

PAPER • OPEN ACCESS

Challenges with gas hydrate formation

To cite this article: M A Kelland 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **700** 012057

View the [article online](#) for updates and enhancements.

Challenges with gas hydrate formation

M A Kelland

University of Stavanger, Norway

Contact address (E-mail): malcolm.kelland@uis.no

Abstract. Many multiphase flow lines are prone to hydrate formation unless prevention methods are put in place. Chemical management of hydrate formation is traditionally done with thermodynamic hydrate inhibitors but in the last 25 years low dosage hydrate inhibitors (LDHIs) have been developed which can offer economic, environmental and other benefits. LDHIs are divided into two main categories, kinetic inhibitors (KHIs) and anti-agglomerants (AAs), both of which are successfully being used in field applications. This paper briefly reviews the hydrate management tools available to the operator. Then the review focuses on LDHIs, their structure-performance relationships and the various classes that have been designed and tested. The environmental challenges of both AAs and KHIs are also discussed.

1. Introduction

Natural gas hydrates are ice-like solids made of natural gas molecules inside the cages of a clathrate water lattice [1, 2]. Gas hydrate structures I and II are known to be formed in pipelines, with structure I being formed from very methane-rich natural gas and structure II from natural gas mixtures (Figure 1). Pipeline blockage due to gas hydrate formation is the number one problem to overcome in transporting oil, gas and water mixtures in cold and/or deep water subsea flow lines (Figure 2).

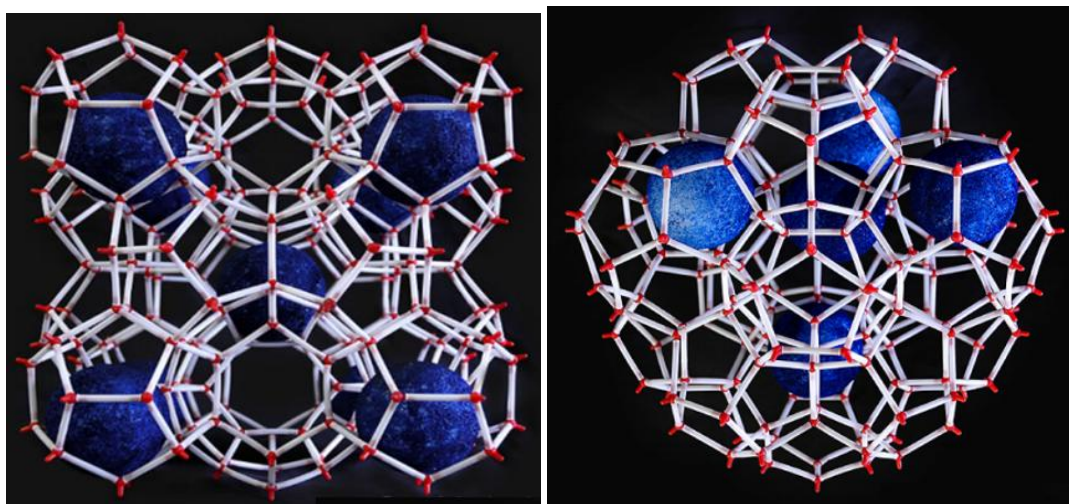


Figure 1. Gas hydrate Structure I (left) and Structure II (right).



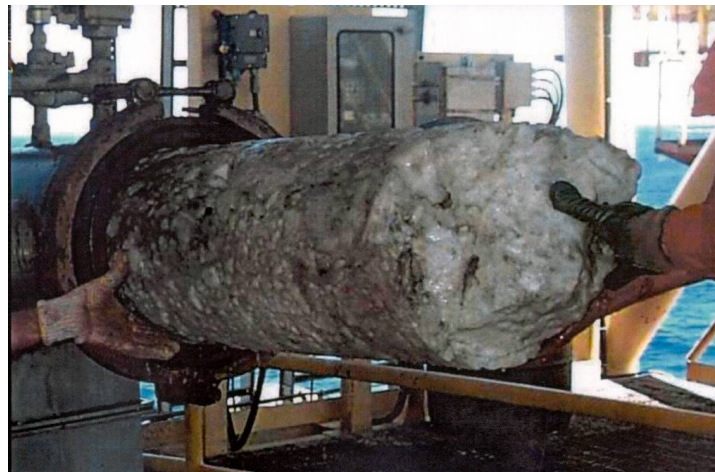


Figure 2. Gas hydrate plug being removed from a flow line.

