiscale Approach for Gas Hydrates Considering Structure, Agglomeration, and Transportability under Multiphase Flow Conditions:

I. Phenomenological Model

Carlos L. Bassani[†,‡]*, Aline M. Melchuna*[#]*, Ana Cameirão*[†*]*, Jean-Michel Herri*[†]*, Rigoberto E.M. Morales*[‡*]*, Amadeu K. Sum*[#*]

[†]Mines Saint-Etienne, Univ Lyon, CNRS, UMR 5307 LGF, Centre SPIN, Departement PEG, F - 42023 Saint-Etienne France

[‡]Multiphase Flow Research Center (NUEM), Federal University of Technology – Paraná (UTFPR), Rua Deputado Heitor Alencar Furtado, 5000, Bloco N, CEP 81280-340, Curitiba/PR, Brazil

[#]Phases to Flow Laboratory, Chemical and Biological Engineering Department, Colorado School of Mines, 1500 Illinois St., Golden, CO 80401, USA

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Abstract. A new topological model on how gas hydrates form, grow and agglomerate for oil and water continuous flow, with and without surfactant additives is presented. A multiscale approach is used to explain how the porous structure of gas hydrates and the affinity between the phases affect the particle morphology and their agglomeration. We propose that gas consumption due to hydrate growth happens mostly in the water trapped inside the capillaries of the hydrate structure near the outer surface of the particles. This approach is herein referred as the 'sponge approach' and is treated as a surface problem, instead of the volume problem often treated in literature (the 'shell approach'). Affinity between phases (which in a macro point-of-view is interpreted as a wetted angle giving rise to capillarity forces and that can be changed by the use of surfactant additives) describe preferential entrapment of oil or water inside the hydrate sponge structure. Yet by splitting agglomeration into smaller processes, and depending on the morphology of the particles and on the evolution of the porous structure of hydrates: (i) capillarity bridges may form causing particles to be sticky, and (ii) water may be available at the outer surface of the particles and promote consolidation of particle-particle (agglomeration) or particle-wall (deposition). Settling of slurries is treated as a separated solid-liquid flow instability problem once mixture deceleration (due to phase consumption during crystallization) and particle size (due to growth and agglomeration) is known. We also propose a new explanation on how surfactants act as Anti-Agglomerants in oil continuous flow, differently from the common DLVO theory used in literature, which can only explain anti-agglomeration of particles much smaller than the ones formed over droplets of a very fine dispersion flow.

Nomenclature

In this article, images with blue color refer to water phase, brown to oil phase, white to hydrate phase and green to gaseous phase. Gray refer to the carrier liquid phase, which can be either oil or water.

1. Introduction

The high pressure and low temperature conditions often found in offshore oil and gas production scenarios favor the formation of gas hydrates. Gas hydrates are crystals formed by the imprisonment of gas molecules inside cages of hydrogen-bonded water molecules[1]. Uncontrolled growth and agglomeration of the particles can cause pipe blockage, with production stop and consequent revenue losses. Plugging due to gas hydrate formation is nowadays considered the most concerning problem of scientists/engineers in the field of *flow assurance*[2] – that is, the ensemble of operations to assure continuous flow in the oil and gas flowlines.

Literature presents diverse thermodynamic studies on phase equilibria to measure and to model the pressure and temperature envelope of hydrate formation of different gases[3–5]. By estimating the temperature and pressure profile of the multiphase gas-oil-water flow along the entire flowline, the flow assurance engineer can predict if ever there is part of the flowline under risk to form hydrates. For long tiebacks, complete avoidance of hydrate formation is usually done: (i) by insulating/heating the flowline walls, related to a high energetic cost; or (ii) by injecting chemical additives that displace the thermodynamic envelope of gas hydrate formation (e.g., salts and alcohols), called *thermodynamic inhibitors*.

With harsher scenarios due to crescent production in deeper and colder waters, continuous injection of thermodynamic inhibitors became prohibitive and the concept of *hydrate management* appeared. In this case, hydrates are expected to form, but the flow assurance engineers shall assure that they will present a stable slurry flow over the entire flowline. Therefore: (i) hydrates shall never form directly in the wall, but in the bulk, otherwise a catastrophic pressure drop increase with further sloughing of the deposited masses may occur, which can quickly plug the flowline[6–8]; and (ii) the flow shall always have enough inertia to carry the particles[9,10]. With this in mind, the best condition is to promote a very fine slurry flow and to avoid any kind of agglomeration of hydrates. For those purposes, additives called *Anti-Agglomerants* (AA) have been developed, which often present surfactants properties, although chemical composition of commercial AAs is undisclosed due to proprietary formulations. These additives are injected in a much lower volumetric fraction than the thermodynamic inhibitors and therefore are broadly called *Low-Dosage Hydrate Inhibitors* (LDHI)[11], which for the case of AAs, the inhibition is due to avoidance of agglomeration.

Although hydrate management can substantially reduce the CAPEX and OPEX, there is still a significant lack of fundamental understanding in the growth and agglomeration phenomena of hydrates in multiphase systems. Different experimental apparatus – e.g., flowloops[12,13], batch reactors[14–18] and rocking cells[19,20] – give different growth kinetic rates (i.e., amount of gas consumed over time) and plugging tendencies (i.e., pressure drop and volumetric flowrate oscillations) even when using similar gases (often methane or synthetic natural gas) and oils. Therefore, the literature still presents a process of trial and error in understanding both phenomena (growth kinetics and agglomeration) for the use of different gases, oils and additives in different conditions of water cut, mixture flowrate, and presence of salt.

We consider that the mass transfer process during kinetics and the agglomeration of particles is mathematically well described in literature for gas-water systems[14,17], whereas there is still a lack of experimental data of micro-scale parameters for a complete model validation (e.g., evolution of particle size distribution in time, especially for dense populations[14]; constant of proportionality of crystal integration, known as well as *intrinsic kinetics*[16,17,21]). When it comes to gas-oil-water systems, the phenomena are more complex. Literature converges to the use of the shell approach[11,15,16,22,23], where hydrates are considered to form encompassing the droplets, forming a hydrate shell with an inner liquid core (often applied to water-in-oil dispersion flow). Mathematical description has been formulated in the literature on the core shrinkage due to gas diffusion through the solid shell[15], outer growth due to water permeation[16] and gas consumption due to crystallization in the water trapped inside the porous structure[24].

Experimental evidence of the existence of this hydrate shell is presented for static systems[25–28], but has never been presented for non-static systems due to the lack of instrumentation capable of tracking one single particle along the flow during the time-scale a particle takes to initially form and grow. Recent studies in flowing systems put in question the stability of the formed shell, with probable splitting and rearrangement of the particles into a hydrate-water-oil network[29–31], which in a macro-scale form a cream/gel-like non-Newtonian mixture[32,33] (see as well videos published by Chen et al.[29]). Shell formation is associated to heterogeneous kinetics (that is, the existence of a preferential growth direction) and is reasonable in the point-of-view that hydrates will mostly grow tangentially over the droplet, where contact between water and gas is facilitated. This may not be however the case when rotational and translational movements exist between the just formed hydrate seeds and the droplet. This is in the center of discussion of this paper, where cases of non-existence of the liquid core in the particles should be, in the future, mathematically modeled using a different approach to the one that has persisted in literature so far.

The second axis of discussion of this paper is on the comprehension of how multiphase flow prior to initial formation and affinity between the phases (water, oil, hydrates) affect growth kinetics and agglomeration. A macro scale comprehension of those phenomena is widely diffused in the literature[11,19,22], based mainly on visual observation. However, the trial and error methodology is still used in order to understand slurry stability for different oils, additives, salts, etc., and major conclusions say that some additives can lose efficiency in very similar cases (e.g., salt fraction and continuous phase of the slurry can change the efficiency of the AAs). This trial and error experimentations with non-deterministic results should be interpreted as not-well comprehended phenomena that happen in a smaller scale than the ones being studied nowadays, in part due to the lack of instrumentation in such small scales.

In this sense, this study introduce new insights on phenomena description (that is, a *topological model*) of how gas hydrates form, grow and agglomerate in a much smaller scale than the ones presented so far in literature for gas-oil-water systems (focus is liquid-dominant systems). This paper is theoretical and based on the following observations given in the literature: (A) water is never entirely converted into hydrates, but gas consumption presents an asymptote, proving that a phenomenon of kinetic limitation occurs[12,13,15,16], usually interpreted as a limitation due to the mass or heat transfer processes; (B) hydrates present a highly porous structure, visualized through microscope[34,35]; (C) particles formed are visually much more voluminous than a perfect crystal should be in means of the amount of gas consumed[19,36]; (D) gas hydrates present a hydrophilic nature[16,27,37]; (E) when hydrates form, the oil-water emulsion can present a phase separation or inversion[19,36,38,39]; (F) vanishing of water phase once hydrates form[20]; (G) in the presence of surfactant additives, the hydrates structure can completely trap all liquid in the system (water and oil), called *dry-up phenomenon*[20]; (H) higher driving forces can cause stable slurries for longer time without the presence of surfactant additives (cold flow concept[40]); (I) the use of additives can change the wetted angle of water-oil-hydrates[41]; and (J) multiphase flow pattern can change all the steps of gas hydrate formation and agglomeration[7], whereas the existence of hydrates can consequently change the flow patterns and structure characteristics[42–44].

This is the first part of a series of articles intended to describe a multiscale model coupling gas hydrate formation in multiphase flow conditions. Mathematical description will be published, in a near future, in the subsequent parts of this series of articles.

2. Topological model for gas hydrate formation, growth and agglomeration

Figure 1 depicts the multiscale problem of gas hydrate formation, growth and agglomeration up to flowline plugging. The topological models available in the literature[11,19,22] explain how the first particles form (length scale in the order of $\sim 10^{2-3}\ \mu\text{m}$) and agglomerate ($\sim 10^{1-2}\ \text{mm}$) up to cause pressure drop and mixture flowrate oscillations ($\sim 10^{1-3}\ \text{m}$), which leads to plugging if the mixture shall flow through long distances before exiting the flowline ($\sim 10^{1-2}\ \text{km}$). The trend of the main parameters of the flow with hydrate formation are depicted in Figure 1(f): (i) as hydrates form, gas is consumed, with an asymptotic trend due to mass and heat transfer limitation processes[12,13,15,16]; (ii) the slurry viscosity increase as hydrates form[9,45]; (iii) pressure oscillations occur at higher hydrate fractions due to partial deposition and sloughing of hydrate masses[8,46], with an average increase in time; (iv) which is related to flowrate oscillations, with an average decrease in time up to flowline plugging. Gas hydrates form over time, which can be interpreted as a length scale since the mixture is flowing and carrying the hydrate particles as they form. As well, this time/length scale can be interpreted as dependent of the volumetric fraction of particles, as shown in the abscissa of Figure 1(f).