Once the transported multiphase fluids are inside the equilibrium boundary for gas hydrate formation, hydrate crystals can occur and build up as deposits in the flow line (Figure 3). Formation of a hydrate plug, especially in a subsea flow line is a serious problem and removal of the plug requires specialist skills. Therefore, many methods to avoid hydrate plug formation have been developed (Figure 4). Due to the real fear of having to deal with a hydrate plug, the operator usually wants a method that gives total prevention of hydrate formation under all field conditions, over the field lifetime, and both during production and shut-in. These methods usually rely on keeping outside the thermodynamic region for hydrate formation, either by pressure or temperature control or by shifting the equilibrium for hydrate formation.

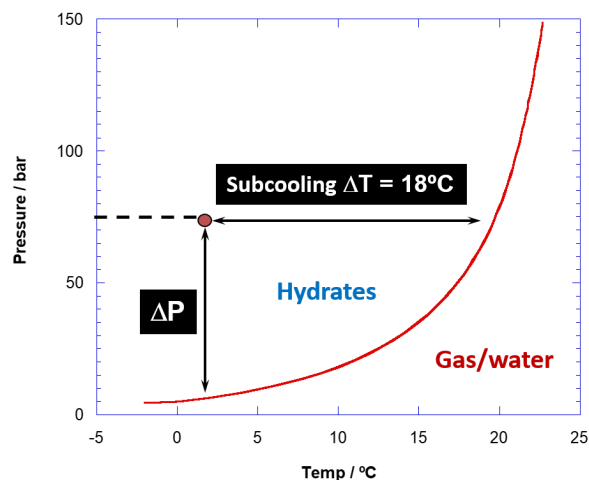


Figure 3. Pressure-temperature diagram for gas hydrate formation, illustrating determination of subcooling (ΔT).

If the field is large and water production high, chemical methods tend to be too expensive even if chemical recovery and regeneration is used. In such cases engineering solutions are usually applied based on an understanding of the flow conditions expected and the pressure and temperature changes across the whole flow line. Multiphase flow simulators are used for these calculations. If the volume of fluids is high (usually for oilfields), hydrate problems can often be avoided under normal production flow rates because the temperature does not drop sufficiently to enter the hydrate formation region. For many fields, only in planned or unplanned shut-ins will the temperature be low enough for hydrates to form. Some form of fluid heating during the shut-in, such as electrical heating, can be used. This can be fairly expensive in terms of both CAPEX and OPEX, especially for very long subsea flow lines.

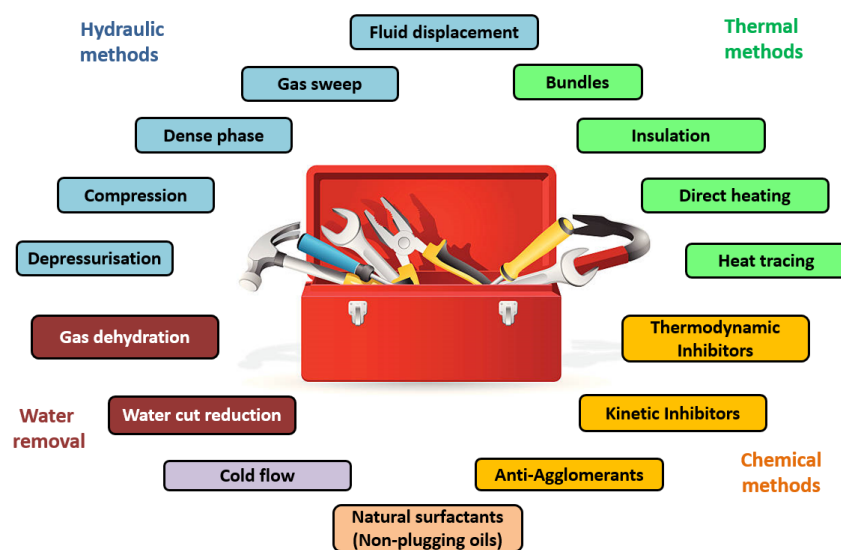


Figure 4. Gas hydrate management tools available to the operator.

2. Chemical Hydrate Inhibition

2.1 Thermodynamic Inhibitors (THIs)

If the volume of produced water is relatively low (usually for gas or gas condensate fields), chemical methods to protect from hydrate formation can be used. The standard chemical method is to shift the equilibrium conditions for hydrate formation by adding a thermodynamic hydrate inhibitor (THI). Common examples are methanol (MeOH), ethanol or monoethyleneglycol (MEG) but even salts such as sodium chloride or potassium formate will work although they are mostly used to prevent hydrate formation in drilling or completion fluids. High concentrations of THIs are needed to shift the equilibrium, maybe 20-80 wt.% of the water phase needs to be added in some cases. Methanol is sufficiently cheap that in some parts of the world it is discharged overboard with the produced water. MEG is relatively more expensive and a less powerful THI than methanol and is often regenerated for reuse.

However, there are other tools available to the operator. For example, some oils are so-called non-plugging oils at certain water cuts [3]. These oils contain natural surfactants which prevent any formed hydrates from agglomerating and depositing in the line. The exact structure of the active components in these oils is still unknown but some characterisation of the functional groups and molecular weights of these resin fractions has been reported. Model natural surfactants have been investigated but it still looks a long way to go as to when chemists can develop AAs based on our understanding of non-plugging oils [4, 5].

2.2 Anti-Agglomerants (AAs)

The artificial equivalent of these natural surfactants are known as anti-agglomerants (AAs) and are a class of low dosage hydrate inhibitor (LDHI).[6] AAs are also surfactants but were not originally developed based on the knowledge of natural surfactants in oil; instead they came out of projects to find gas hydrate crystal growth inhibitors. These crystal-modifying AAs were first invented by Shell energy company [7, 8]. Various classes of AA surfactants are now used commercially on fields worldwide, particularly for the start-up of new subsea wells. The key feature of these AA surfactants appears to be a hydrophilic head group, which can interact with hydrate crystal surfaces, slowing down the crystal growth rate at the same time as making the hydrate particles oleophilic by coating them with the hydrophobic AA tails (Figure 5). The AAs will also accumulate at the oil-water interface where hydrates first form as well as coating the steel walls of the flow line making it less likely for hydrates to deposit. AA surfactants are therefore “hydrate-philic” [9-13].

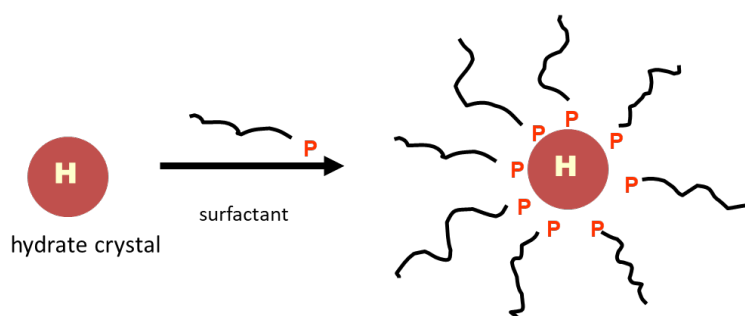


Figure 5. Possible mechanism for hydrate-philic AAs.

The classic head group used in many commercial AA surfactants is a quaternary ammonium or phosphonium group, usually with two or 3 alkyl groups of a particular size for best interaction with open hydrate cavities on the growing hydrate crystal surface (Figure 6). Typical alkyl groups are n-butyl or pentyl groups. Butyl groups are often used because they are cheaper and easier to attach to a nitrogen atom on an industrial scale.

The drawback with AAs is that to transport the crystals of hydrates you need a carrier fluid, and enough fluid so that the “slurry” of crystals is not too viscous but moves smoothly down the flow line. Strongly hydrate-philic AAs keep the crystals small, and often with no sharp edges, which helps keep viscosity low. High water cuts could be a problem if all the water converted to hydrates. Misleading laboratory results in closed systems can be obtained if all the water that could be converted to hydrates is not fully converted. However, as hydrates form the remaining free water becomes more concentrated in any produced salts and at some point can be outside the thermodynamic hydrate formation boundary. Both liquid hydrocarbon and unconverted concentrated produced water can thus be the lubricant for the hydrate crystals.