We propose in this study that further micro-scales shall be used to a more complete explanation of the phenomena, e.g., to understand the influence of a surfactant additive. The length scale of the flowing structures ($\sim 10^{0-3}$ mm) explains: (i) interactions of the multiphase flow pattern prior to formation with the initial particle size and particle morphology; and (ii) slurry stability, that is, the tendency the particles/agglomerates have to settle down depending on their size and on the flowrate of the mixture. However, agglomeration and flow deceleration (mainly due to gas consumption[47]) will act on destabilizing the slurry. Those phenomena are dependent on micro scale phenomena.

For the opposite direction of the length scale, we assume that gas hydrates are porous due to the high driving forces (subcoolings) and to the high amount of impurities present in production fluids. In the inter-molecular length scale (~ 1–20 Å, i.e., 0.1–2 nm, Figure 1(a)), the water molecules of the hydrate structure are in harmony with the water molecules in the liquid form, whereas in contact with the non-polar hydrocarbons, the water molecules tend to structure to minimize the energy. This cause a concavity on the water-oil interface near the hydrate surface ($\sim 10^{0-1}$ nm), which in a macro-scale is interpreted as a wetted angle. Inside of a capillary of the porous structure ($\sim 10^{2-3}$ nm, Figure 1(b)), this interface concavity cause acceleration of the water body, called capillarity force, which tends to expulse water from the porous structure of the particles to the outer surface. Water availability on the outer surface of the particles ($\sim 10^{0-1}$ μm, Figure 1(c)) causes capillarity bridges to form after particles collision. Particles collision, by its turn, is due to relative motion in the particle size scale ($\sim 10^{2-3}$ μm, Figure 1(d)). The capillarity bridges explain why particles can be sticky (often called *wet particles*). The available water will as well crystallize, consolidating the particles into an agglomerate, which can then destabilize the slurry in the length scale of the multiphase flow ($\sim 10^{0-3}$ mm, Figure 1(e)).

The presence of a surfactant can act at changing the interfacial properties near the water-oil-hydrate interface (Figure 1(a)), thus causing oil to penetrate the capillaries (Figure 1(b)), sealing water into the porous structure of the hydrate particles. Therefore, water is unavailable: (i) for capillary bridge formation, that is, particles are not sticky anymore and are called *dry particles;* and (ii) for particle consolidation into agglomerates. In this sense, affinity between phases (inter-molecular scale) and interaction of phases inside the porous structure (capillary scale) explain agglomeration tendencies (particle and inter-particle scales) which will later be important in predicting plugging at the flowline scale. Flow deceleration due to gas consumption destabilize as well the slurry. Gas consumption comes from mass transfer of gas up to the crystallization surface, which herein is considered as being the capillary walls (capillary scale).

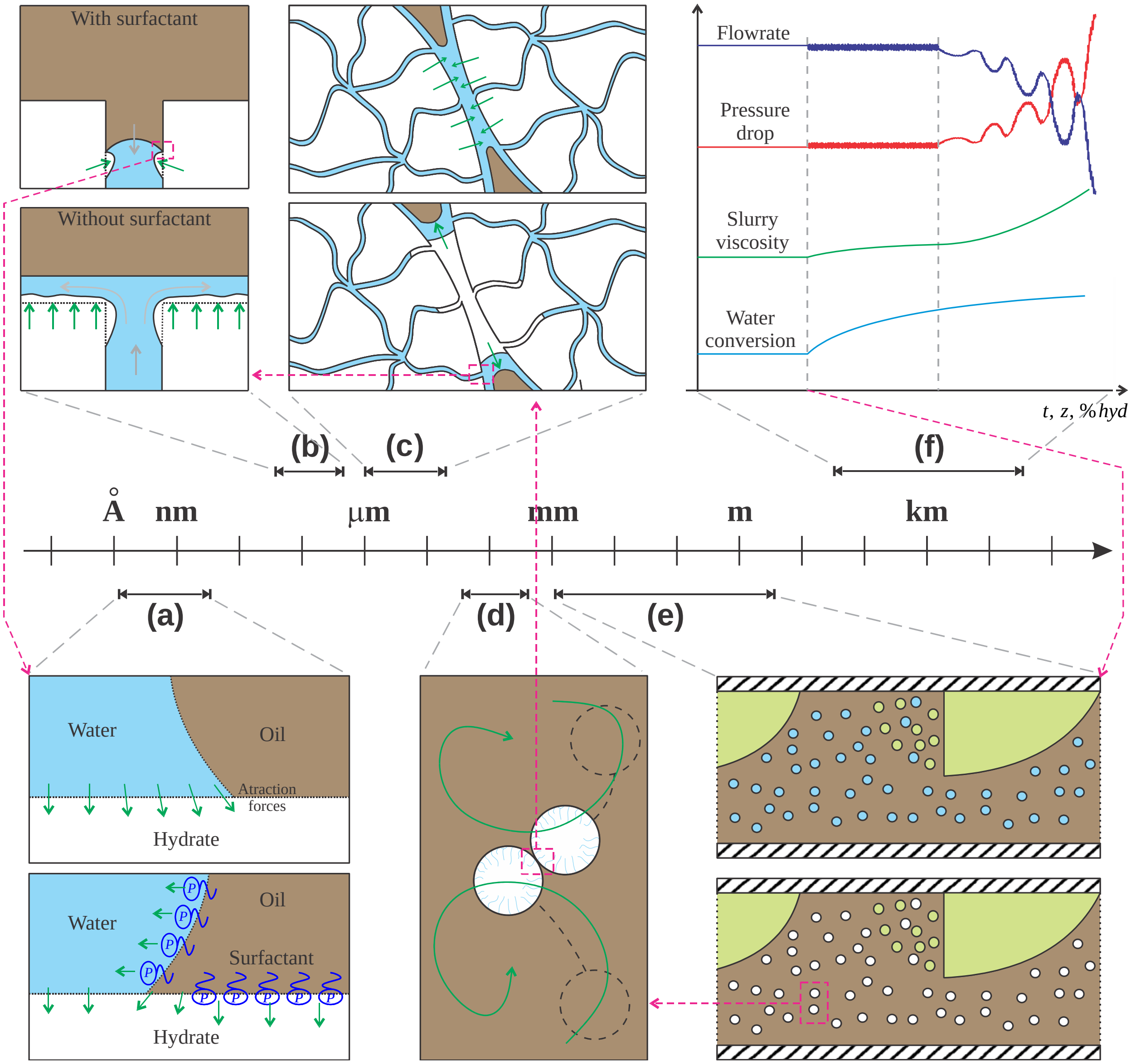


Figure 1. Depiction of the multiscale problem of hydrate formation under multiphase flow. (a) Inter-molecular scale: affinity between water, oil and hydrate is explained by distortion of the polarity in the inter-molecular length scale. The use of a surfactant additive can cause affinity inversion of hydrates from hydrophilic to oleophilic. (b) Capillary scale: without the use of a surfactant, capillarity forces expulse water from the porous structure. With a surfactant, oil tends to penetrate the capillaries. (c) Particle outer surface scale: water availability in the outer surface of hydrate particles explain existence of capillarity bridges (stickiness of particles). If particles

remain together for enough time, crystalline bridges consolidate the particles into an agglomerate. (d) Particle scale: collision between hydrate particles depends on the length scale of the particle size and of the turbulent eddies. (e) Multiphase flow scale: initial size of hydrate particles is related to the size of the droplets in dilute dispersed flows. Slurry stability depends on the size of the particles and flowrate of the carrier phase. (f) Flowline scale: uncontrolled hydrate formation causes pressure drop oscillations related to flowrate decrease up to complete blockage (plugging).

Multiphase flow pattern and particle morphology

Gas hydrates form at the energetically most favorable sites, which are usually located: (i) where gas and water are available in abundance, (ii) where the temperature is lower and/or (iii) where the increase in energy due to the creation of a new surface (the crystal) is minimum, that is, over impurities or wall imperfections. Hydrate formation over the flowline walls is therefore one energetically favorable site due to material roughness and to lower temperature compared to the mixture bulk. However, in order for hydrates to form at the wall, water needs to be present at the wall (that is, water should be the continuous phase) and gas should present a considerable solubility in water (e.g., CO_2 presents solubilities of one order of magnitude higher than CH_4 for the same temperature and pressure conditions[48]). Hydrate formation and deposition directly in the wall will gradually increase pressure drop over the flowline, decreasing the mixture flowrate, and can afterwards be submitted to sloughing with a fast plugging[7,8]. As a rule-of-thumb, simple hydrocarbons (methane, ethane, propane…) are non-polar and therefore present low solubility in water compared to its solubility in oil. Therefore, the interfaces between water and a phase abundant in gas (the gas free phase or the oil) are energetically favorable for initial hydrate formation. In this study, only hydrate formation in the interfaces are considered.

The gas-water and water-oil interfaces depend on the three-phase flow pattern assumed by the mixture before hydrate formation. The flow patterns are mainly dependent on the superficial velocities of the phases, flowline diameter and liquid viscosity[49,50]. Gas-liquid flow patterns are represented in Figure 2(a-d) and have a high influence of the flowline inclinations due to the high density ratio between the phases. The liquid in gray represents the oil-water flow. Literature (mostly) converges to the classification of the flow patterns into: (a) stratified flow, (b) dispersed bubbles flow, (c) intermittent/slug flow and (d) annular flow[49,51,52]. Sub-classifications can as well be done due to the interfaces of the stratified flow (smooth or wavy)[51,53], to the size and homogeneity of the dispersed bubbles (bubbles or dispersed bubbles)[53], to the presence of a wake zone with dispersed bubbles in the intermittent flow pattern (plug or slug flow)[54] and to the presence of wavy interfaces and entrained droplets in the gas core (wispy, wavy annular)[55,56], which sometimes is classified as an alternative flow pattern called *churn flow* (churn flow can as well be classified as a sub-pattern of intermittent flow or as a transition flow between intermittent and annular[52,55]).

When it comes to liquid-liquid flow patterns (that is, water-oil flow patterns), classification is disparate in literature[50,57–59]. Flowline inclination is not so important due to similar density between the phases, and therefore interfacial forces become important. That is, interfacial tension between the liquids and flowline wettability by both liquids is of most importance[50]. Figure 2(e-n) presents some reported liquid-liquid flow patterns. Dispersion flow can either be: (e-f) dilute or (g-h) dense. Stratified flow can have: (i) no mixing or very low mixing at the interface, (j) one layer of dispersion or (k) two layers of dispersion, called as well as dual flow. Intermittent flow is related to a swarm of drops (l) instead of an elongated body such as in gas-liquid flow patterns. Annular flow (m), also known as core flow, is related to highly viscous oils. Free phase flow (n) is related to low mixture velocities.