The best AAs are claimed to work at very high subcoolings, if dosed sufficiently. This makes them useful for deep water (high pressure and cold water) applications where the subcooling can be 20+ °C. However, some AAs do not perform well in fresh water. Another drawback of using AAs is the quality of the produced water, i.e. the strong surface-active property of the AA may challenge the oil-water separation processes and lead to too much oil-in-water for discharge approval. This, several AAs from different vendors may pass the hydrate tests but could fail on the water quality. However, more recent AAs have overcome this drawback [14].

As AAs are surfactants they are generally quite toxic, especially the quaternary ammonium and phosphonium surfactants. To avoid long term ecotoxicological problems it is desirable if the AA degrades quickly. Recently, an AA was developed with over 60% biodegradation in the OECD306 seawater test [15].

2.3 Hydrate slurry transportation without chemicals

The ideal method to produce a transportable slurry of hydrate particles would be to avoid the use of chemicals altogether. As mentioned earlier some crudes won't give hydrate plugs under certain conditions, thus avoiding any extra chemical need, but the majority of crudes will cause a plug. In such cases a new method has been developed which requires no additives. The idea is to get the hydrates to nucleate fast under special conditions so that the “sticky” phase when hydrates would normally aggregate and agglomerate is prevented from occurring [16-18].

The method can involve seeding to accelerate the hydrate process to such an extent that the particles have no time to agglomerate before all the water is converted. Some researchers call the method “cold flow”. Field trials have been performed with partial success. Naturally, operators will need to see fully successful and reliable field data before they will be willing to risk using this method in the field. Having back-up storage of AA chemical may help reduce the risk.

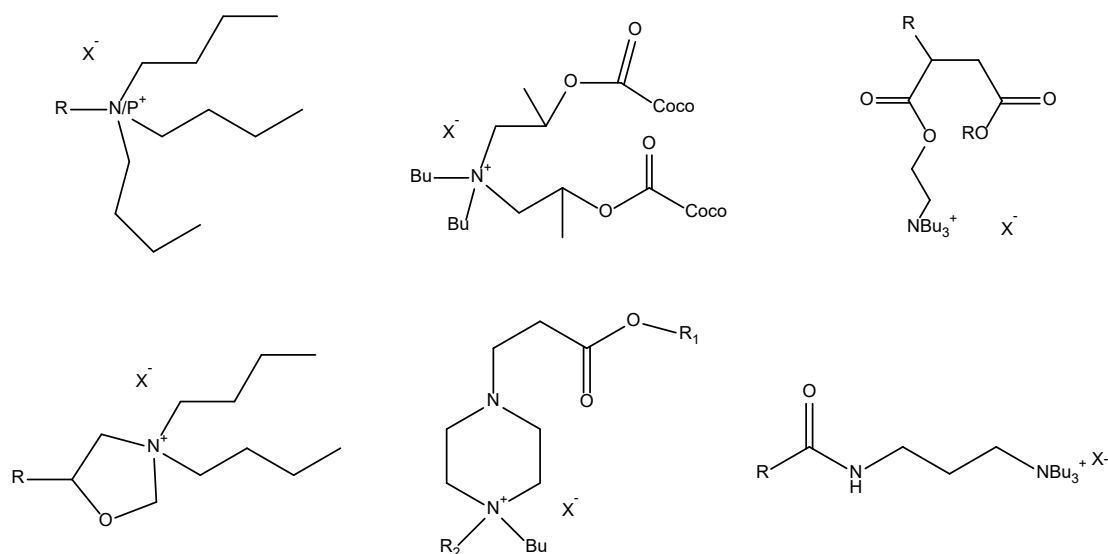


Figure 6. Typical structures of hydrate-philic AA surfactants (R = C12-18).

2.4 Kinetic Hydrate Inhibitors (KHIs)

For fields where there is no or very little liquid hydrocarbons and low produced water volumes (typically gas or gas condensate fields), an alternative LDHI known as a kinetic hydrate inhibitor (KHI) can be used.[1,6,14,19-21] KHIs typically consist of water-soluble polymers as the main component, often containing amide or imide functional groups, as formulations in solvents, and are applied at low concentrations, typically 0.1–2 wt. % based on the amount of produced water. The commonest KHI polymer classes are poly(N-vinyl lactam)s, poly(N-alkyl (meth)acrylamide)s, and copolymers thereof, and hyperbranched polyesteramides (Figure 7).