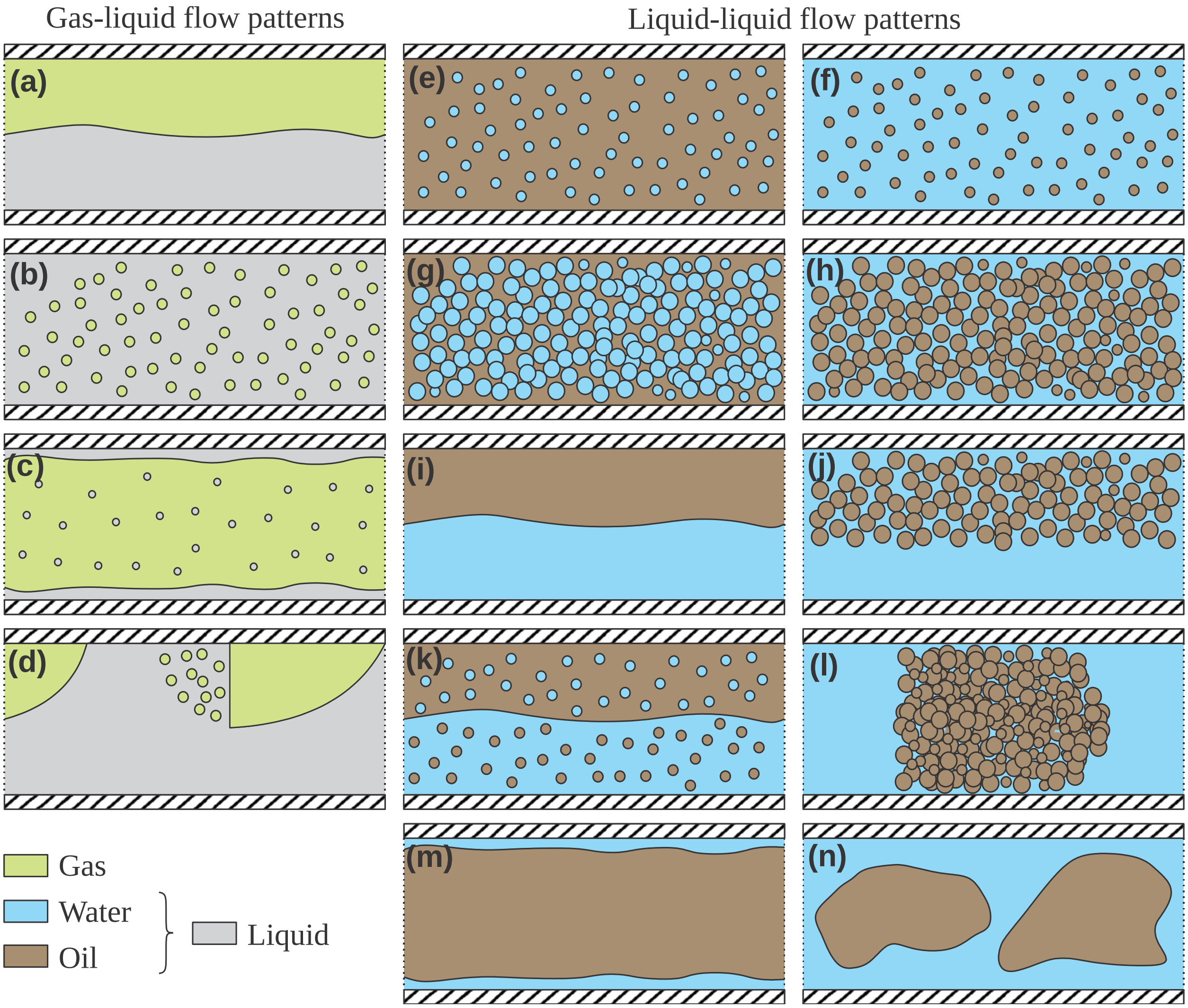


Figure 2. Gas-liquid flow patterns: (a) stratified flow, (b) dispersed bubble flow, (c) annular flow and (d) intermittent/slug flow. Liquid-liquid flow patterns: (e-f) dilute dispersed flow with oil and water continuous phase, (g-h) dense dispersed flow with oil and water continuous phase, (i) completely segregated/stratified flow, (j) stratified flow with one layer of dispersed flow, (k) stratified flow with two layers of dispersed flow, also known as dual flow, (l) intermittent/slug flow, (m) annular/core flow and (n) free phase flow.

Classification of the gas-oil-water flow before hydrate formation is key to understand where hydrates will nucleate and the initial morphology of the particles. It is not the purpose of this work to present flow pattern classification. Literature already present studies on stability criteria for flow pattern transitions for gas-liquid[49,51,52] and liquid-liquid flow systems[50], and as well correlations for the size of droplets[60–62], the phase fraction and lengths of the different regions of the intermittent flow[63,64] and phase inversion criteria[50,65,66].

Although a perfect characterization of all the structure sizes and all boundary conditions of three-phase gas-oil-water flow patterns is not yet established in the literature, herein we discuss the expected particle morphology that may happen over large and small surfaces and in dilute and dense flows, experimental evidence (J). Hydrate formation in large surfaces as presented in Figure 3(a) will generate flaked particles that will most probably detach from the interface due to shear of the liquid phase. Representation of oil-water interface is done in Figure 3(a), but the concept can be extended for a gas-water interface as well. Large interfaces happen mostly in stratified, intermittent (in the elongated bodies) and free phase flows. In cases of large interfaces where the gas is the predominant phase at the bulk (e.g., annular flow), the particles grow directly over the wall as a deposit[7,67–70], and a slurry flow will not be present. In smaller interfaces, the hydrates are considered to quickly encompass the entire drops/droplets. In the case of a dense flow (Figure 3(b-c)), the drops are very close to each other or even touching themselves, and hydrate formation of an 'agglomerate' happens from the beginning (see experimental observation of these particles in Fig. 4 of Chen et al.[29]).

For dilute dispersed flow, each droplet is considered as forming hydrates separately (Figure 3(d-e)). For water-in-oil emulsion flow, literature considers that gas hydrates form as shells surrounding the water droplets[11,16,71–74] (Figure 3(g)). Tangential growth is considered as predominant over radial growth (Figure 3(f)) because there is no need of diffusion through the hydrate layer just created. This preferential growth is called heterogeneous kinetics and leads to the formation of a shell of hydrate, which traps a water core (Figure 3(g)). Whereas experimental evidences of this shell formation exist for droplets of water in static fluid[25–27], there is no experimental evidence when the continuous phase is in movement and the interfaces (gas-liquid, liquid-liquid, solid-liquid) are constantly deformed/renewed.

If the continuous phase is not static, it can promote relative motion between the hydrate seed crystal and the water droplet (Figure 3(h)). In this case, the just formed crystal can freely rotate and/or be removed from the surface (as observed at the water/gas interface in batch reactor[14]) and no preferential growth will happen. This is called homogeneous kinetics and, in this case, a water core will not be formed (Figure 3(i)). The particles will therefore form a sponge-like structure. Experimental evidences (A) and (C) (presented in the introductory section of the article) were used in literature to support the shell approach (Figure 3(g)); however, the same evidence can come from water entrapment in the hydrate porous structure and support the sponge approach (Figure 3(i)). See further evidence of water sealing into the porous structure in Fig. 7 of Adamova et al.[75].

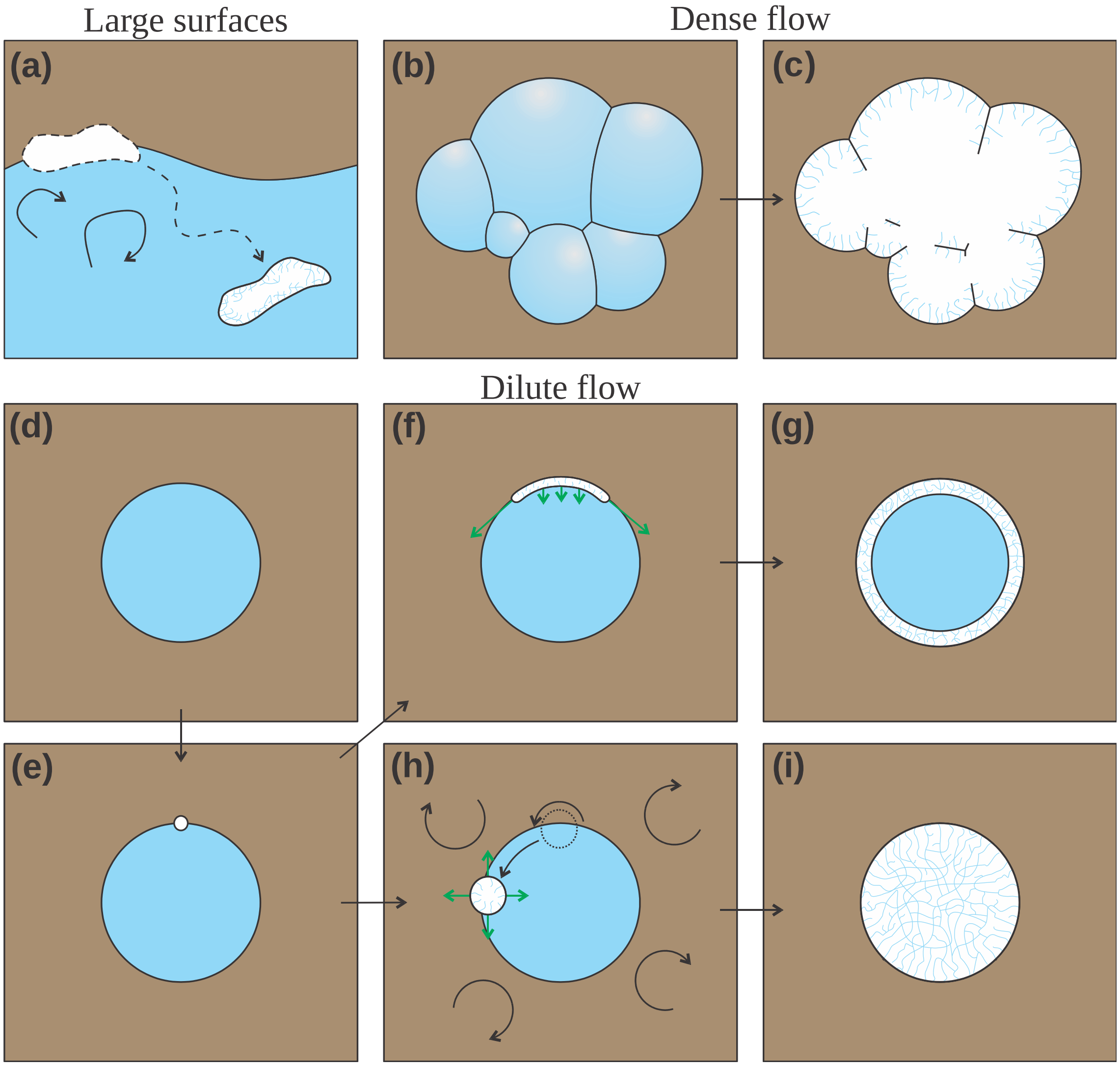


Figure 3. (a) In large interfaces (e.g., stratified flow), the particles form as a flake and easily detach due to flow shear. (b-c) In dense flow, drops are very close to each other and initial particles are related to the size of the aggregates of drops. In dilute flow: (d-e) first seed crystal in the droplet interface; (f-g) in static systems, tangential growth prevails (heterogeneous kinetics), forming a hydrate shell that encompasses a water core; (h-i) in non-static systems, relative motion between crystal and particle do not promote any preferential growth (homogeneous kinetics) and water core is not created (called sponge-like particle).