Synergists, such as other polymers or smaller nonpolymeric compounds, are often added to the formulation to enhance the KHI activity of the water-soluble polymer. Sometimes the solvent itself functions as a synergist. The mechanism by which KHIs and synergists work is still somewhat unclear, but is usually assumed to include a combination of nucleation and crystal growth inhibition.[22-23] KHIs are fairly expensive products, the base polymers can often cost 10-20 Euro/kg. However, they can still be a cheaper method of hydrate control than more traditional methods where the water production is low. Recently, methods to capture and recycle the KHI have been reported.[24-25] This could open up the use of KHIs at much higher water production rates.

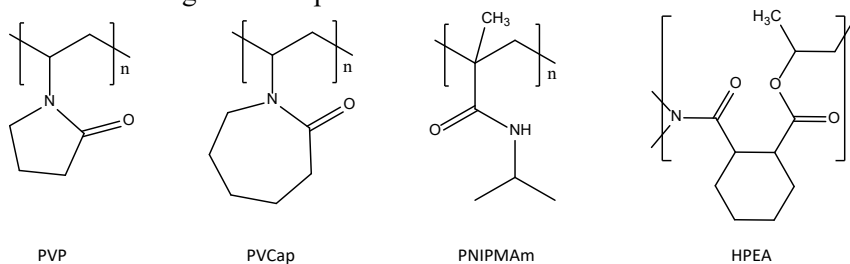


Figure 7. Common monomer units in commercial KHI polymers.

The performance usually increases with increasing concentration in the range 0.1-2.0 wt.% but the improvement generally becomes less and less. The performance limit is often quoted as a combination of time and subcooling. The best SII hydrate KHIs can prevent hydrate formation for 48 h at 12-14 °C subcooling. However, there are many other factors that will affect the performance that must be considered, including:

- Temperature profile during the residence time
- Shut-in/start-up situations

- Pressure
- Total salinity (TDS)
- Brine composition e.g. monovalent vs. divalent cations
- pH
- Gas composition
 - SI vs. SII
 - Acid gases (H₂S, CO₂)
- Condensate or crude composition
 - aromatics vs. aliphatic content, resins and natural surfactants
 - emulsion properties
- GOR, water cut
- Flow regime (laminar, slug etc.)
- Solid surfaces
 - Clay, formation fines, scale, corrosion products
- Other production chemicals
 - Particularly corrosion inhibitors

In the last 15 years, our group has studied a range of other water-soluble polymers in order to understand the key features for best KHI performance. These studies have shown that many structural features can affect KHI polymer performance. Here we only list the main factors as this is not the place for a full discussion.

- Amphiphilic functional groups
 - They should contain hydrophilic groups, probably with strong hydrogen-bonding e.g. amide or amine oxide
 - The hydrophobic groups should be bonded to or neighbouring to the hydrophilic groups
 - The size and shape of the hydrophobic groups must be optimised. 3-6 carbon atoms acyclic or cyclic aliphatic groups is most common.
 - There is recent evidence that low cloud point is beneficial if the criteria above are satisfied [26].
 - The functional groups should be part of or attached to the backbone of the polymer. This reduces the degrees of freedom and therefore loss of entropy, making the local change in Gibbs free energy less negative
- Polymer molecular weight
 - Low molecular weight is best for polyamides. PVCap with Mw as low as 500 g/mole (i.e. only 4 repeat units) appears to work well as a KHI [27]. However, the method of molecular weight determination is critical. Gel permeation (size exclusion) chromatography is often done with a calibrating polymer with very different characteristics from the KHI polymer. Absolute molecular weight determination without the need for a calibrating polymer can give very different results [28].
 - A bimodal molecular weight distribution has been shown to work better than a monomodal distribution [29].
- Maximising the hydrodynamic surface area:volume ratio appears to be important [26].
- Tacticity (of vinyl polymers) – syndiotactic is best due to maximising the surface area:hydrodynamic volume ratio [30, 31].
- Polymer end groups – type of initiator and chain transfer agent can make a difference [32].
- Copolymer – monomer distribution, block vs. statistical (random) [33, 34].
- Unknown effects from the polymerisation procedure – this is well known from the chemical companies and can cause poor quality control if the exact procedure is not adhered to each time. Even two polymer samples with similar molecular weight distributions can have different performances due to the method of manufacture, i.e. temperature, solvent, polymer concentration, initiator, method of mixing, reaction time etc.

3. Conclusion

Many methods have been developed to combat the potential of hydrate blockages in flow lines. No one method is a panacea for all fields and therefore different methods are used for different field scenarios for the best economics for the owner companies. It is akin to picking the appropriate tool from the toolbox for the job in question. For large oilfields with high produced water volumes, operators tend to use engineering methods to avoid hydrate formation. For low amounts of water production, chemicals become more of an option. Low dosage hydrate inhibitors (both AAs and KHIs) are useful tools for certain scenarios but have limitations which were discussed. KHIs that perform at higher subcoolings, are a challenge that would be very welcome to overcome, for either SI or SII hydrates. Finding low toxic AAs may be an unsurmountable challenge as they are so surface-active, but biodegradable AAs are now available. KHI polymers tend to be low in toxicity but not very biodegradable, although some are now available although their performance is not as high as the best KHIs [35-36].

4. References

- [1] Sloan E D and Koh C A 2008, *Clathrate Hydrates of Natural Gases*, 3rd ed.; CRC Press: Boca Raton, FL.
- [2] Carroll J J 2009 *Natural Gas Hydrates: A Guide for Engineers*, 2nd ed.; Elsevier Gulf Professional: Amsterdam.
- [3] Sjöblom J, Øvrevoll B et al. 2010, Investigation of the hydrate plugging and non-plugging properties of oils. *J. Disp. Sci. Techn.* **31**(8), 1100-1119.
- [4] Aman Z M, Sloan E D, Sum A K, and Koh C A 2012 Lowering of clathrate hydrate cohesive forces by surface active carboxylic acids. *Energy Fuels* **26**(8), 5102-5108.
- [5] Syddall W G T, Haber A, Qin Y, Graham B, Aman Z M, May E F, Johns M J and Pickering P F, 2017, Characterization of crude oils that naturally resist hydrate plug formation. *Energy Fuels* **31**(6), 5806-5816.
- [6] Kelland M A 2006, History of the development of low dosage hydrate inhibitors. *Energy Fuels* **20**, 825–847.
- [7] Klomp U C, Kruka V C and Reijnhart R 1995 WO Patent Application 95/17579.
- [8] Klomp U C and Reijnhart R 1996 International Patent Application WO 96/34177.
- [9] Delroisse H, Torr e J-P and Dicharry C 2019 Effects of a quaternary ammonium salt on the growth, wettability, and agglomeration of structure II hydrate crystals. *Energy Fuels* **32**, 12277-88.
- [10] Bellucci M A, Walsh M R and Trout B L 2018 Molecular dynamics analysis of anti-agglomerant surface adsorption in natural gas hydrates. *J. Phys. Chem. C*, **122**(5), 2673-83.
- [11] Chua P C and Kelland M A 2013 Study of the gas hydrate anti-agglomerant performance of a series of n-Alkyl-tri(n-butyl)ammonium bromides. *Energy Fuels* **27**, 1285–92.
- [12] Sicard F, Bui T, Monteiro D, Lan Q, Ceglie M, Burress C and Striolo A 2018, Emergent properties of antiagglomerant films control methane transport: Implications for hydrate management. *Langmuir* **34** (33), 9701-10.
- [13] Mehrabian H, Bellucci M A, Walsh M R, Trout B L, 2018, Effect of salt on antiagglomerant surface adsorption in natural gas hydrates. *J. Phys. Chem. C*, **122**(24), 12839- 49.
- [14] Kelland M A 2014 *Production Chemicals for the Oil and Gas Industry*, 2nd ed.; CRC Press: Boca Raton, FL.
- [15] Li X, Amundsen Ø, Kinnari K, Cely A, Askvik K, Kelland M A and Abrahamsen E 2017 *Discovery of an environmentally friendly low dosage hydrate inhibitor anti-agglomerant for NCS*, Proceedings of the Oil Field Chemistry Symposium 2017 Geilo, Norway, 26-29th March.
- [16] Straume E O, Morales R E M and Sum A K 2019 Perspectives on gas hydrates cold flow technology, *Energy Fuels*. **33**(1), 1–15.
- [17] Talley L D, Turner D J and Priedeman D K 2007 *Method of Generating a non-plugging hydrate*