Affinity between phases and liquid entrapment in the hydrate porous structure

In any of the cases of hydrate formation (over large surfaces, over drops in dense flows or droplets in dilute flows), the particles will present different length scales of porosity (see Fig. 1 of Staykova et al.[34]). The smaller length scale of porosity is due to crystal growth. High driving forces, ionic force and impurities (often present in any hydrocarbon production) promote initial preferential growth directions (Figure 4(a-b)). After that, the heat release and gas consumption due to hydrate growth of the far end of the dendrites reduce the driving force for their lateral growth, forming the porous structure (Figure 4(c-d)). This dendritic growth of gas hydrates towards the water phase is observed experimentally in Fig. 2 of Adamova et al.[75], but the dendrites are in a much larger scale since their experiments are for static systems.

Larger porous length scales are due to agglomeration and consequent imprisonment of the interstitial liquid (Figure 4(e-f)). Agglomeration of different sizes of particles will cause different porous length scales, e.g., agglomeration of small crystals seeds just formed over a droplet, agglomeration of particles formed encompassing a droplet, agglomeration of agglomerates at different levels.

Gas hydrates have hydrophilic nature[16,37], experimental evidence (D). The oil is herein considered totally non-polar and therefore with no affinity with water and hydrates. This is mainly valid for an oil composition of simple hydrocarbons only. The use of a surfactant can change affinity between the phases. Some oils already present natural surfactants in their composition[38], but effects shall be similar to the use of a surfactant into a non-polar oil.

Figure 5(a) shows that near the water-oil-hydrate interface, the water molecules of the crystal tend to form hydrogen bonds with the water molecules in the liquid phase. Meanwhile, the non-polar molecules of the oil phase do not interact with the crystal. This promotes an asymmetry in the polarity near the water-oil-hydrate interface, pushing forward the water and causing a better wettability of water over the crystal surface. If this happens inside of a capillary of the porous structure, then the water-oil interfacial tension promotes displacement of the entire body of water, Figure 5(b). In a macro point-of-view, this is called capillarity force and tends to expulse the water that is initially trapped inside of the particle.

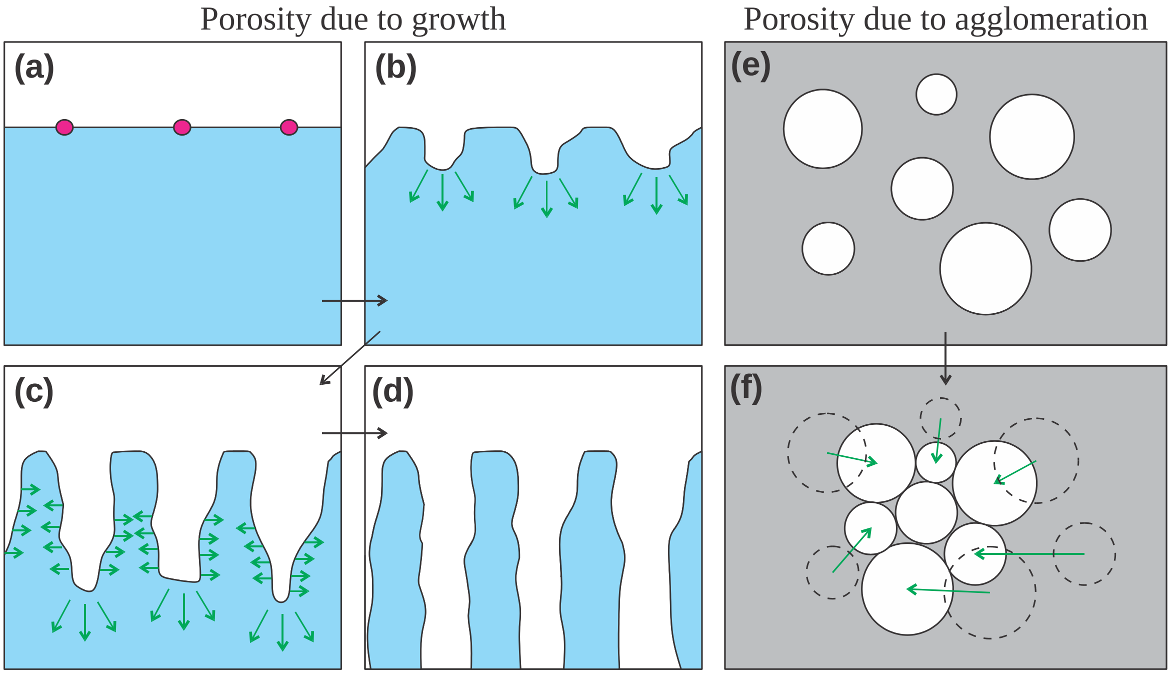


Figure 4. Gas hydrates present porous structure. Porosities due to crystal growth: (a-b) The presence of impurities, ionic forces and/or high driving forces induce initial preferential growth directions; (c-d) the gas cannot reach deeper regions of the formed grooves due to heat generation and gas consumption, forming the porous. (e-f) Agglomeration traps interstitial liquid forming another scale of porosity.

The introduction of surfactants can promote the inversion of ‘nature’ of gas hydrates from hydrophilic to oleophilic, thus entrapping oil into the capillaries. Figure 5(d) show that surfactants may stick to the interfaces between a polar phase (water, hydrate) and a non-polar phase (oil). Those attractions make the asymmetry of the polarity near the water-oil-hydrate interface to decrease (causing less water permeation), to vanish (causing capillarity forces to cease) or even to invert (inverting capillarity forces and causing oil to penetrate the capillaries). Here we consider that surfactants invert the concavity of the oil-water interface, experimental evidence (I), thus entrapping oil into the capillaries. Furthermore, evidence (G) show that the hydrate structure can completely absorb all liquid in the system (water and oil) if a surfactant is used (for low liquid loading systems), which supports the affinity inversion.

It is important to notice that Figure 5 is valid for small length scales of the porous structure, where capillary forces are important. In the case of porous scales formed by agglomeration (Figure 4(e-f)), the interstitial liquid entrapped is preferably the liquid that has affinity with hydrates (e.g., water when no surfactants are used), but can as well be the other one if the created pores attain larger sizes (that is, agglomeration of agglomerates). An example is the imprisonment of oil observed by Chen et al.[29] even without the use of surfactants. Still in the same article, the authors discuss the appearance of an “ice cream-like” non-Newtonian fluid in the presence of additives, explained by a higher degree of entrapment of oil in the hydrate network formed. This is further evidence of easier oil entrapment when hydrate affinity is inversed (Figure 5(d-f)). In any case, in this study we focus on the small porous scales formed prior to agglomeration, which are determinant on understanding the agglomeration process as will be discussed in the later sections. In this case, the entrapped liquid is water only if no surfactant is used; or preferentially oil if an effective surfactant is used, but yet with a degree of affinity with water.

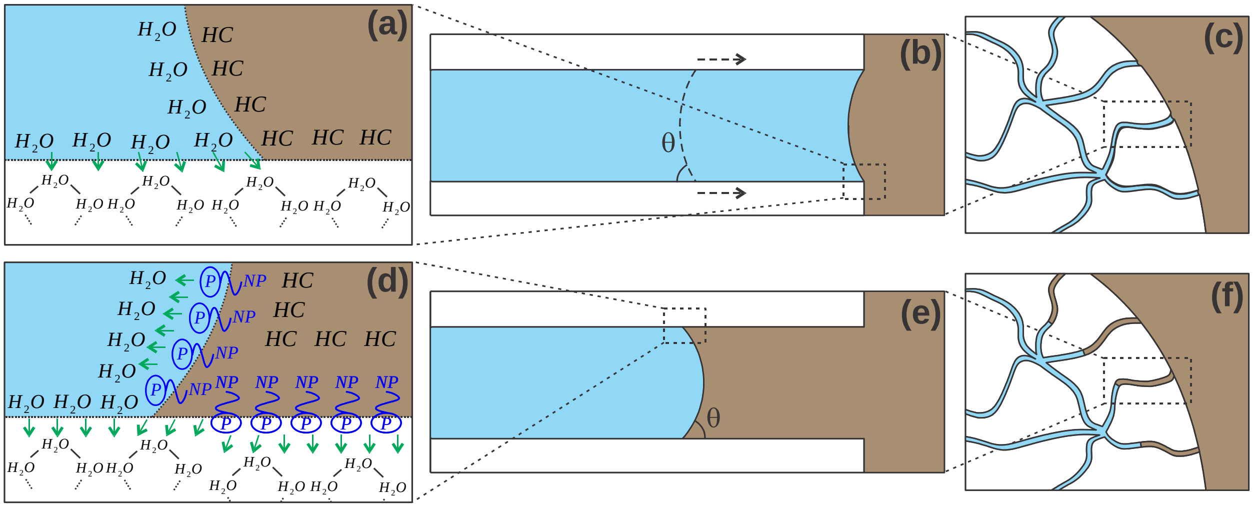


Figure 5. Depiction of liquid entrapment inside hydrate porous structure without (a,b,c) and with (d,e,f) the presence of surfactant. Without surfactant: (a) affinity between water and hydrate surface create a distortion in the electromagnetic field near the hydrate-water-oil interface. This attracts water, curving the water-oil interface. (b) If the capillary is small enough, this curved surface pushes forward the water body to the exit of the capillary (outer surface of the particle). (c) Water fills-up the entire capillaries of the hydrate porous structure. With surfactant: (d) the polar part of the surfactant can invert the polarity distortion, (e) resulting in an inversion of capillarity forces and (f) oil penetrates part of the capillaries. (Legend: HC = Hydrocarbon, P = Polar end of the surfactant, NP = Non-polar end of the surfactant).

Figure 6 presents the topological model of initial formation of hydrate particles with and without surfactant additive for oil and water continuous flow. Representation of initial hydrate formation over small droplets of a fine dispersed flow is done, but the concept can be applied to any kind of flow pattern (since capillary-scale and particle-scale are in different order of magnitude). Without surfactant, the hydrate porous structure will entrap only water (Figure 6(a-b) for oil continuous flow; Figure 6(e-g) for water continuous flow). This porous structure acts as a *sponge*, making all water of the system to vanish almost instantly, experimental evidence (F). In the case of water continuous phase, water consumption due to crystal growth plus water entrapment in the sponge can cause a phase separation for high water cut systems (Figure 6(f)) or a phase inversion in the case of intermediary water cut (Figure 6(g)), supported by experimental evidence (E). It is important to notice that an initial case of water continuous flow (Figure 6(e)) can, after the onset of hydrate formation, behave similarly to a case of oil continuous flow (since Figure 6(b,g) present similar morphologies).