- slurry*. International Patent No. WO 2007/095399.
- [18] Larsen R, Lund A, Hjarbo K W and Wolden M 2009 *Robustness Testing of Cold Flow*, 20th International Oilfield Chemistry Symposium, Geilo, Norway, March 22–25.
- [19] Kelland M A 2011 *A review of kinetic hydrate inhibitors: Tailormade water-soluble polymers for oil and gas industry applications*. In *Advances in Materials Science Research*; Wytherst, M. C., Ed.; Nova Science Publishers, Inc.: New York, 2011; Vol. 8.
- [20] Perrin A, Musa O M and Steed J W 2013 The chemistry of low dosage clathrate hydrate inhibitors. *Chem. Soc. Rev.*, **42**(5), 1996–2015.
- [21] Shahnazar S, Bagheri S, TermehYousefi A, Mehrmashhadi J, Abd Karim M S and Kadri N A 2018 Structure, mechanism, and performance evaluation of natural gas hydrate kinetic inhibitors. *Rev. Inorg. Chem.* **38**(1), 1-19.
- [22] Yagasaki T, Matsumoto M and Tanaka H 2019 Molecular dynamics study of kinetic hydrate inhibitors: The optimal inhibitor size and effect of guest species. *J. Phys. Chem. C* **123**, 1806-16.
- [23] Xu J F, Li L W, Liu J X, Wang X P, Yan Y G, Zhang J 2018 The molecular mechanism of the inhibition effects of PVCaps on the growth of sI hydrate: an unstable adsorption mechanism, *J. Phys. Chem. Chem. Phys.* **20**, 8326-32.
- [24] Tohidi F, Anderson R and Tohidi B 2018 Evaluation of a novel water-immiscible kinetic hydrate inhibitor formulation. *Energy Fuels* **32**(6), 6518–23.
- [25] Rithauddeen M A, Al-Adel S I and Mohammad A F 2019 *Removal of Kinetic Hydrate Inhibitors*, US Patent Application US20190118114.
- [26] Dirdal E G and Kelland M A 2019 Does the cloud point temperature of a polymer correlate with its kinetic hydrate inhibitor performance? *Energy Fuels* **33**(8), 7127-37.
- [27] Clements J, Pakulski M K, Riethmayer J and Lewis D C 2017 International Patent Application WO2017/048424.
- [28] Ree LHS, Opsahl E & Kelland M A 2019 N-Alkyl methacrylamide polymers as high performing kinetic hydrate inhibitors. *Energy Fuels* **33**, 4190–201.
- [29] Colle K, Talley L D and Longo J M 2005 World Patent Application WO 2005/005567.
- [30] Chua P C, Kelland M A, Hirano T and Yamamoto H 2012 Kinetic hydrate inhibition of poly(N-isopropylacrylamide)s with different tacticities. *Energy Fuels* **26**, 4961-67.
- [31] Chua P C, Kelland M A, Ishitake K, Satoh K, Kamigaito M and Okamoto Y 2012 Kinetic hydrate inhibition of poly(N-isopropylmethacrylamide)s with different tacticities. *Energy Fuels* **26**, 3577–85.
- [32] Zhang Q and Kelland M A 2018 Study of the kinetic hydrate inhibitor performance of poly(N-vinylcaprolactam) and poly(N-isopropylmethacrylamide) with varying end caps. *Energy Fuels* **32**, 9211–19.
- [33] Ree L, Kelland M A, Haddleton D and Alsubaie F 2017 Comparison of the kinetic hydrate inhibition performance of block and statistical N-Alkylacrylamide copolymers. *Energy Fuels*, **31**, 1355–61.
- [34] Reyes F T, Kelland M A, Kumar N & Jia L 2015 First investigation of the kinetic hydrate inhibition of a series of poly(β -peptoid)s on structure II gas hydrate, including the comparison of block and random copolymers. *Energy Fuels* **29**(2), 695–701.
- [35] Kelland M A 2018 A review of kinetic hydrate inhibitors from an environmental perspective. *Energy Fuels* **32**, 12001–12.
- [36] Magnusson C, Abrahamsen E, Kelland M A, Cely A, Kinnari K, Li, X & Askvik K M, 2018, As green as it gets: An abundant kinetic hydrate inhibitor from nature. *Energy Fuels* **32**, 5772–8.