In a macro-scale, the use of surfactants will decrease the size of the droplets prior to the onset of hydrate formation, as to be discussed in the agglomeration section. In the capillary scale, the use of surfactants enhance the affinity of the oil phase with hydrates and, as the first crystals rotate and translate over the droplets (Figure 6(c) for oil continuous; and Figure 6(h) for water continuous flow), the sponge structure absorbs both oil and water (although with surfactant the hydrate is preferentially oleophilic, it still has affinity with water, so both oil and water can be entrapped in the porous media). We consider here that the inner volume of the particle will present the liquid contained in the droplet, whereas the outside of the particle will contain the continuous phase (Figure 6(d,i)). In the oil continuous case (Figure 6(d)), the oil will always penetrate the capillaries, thus turning water unavailable in the outer surface of the particle. This has an important role on the growing surface for kinetics and on disruption and consolidation rates for the agglomeration process, discussed in the next sections.

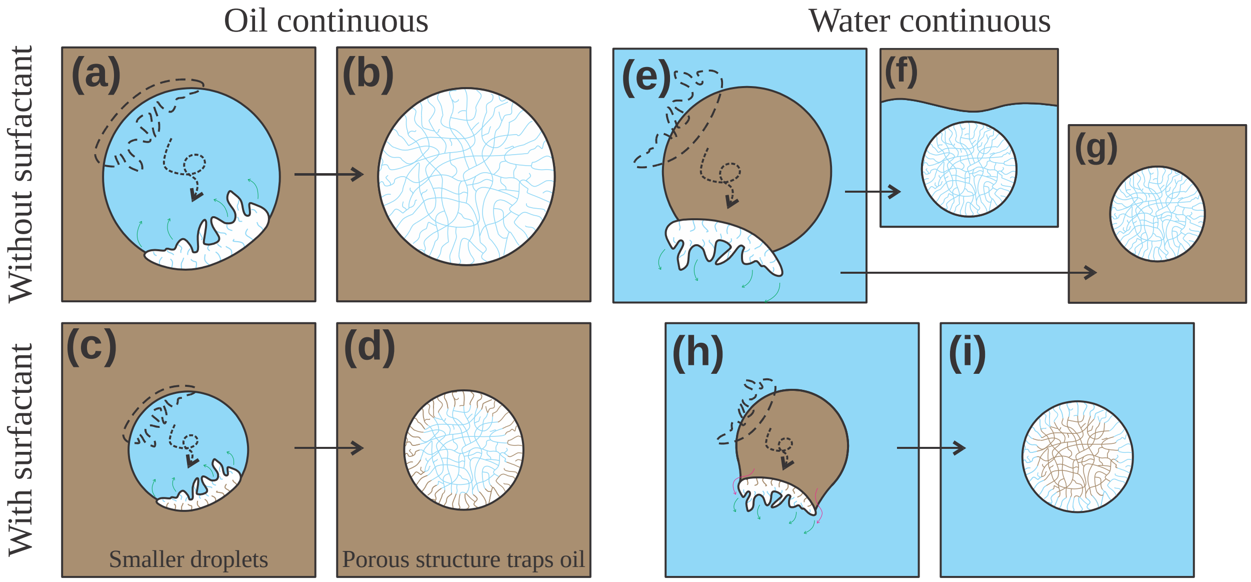


Figure 6. Surfactants cause hydrate porous structure to trap oil and droplet size to decrease. Oil continuous: (a-b) without surfactant, the hydrate porous structure traps only water; (c-d) with surfactant, the hydrate structure traps oil mostly in the outer surface, and the inner particle traps water. Water continuous without surfactant: (e) the hydrate porous structure traps water only, which can cause (f) phase separation or (g) total phase inversion. Water continuous with surfactant: (h) as the first crystals are formed and grow in the droplet interface, the oleophilic nature of hydrates makes oil to constantly wet the particle, (i) trapping oil in the inner of the particle and water near the outer surface.

Water permeation vs. crystallization in the capillary walls

Crystal growth occurs preferentially at the water-oil-hydrate surface, which can be: (i) in the outer surface of the particle, if water is available at this surface, especially in the case of water continuous flow (Figure 7(a)); or (ii) in the capillary walls, with consequent filling-up of the porous structure (Figure 7(b-c)). The case of oil continuous flow without surfactant (Figure 7(c)) can be submitted to both outer growth and capillary filling-up depending on the competition between gas diffusion into the capillaries and water permeation through the porous structure.

Figure 8 show insight at the capillary scale near the outer surface of the particle for the case of oil continuous flow without surfactant. In this case, capillarity forces act on expulsing water from the sponge, as already discussed from Figure 5(a). For slow water permeation (Figure 8(a)), the gas penetrates into the capillary due to diffusion through water, crystallizing at the capillary walls (Figure 8(b-c)). Therefore, the porous structure is sealed, trapping all water inside the particle (Figure 8(d)), and the particle is called *dry*. Once the capillaries are closed, water and gas have no contact anymore, which is a mechanism of mass transfer limitation and could explain experimental evidence (A).

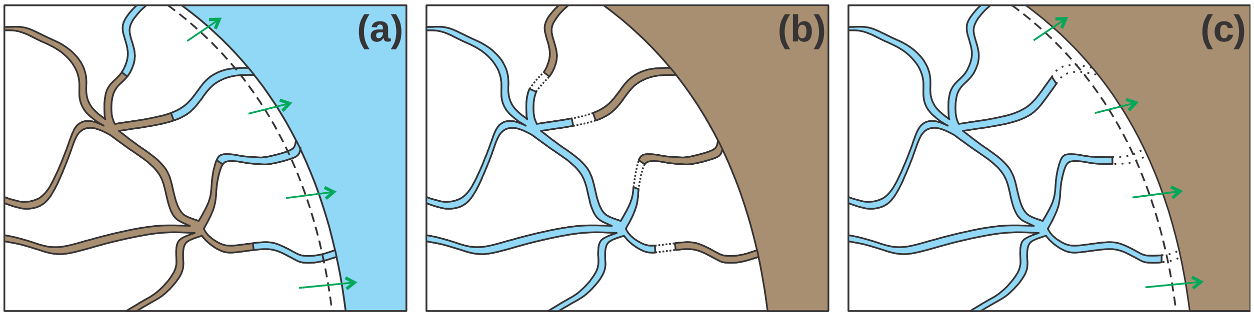


Figure 7. Surface where crystal growth takes place. (a) In water continuous flow, crystal growth occurs in the outward surface of the particle. (b) In oil continuous flow with surfactant, capillaries are filled-up. (c) In oil continuous flow without surfactant, both outward growth and capillary filling-up can occur depending on the competition between gas diffusion into the capillaries and water permeation through the porous structure.

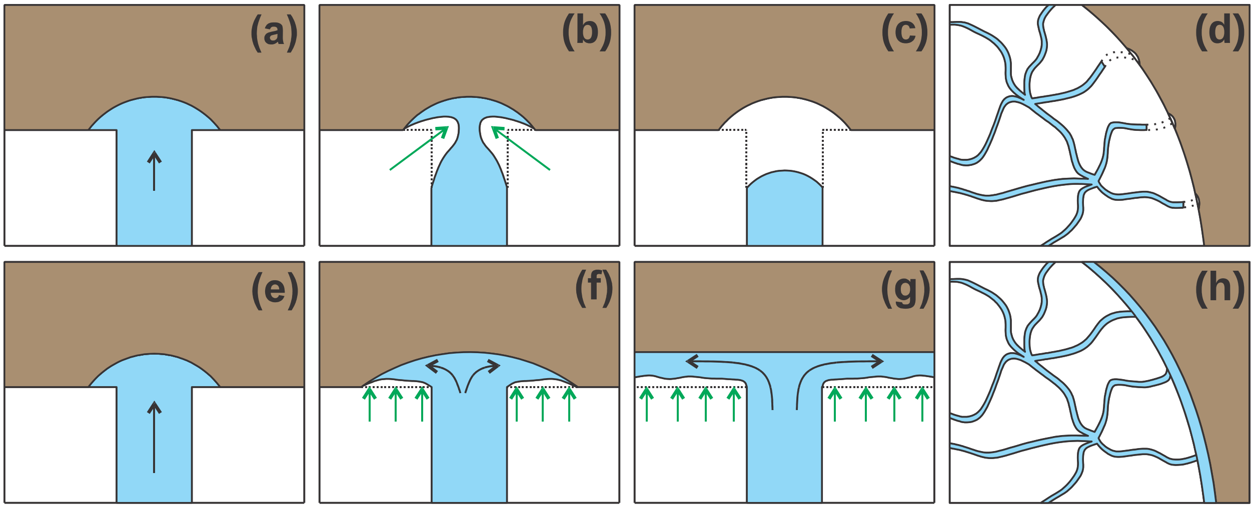


Figure 8. Depiction of the interaction between the hydrate porous structure and the solid bridge formation in oil continuous flow without surfactant. If gas diffusion in water is faster than water permeation: (a) water is slowly expulsed from the capillary; (b) gas diffuses in water and reach the capillary wall near the capillary entrance zone, where crystal growth happens; (c) a hydrate cap/solid bridge is formed, blocking the capillary entrance; (d) the water is sealed inside the porous structure, and the particle is called *dry*. If water permeation is faster than gas diffusion in water: (e) water is expulsed from the capillary at a considerable velocity; (f) gas cannot diffuse in the direction of the capillary walls because it is constantly expulsed due to convection of the water stream in the capillary; (g) water starts to accumulate in the outer surface of the particle and outer growth takes place; and (h) a water layer covers the outer surface of the particle, which is called a *wet* particle.

For high velocities of water permeation, convection does not let gas to diffuse and to accumulate near the entrance of the capillary (Figure 8(e)). In this case, water starts to accumulate at the outer surface (Figure 8(f-g)). Gas can then penetrate this water layer and crystallize with consequent outer growth of the particle. In this case, a water layer will always be available at the outer surface of the particle (Figure 8(h)), and the particle is called *wet*. The influence of a dry or wet particle in the agglomeration process is discussed in the next section.

Most probably both mechanisms of Figure 8 will compete and change predominance over time. In the beginning, the higher amount of capillaries, with related larger radiuses and smaller lengths (that is, smaller head losses) cause higher water permeation rates. As the particle starts to grow outwardly, the capillaries increase in length, increasing head losses as well. Then gas starts to gradually penetrate, forming caps over some of the capillaries. These caps are fragile and may present easy cracking due to turbulent flow and consequent particle squeezing (Figure 9(a,b)), turning it possible for water to permeate again. The filling-up process of the capillaries can itself cause water squeezing from the particle, since the formed gas hydrate is more voluminous than the consumed water (Figure 9(c-e)). Filling-up occurs from outward to inward in the capillary (Figure 9(e)), which traps water and locally increase its pressure. This can cause cracking of the just formed caps or the formation of new capillaries.

With time, the predominance changes from water permeation to gas diffusion into the capillaries and the particle starts to seal by a layer of hydrate crystal, which traps a sometimes considerable amount of water inside the particle far from the contact with the gaseous phase dissolved in oil (experimental evidence (A)). For further hydrate formation, gas diffusion through the solid bridges is needed (which is negligible at the temperature range where hydrates form), or enough particles squeezing should exist to break the (every time stronger and stronger) solid bridges. Another way of exposing new capillaries filled with water to the oil continuous phase is due to breakage of the particles, as discussed in the next section.

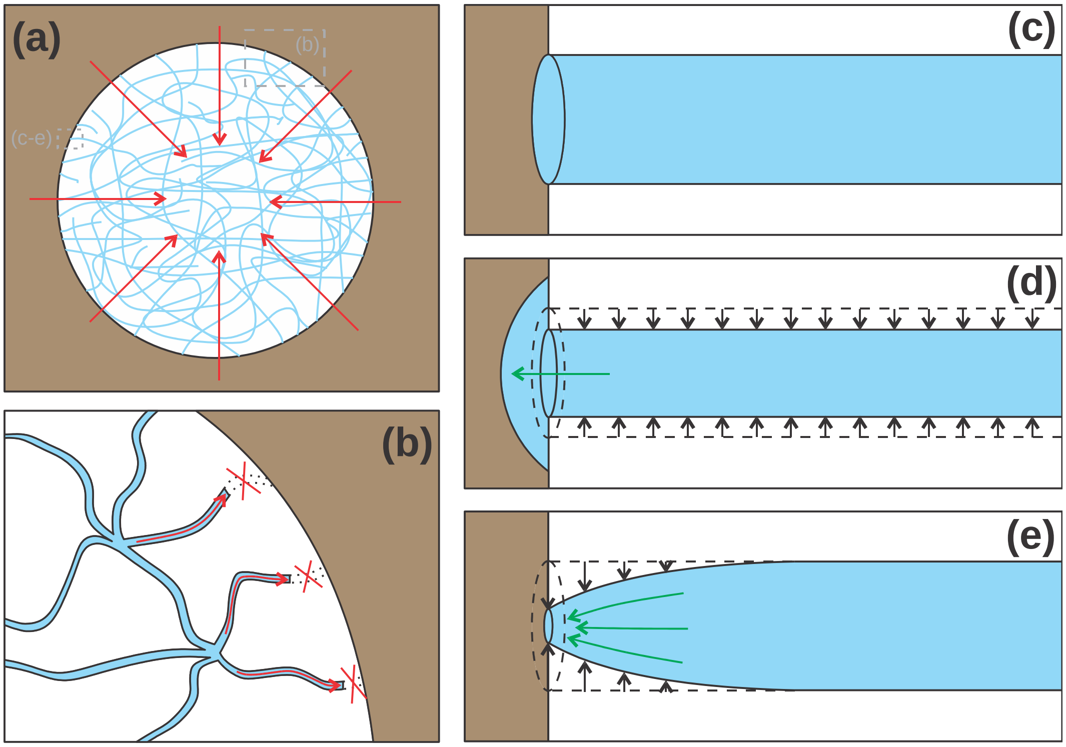


Figure 9. The hydrate porous structure is said to be 'alive', since capillaries close-up due to crystallization in their walls and the capillaries may reopen (or new capillaries may be formed) by crystalline cracking. (a-b) Flow oscillations squeeze the particle, causing crystalline cracking. (c-e) Crystallization in the capillary walls cause water expulsion, since the volumetric rate of hydrate formation is higher than the volumetric rate of water consumption. (d) If the growth is slow and homogeneous, then water is slowly expulsed from the capillary. (e) However, usually higher growth rates are present near the entrance zone of the capillary, causing water to be entrapped and squeezed with consequent crystalline cracking.

The role of surfactants in avoiding agglomeration

In order for hydrate particles to agglomerate, they firstly need to collide. In a simplified way, this can be estimated through a collision probability. The collision probability between three or more particles is considered very improbable and therefore is neglected[76]. So far in the literature of gas hydrates, population balance models that take agglomeration into account considered turbulent regime for particles collision[14,77,78]. Particle regime of relative movement is dependent on the continuous flow regime and on the particle size. Although transition from laminar to turbulent flow of the continuous phase in multiphase flow is an open question in literature, as a rule-of-thumb the continuous phase can be considered in turbulent regime due to the interactions that one phase introduce into another. That is, it is expected that transition from laminar to turbulent flow in multiphase systems occurs in considerable lower velocities than in single phase systems[79].

Independent on the continuous phase being in turbulent regime, the movement between particles can be submitted to different regimes depending on their size, as depicted in Figure 10(a.1). Particles smaller than the Batchelor scale[80] are not influenced by the flow and assume a diffusive-driven movement, called Brownian motion. Particles with size in between Batchelor and Komolgorov scales[80] are carried out by the turbulent eddies, without ever escaping them. From the point-of-view of the particles, they flow inside the turbulent eddies as in a laminar regime. For particles larger than Komolgorov scale, the particles escape the turbulent eddies and particles from different eddies can collide. In this case, particle movement is said turbulent. Since hydrate particles grow and agglomerate over time, a regime transition can occur. For particles formed over very fine dispersion flow (that is, over shear stabilized emulsions), the initial particle size is small and collision can occur at a laminar regime. The initial particles formed over the droplets are usually too large to reach Brownian regime, unless we consider the movement of the seed crystals formed over one droplet.

But not just because two particles collide that they will form an agglomerate. For simplification purposes of population balance models, there is the concept of agglomeration efficiency, which is a value in between zero and one that relates the amount of particles that collide with the amount of particles that actually agglomerate. The agglomeration efficiency can be split in other smaller processes, as pointed out in Figure 10.

The well-stablished models of collision probability[76,81,82] shall be corrected by a collision efficiency, since they do not capture the interactions between particles as they approach themselves. Those interactions are well stablished in means of London-van der Waals forces[83] (Figure 10(a.2)) coupled with double layer of counterions over the outer surface of particles (Figure 10(a.2)), which together are called *DLVO theory*[76]. In this theory, relative motion between particles shall overcome an energy barrier due to the electrostatic interaction once particles are close to each other. Further corrections on the collision probability is done in means of the inertia of the expulsed water as the particles approach themselves, called drainage forces.

So far, literature considers that surfactants act at neutralizing the DLVO attractive forces[46,84]. The DLVO theory explains forces in between very small particles, for inter-particular distances of up to 100 nm[76], and therefore particles larger than 1 μm do not have enough surface of contact in this inter-particular scale length. The droplets of the finest dispersion flows that give the initial size scale of the formed particles/sponges are usually higher than 30 μm. Therefore *DLVO theory should not be used to explain the role of surfactants as Anti-Agglomerants of hydrates in water-oil dispersed systems*.

We should outline that DLVO theory has its niche into explaining agglomeration of seed crystals formed over a water droplet (Figure 3(h) for more than one seed crystal). DLVO theory can as well explain the aggregation of small-with-large particles, being the small particle a solitary seed crystal flowing in the continuous phase. Solitary seed can nucleate in the bulk when water is the continuous phase; or can come from attrition (fine breakage)[14,83,85]. However, the main phenomenon for pipeline plugging is due to aggregation of large-with-large particles. Therefore, we emphasize the importance of the mechanism that is proposed next for Anti-Agglomeration rather than the use of DLVO theory for water-oil flowing systems.

Once particles collide, they flow together for some time. This is called an aggregate and can be easily disrupted due to shear stresses of the flow (Figure 10(b)). When oil and water are available near the outer surface of the particles, there is formation of a capillarity bridge in between them. This only happens if oil is the continuous phase, surfactants are not used, and the porous structure is not yet sealed (Figure 8(f)). In the case of the formation of this capillarity bridge, aggregate disruption is considerably harder and the particles are said to be sticky. That is, once particles collide, they remain aggregated for a much longer time.

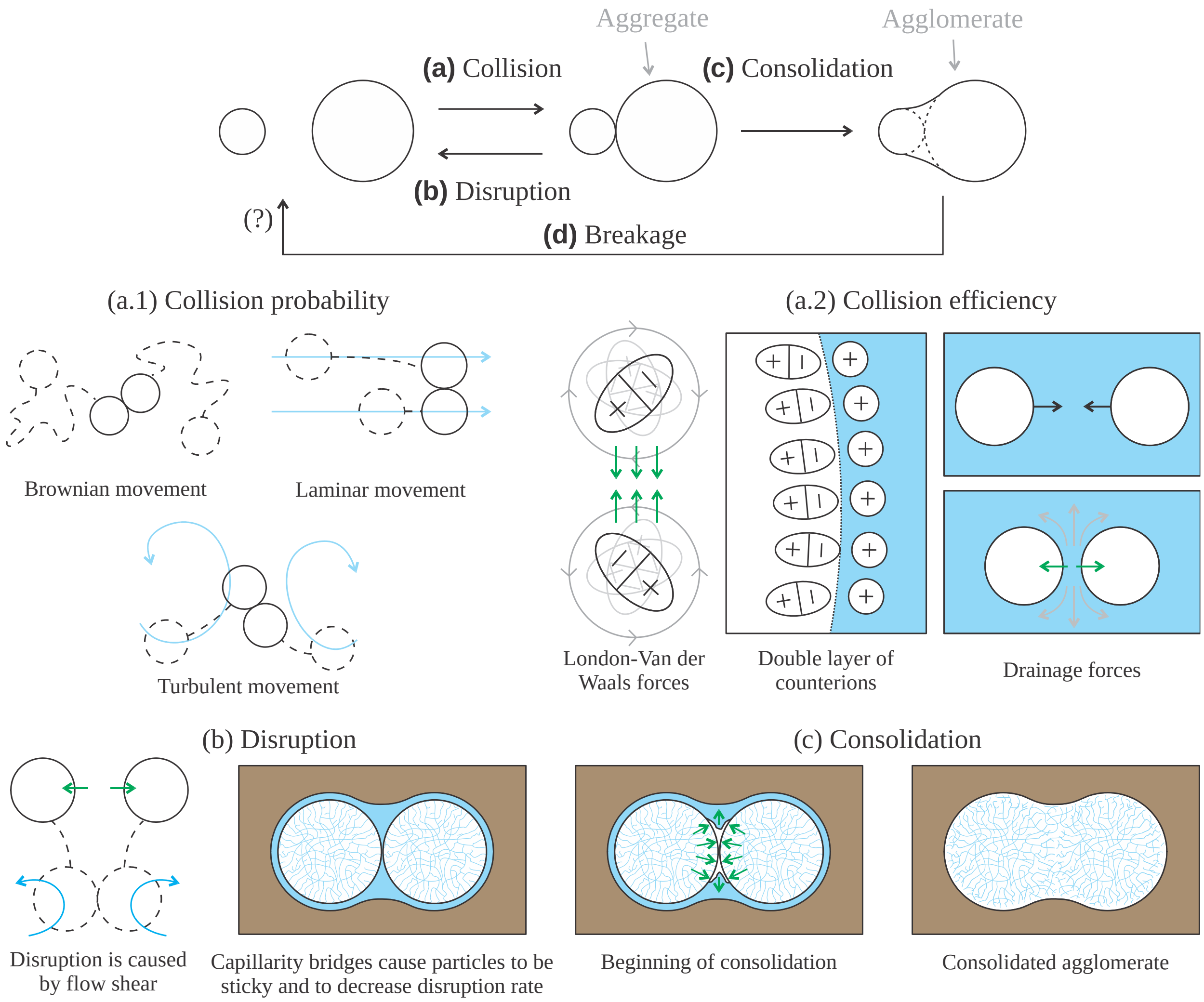


Figure 10. Depiction of agglomeration steps. (a) Two particles have a deterministic probability of collision dependent on their relative motion. Forces due to the approaching of two particles are estimated as a collision efficiency. Two particles that collide and remain together are called an aggregate. (b) Aggregates can disrupt due to flow shear. Disruption is decreased if capillarity bridges form due to water availability in the outer surface of the particles for oil continuous flow. In this case, particles are sticky. (c) Aggregates can consolidate into an agglomerate due to crystal bridge formation in between the initial particles. (d) Splitting of agglomerates due to flow shear is called breakage and not necessarily makes particles to return to the same initial size as they were before agglomeration.

With particles aggregated and with water available at their outer surface, crystal growth happens, consolidating the particles, (Figure 10(c)). This process is called *crystal bridge construction* or *consolidation*, which forms an agglomerate. The agglomerate is much harder to split than the aggregate; therefore, splitting of agglomerates is called breakage (Figure 10(d)), whereas splitting of aggregates is called disruption (Figure 10(b)). It is important to notice that breakage not necessarily will cause the agglomerate to return to the same initial particles as before collision, which is one of the problems of modeling breakage using population balance approach[14].

From the above-mentioned phenomena, probably the most important ones for catastrophic agglomeration of gas hydrates up to flowline plugging are collision of particles, formation of capillarity bridges, and consolidation. Collision of particles is enhanced by the formation of larger initial particles. The larger the drops/droplets of the water-oil dispersion prior to hydrate formation, the larger the initial particles. Surfactant acts into decreasing oil-water interfacial tension, thus decreasing droplets size/initial size of particles[61,62], with related smaller collision rates, as depicted in Figure 11.

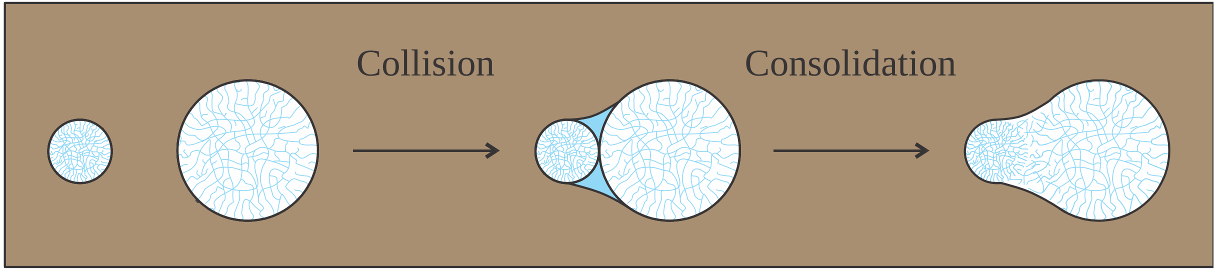
Capillarity bridges will cause the particles to be sticky. With the use of surfactant in oil continuous flow, oil always permeate into the capillaries (Figure 5(f) and Figure 6(d)). In this case, particles are not sticky and then remain aggregated for less time. This causes the disruption rate to increase, as pointed out in Figure 11(a-b). Furthermore, this stickiness (existence of capillarity bridges) also explain deposition of particles into the wall, as to be discussed in the next section. In water continuous flow, the use of surfactant is not related to changes in the disruption rate, since the sponges are considered as always trapping all the oil inside of the porous structure, far from the outer surface.

Finally, consolidation of particles into agglomerates will only happen if water is available at the outer surface of the aggregate. For the case of water continuous flow, there will always exist a degree of consolidation. The consolidation rate can however be reduced if ever crystal integration is decreased in the presence of the surfactant additive, that is, if the surfactant act as a kinetic inhibitor[86]. This can be interpreted as the surfactant blocking the active surface for crystallization or disturbing the electromagnetic field for the formation of the hydrogen bonds of the new hydrate cages.

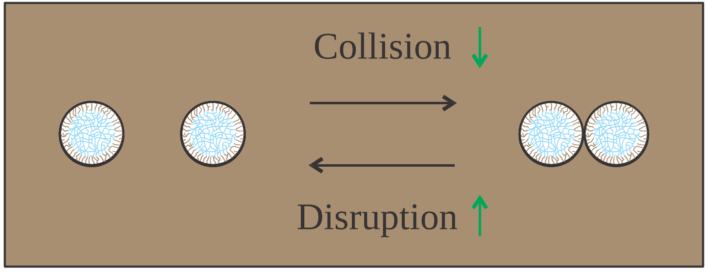
In the case of oil continuous flow without surfactant, the only way to block water availability in the outer surface is by promoting complete capillary filling-up in the outer surface of the particle. That is, the particles need to be sealed by the exterior, trapping all the water inside of the sponge. This will depend, of course, on the driving force and diffusion resistances of the system in order to promote a quick filling-up of the particles before they collide and consolidate. This explains experimental evidence (H), where higher driving forces cause faster capillaries filling-up processes, with consequent enhanced slurry stability.

The easiest way then to avoid consolidation in an oil continuous flow is by the use of surfactants, where oil will permeate the sponge near the outer surface of the particles and water will never be available, as pointed out in Figure 6(d). This causes the consolidation rate to vanish, as presented in Figure 11(b).

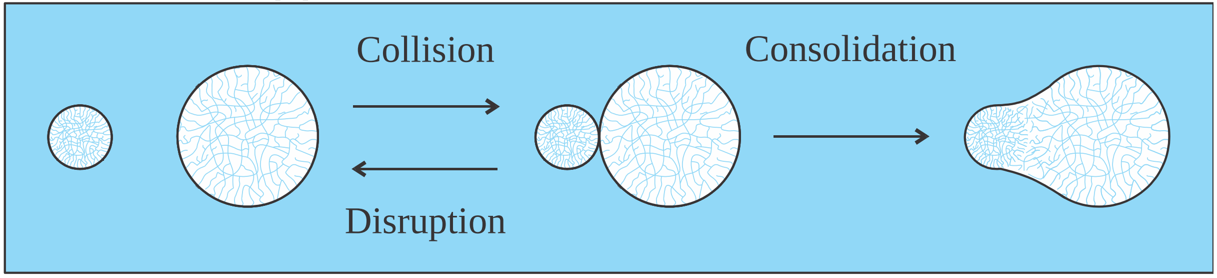
(a) Oil continuous flow without surfactant



(b) Oil continuous flow with surfactant



(c) Water continuous flow without surfactant



(d) Water continuous flow with surfactant

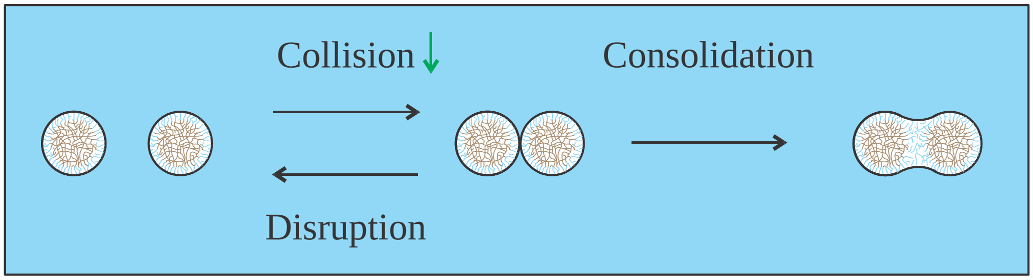


Figure 11. Presence of surfactant decrease and homogenize the droplets sizes, decreasing collision rate. (a-b) The presence of surfactant in oil continuous flow act on eliminating the capillary bridges, enhancing disruption of aggregates; and in eliminating consolidation of particles into agglomerates due to water unavailability in the outer surface of the particles. (c-d) The presence of surfactants in water continuous flow is less important in the agglomeration steps.

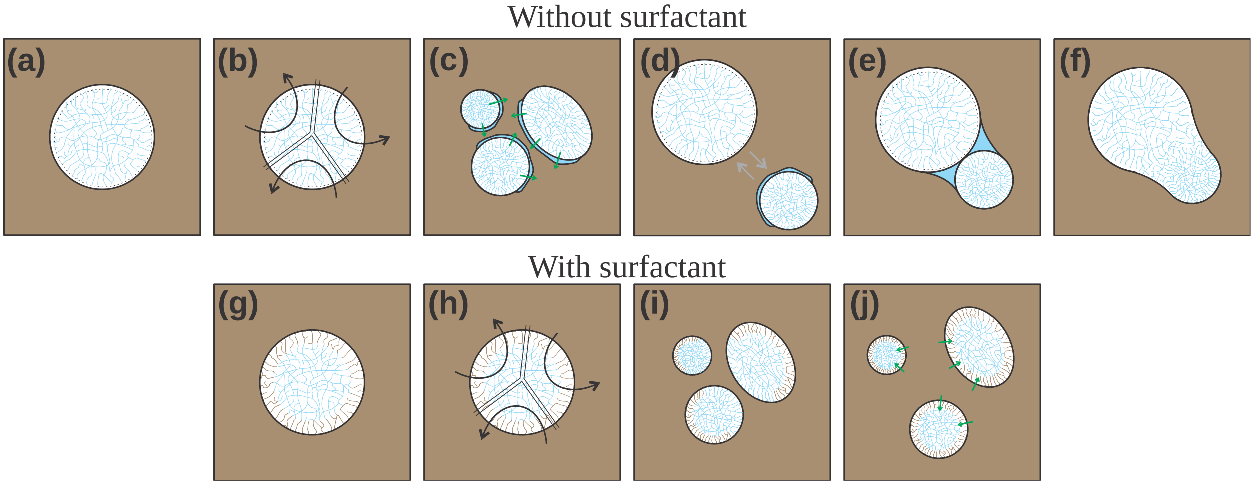


Figure 12. Breakage and agglomeration of particles in oil continuous flow. Without surfactant: (a-b) Even if capillaries are already sealed-up, breakage of particles expose new capillaries; (c) water accumulates in the new exposed surfaces; (d-f) if ever collision happens, those surfaces are sticky (form capillary bridges) and can consolidate into agglomerates. With surfactant: (g-j) even if particles break, oil will almost instantaneously penetrate the just exposed capillaries, avoiding any particle stickiness and consolidation.

Yet, it is important to understand the *dynamic aspect* of the population of hydrate particles. Figure 12(a-f) shows that, although particles in oil continuous flow without the use surfactant can be sealed due to capillary filling-up (Figure 12(a)), they can eventually break-up due to shear stresses of the flow (Figure 12(b)). In this case, exposure of capillaries filled with water happens again (Figure 12(c)), and therefore the new surfaces will be sticky (Figure 12(d-e)), which can cause aggregation and consolidation (Figure 12(f)). That is, more than controlling capillary filling-up in the beginning of the process of hydrate formation, breakage of particles shall as well be controlled in order to avoid exposure of those new sticky surfaces. This high filling-up of the porous structure and low breakage rate (due to low shear stresses in rocking cells) is the case of experimental evidence (H).

The use of surfactant in oil continuous flow helps the new exposed surfaces after breakage to not be sticky and to not permit water availability for consolidation (Figure 12(g-j)). As pointed out in Figure 12(i-j)), even if particles break-up, oil will almost instantaneously penetrate into the capillaries, avoiding further agglomeration. It is important however to notice that, as the particles break-up exposing new capillaries, the oil-water-hydrate interfacial surface that the surfactant needs to cover increases. The theory of Figure 12(g-j) is applicable if the surfactant can cover all the oil-water-hydrate interfacial surface in any moment of the flow. Furthermore, one should yet account to flow shear causing water squeezing to the outer surface of particles (Figure 9(a)) even in the presence of surfactant, which points again to the use of systems with lower agitation.

The avoidance of agglomeration (at least for oil-continuous flows) is then a commitment between: (i) the use of effective surfactant additives at dosages that cover the entire oil-water-hydrate interfacial surface at any moment of the flow (considering the porous structure formed and any eventual particle breakage); (ii) the driving force (subcooling) for a faster sealing-up of the particles; and (iii) an optimal system shear in order to promote finer droplets/initial particles, but that at the same time avoid particle breakage or squeezing.

Settling of slurry

Flowline plugging happens due to instabilities in the slurry flow, thus causing settling of slurry, also called *bedding* or *deposition* (note: deposition is sometimes used as a synonym of hydrate formation directly in the wall in the gas hydrate literature, although in multiphase flow literature it is employed as a synonym to bedding, settling of slurry). Slurry stability criteria are mainly dependent on the mixture velocity and the mean size of particles/agglomerates and come usually in the form of a critical settling velocity[9,10,87,88]. That is, there is a minimum mixture velocity related to the particle/agglomerate size, shape and solid-liquid density ratio for the slurry to be stable, as depicted in Figure 13. Thence, it is key to understand: (i) growth kinetics of gas hydrates, which cause phases consumption with related flow deceleration[7,42,47]; and (ii) particles growth and agglomeration to estimate particle size and slurry viscosity, with consequences in the flowrate as well. With the proposed topological model, growth kinetics is related to gas consumption in the capillary walls, whereas affinity between phases is related to water availability in the outer surface, related to the agglomeration process. Therefore, the mathematical model for growth kinetics and agglomeration shall be coupled with the existent critical settling velocity correlations.

However, there is yet one aspect that shall be incorporated into the said criteria for slurry stability. Once particles that promote capillarity bridges collide with the flowline wall, they may stick to it, Figure 14. The critical case herein analyzed is oil continuous flow without surfactant (Figure 14(a-c)), where a water layer can contour the particles if capillaries are not quickly sealed-out. Stickiness of the particles to the wall will be higher if a hydrophilic flowline material is employed. Yet, if water is available, then a crystal bridge can consolidate this particle to the flowline wall, causing adhesion forces for the deposit[89].

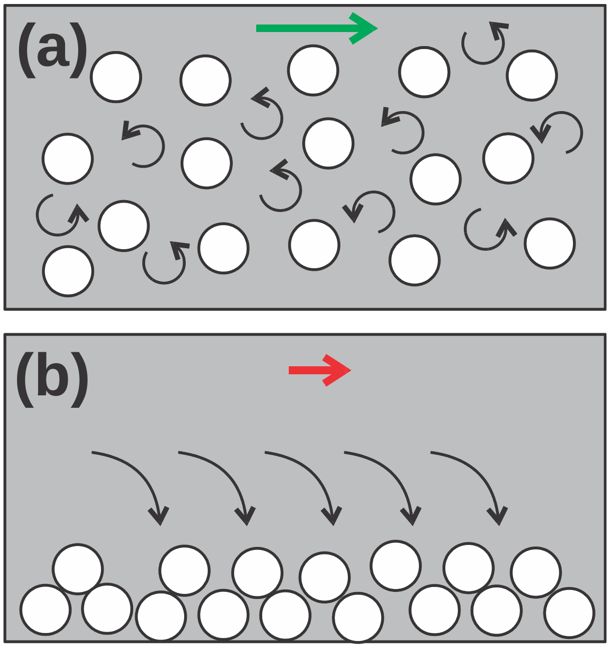


Figure 13. Settling of slurries depends on the estimation of the evolution of particles size and mixture deceleration over time, coupled with a criterion for critical settling velocity. (a) The slurry is stable if the mixture velocity is higher than the critical settling velocity. (b) The slurry settles down if the mixture velocity is lower than the critical settling velocity.

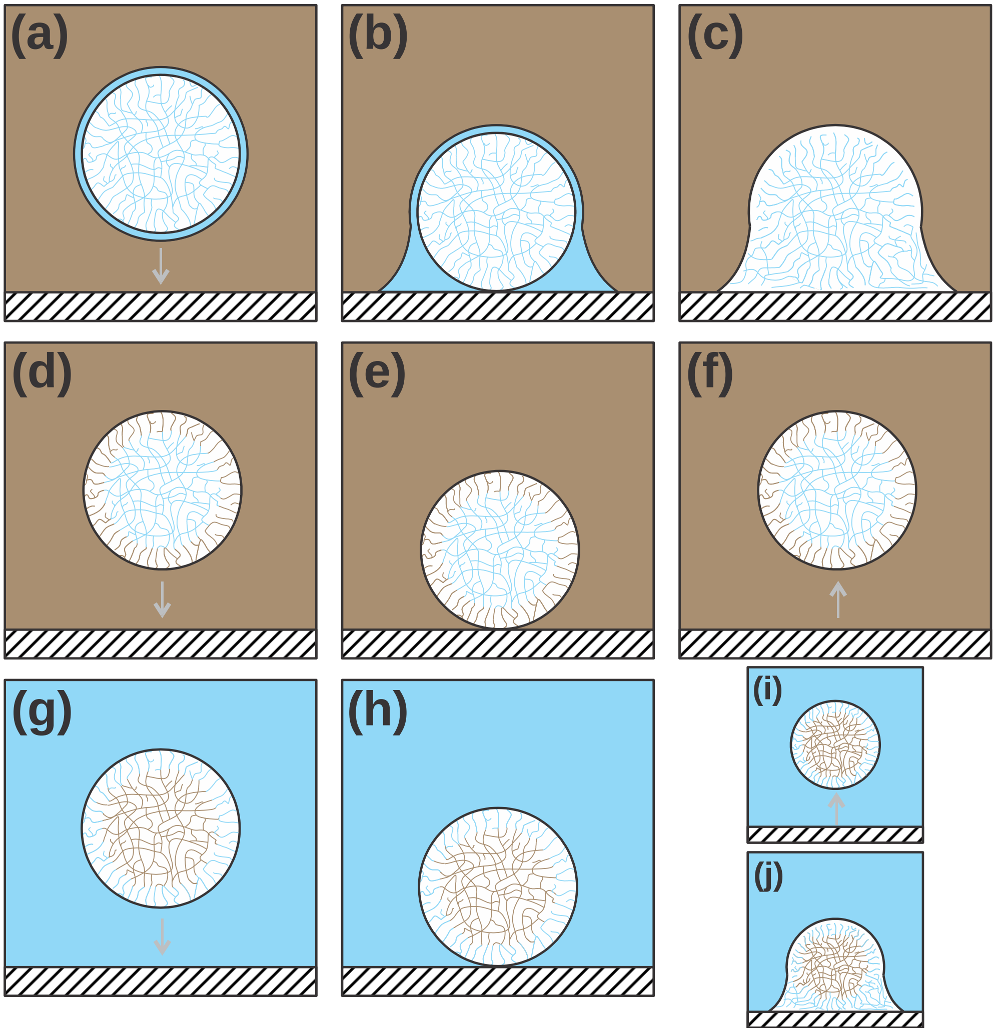


Figure 14. Depiction of interaction of particles during collision with the flowline wall. (a-c) In oil continuous flow without surfactant, if water is available at the outer surface of particles, they stick to the wall and consolidate by creation of a crystal bridge. (d-f) The use of a surfactant in oil continuous flow cause not-sticky particles and prevent consolidation of the particle with the wall. (g-h) In water continuous flow, water is always available for consolidation of the particle in the wall (j), which is however much harder to achieve since there is no capillarity bridge formation (particles are not sticky), and therefore they will most probably detach from the wall due to flow shear before consolidation (i).

3. Conclusions

We propose new insight on how gas hydrates form, grow and agglomerate applied to multiphase flow in oil and gas production. Hydrate particles are interpreted as small sponges that trap oil or water depending on the hydrate affinity. Affinity is dependent on the use of surfactant additives, which will have effects especially in oil continuous flow. In this case, surfactants cause oil to penetrate the capillaries, thus sealing the water inside the sponges. Therefore, a water layer will not be present anymore at the outer surface of the particles, causing particles not to be sticky (called dry particles) and preventing consolidation into agglomerates due to water unavailability for crystal bridge construction. This is a new perspective on how surfactant additives act as Anti-Agglomerants, differently of the DLVO theory explanation persistent in literature, which only explain interaction between particles much smaller than the ones present in gas-oil-water systems. For engineering purposes, trial and error tests in large flowloop in the presence of different additives should be replaced by characterization of interfacial properties in smaller experiments, which will then guide more focused tests in the costly and time-expensive large flowloops. The mathematical description of the herein described phenomena is the focus of the next parts of this series of articles.

Corresponding authors

*Ana Cameirão, cameirao@emse.fr

*Rigoberto E.M. Morales, rmorales@utfpr.edu.br

*Amadeu K. Sum, asum@mines.edu

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