EVALUATING NEW CHEMICALS AND ALTERNATIVES FOR MITIGATING HYDRATES IN OIL & GAS PRODUCTION

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ABSTRACT

The paper presents a review of strategies for hydrate mitigation and remediation focusing on novel chemical inhibitors and the prediction of hydrate formation and dissociation. The application of novel low dosage inhibitors is analysed and the current advantages and disadvantages are highlighted. The predictive modelling of hydrate formation is also discussed and the strengths and weaknesses of the techniques are evaluated. The discussion concludes that the novel hydrate inhibitors offer significant cost and environmental benefits compared to the traditional chemicals, but that they still suffer from a number of important limitations which restrict widespread application. From the modelling perspective, the paper emphasises the need for improved modelling, particularly in black oil systems, and the need for work on the modelling of novel inhibitor effects.

INTRODUCTION

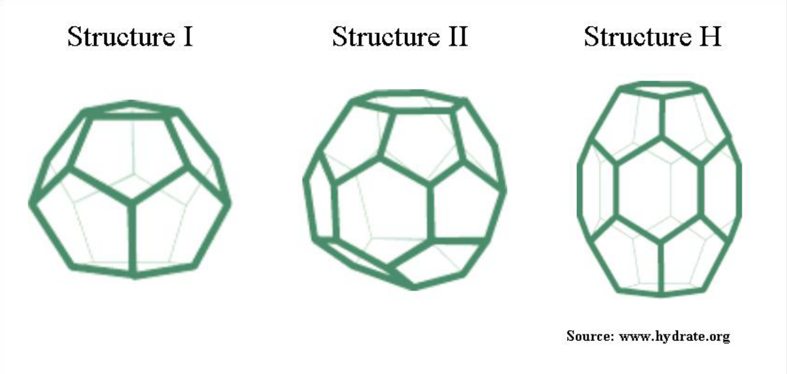
Hydrates of natural gas were first discovered by Sir Humphrey Davy in 1810 but remained somewhat of a scientific curiosity until Hammerschmidt reported in 1934 that they could form in natural gas pipelines leading to blockages and reduced or zero gas flow. The initial work by Hammerschmidt motivated considerable research activity into the formation of hydrates and their prevention in pipelines and led to the development of the first hydrate prediction methods and inhibition techniques.

In this last decade, driven by the need to cut operating costs and reduce the environmental impact of operating oil & gas facilities, research activity has concentrated on the development of novel low dosage hydrate inhibitors (LDHIs). This paper presents are review of alternative hydrate mitigation methods focusing on the prediction methods required for design and the selection criteria applicable for different field development scenarios.

Gas hydrates are crystalline ice-like solids formed from water and a range of lower molecular weight molecules, typically methane, ethane, propane, hydrogen sulphide and carbon dioxide. The structures of the crystals fall into the class of clathrates with the water molecules forming a hydrogen-bonded cage-like structure which is stabilized by ‘guest’ molecules located within the lattice. For more detailed discussions see Makogon (1997) or Sloan (1998).

To date there are three known hydrate structures referred to as structures I, II and H (abbreviated to sI, sII and sH). Figure 1 presents schematics of the three different structures. Structure I hydrates contain 46 water molecules per 8 gas molecules giving a hydrate number of 5.75. The water molecules form two small dodecahedral voids and six large tetradecahedral voids. The sizes of the voids are relatively small meaning that the guest molecules are restricted in size to essentially methane and ethane.

Figure 1, Schematics of Structure I, II and H Gas Hydrates



Source: www.hydrate.org

Structure II hydrates contain 136 water molecules per 24 gas molecules giving a hydrate number of 5.67. The water molecules form 16 small dodecahedral voids and 8 large hexakaidecahedral voids. The larger voids are able to accommodate molecules including propane, isobutane, cyclopentane, benzene and others. Table 1 presents lists of hydrate forming molecules which have been identified to date; it is by no means exhaustive. However, while the larger cavities can accommodate larger molecules the structure is only stable if small 'help' molecules are available to fill the smaller lattice cavities.

Structure H hydrates were discovered recently (Ripmeester *et al*. 1987) and contain 34 water molecules for every 6 gas molecules giving a hydrate number of 5.67. The structure has three cavity sizes with the largest cavity able to accommodate larger molecules than both sI and sII. Once again, stability is only possible in the presence of smaller 'help' molecules such as methane or nitrogen.

Table 1, Molecules Identified as Potential Hydrate Formers

Natural Gas	Condensates / Oils	Process Industry	Academic
Nitrogen	Benzene*	Ethylene	Inert gases
Carbon Dioxide	Cyclopentane*	Propylene	Oxygen
Hydrogen Sulphide	Cyclohexane*	Other olefins	Hexafluorosulphide
Methane	Methylcyclopentane*		Cyclopropane
Ethane	Cycloheptane*		
Propane	Methylcyclohexane*		
Butane*	Ethylcyclopentane*		
Isobutane	Cyclo-octane*		
Neopentane*	1,1 Dimethylcyclohexane*		
	cis 1,2 Dimethylcyclohexane*		
	2 Methyl butane*		
	2,2 Dimethyl butane*		
	2,3 Dimethyl butane*		
	2,2,3 Trimethyl butane*		
	3,3 Dimethyl pentane*		
	2,2 Dimethyl pentane*		
	2,3 Dimethyl-1-butene*		
	3,3 Dimethyl-1-butene*		
	3,3 Dimethyl-1-butyne*		
	cis Cyclo-octene*		
	bicyclo[2,2,2] oct-2-ene*		
	Adamantane*		

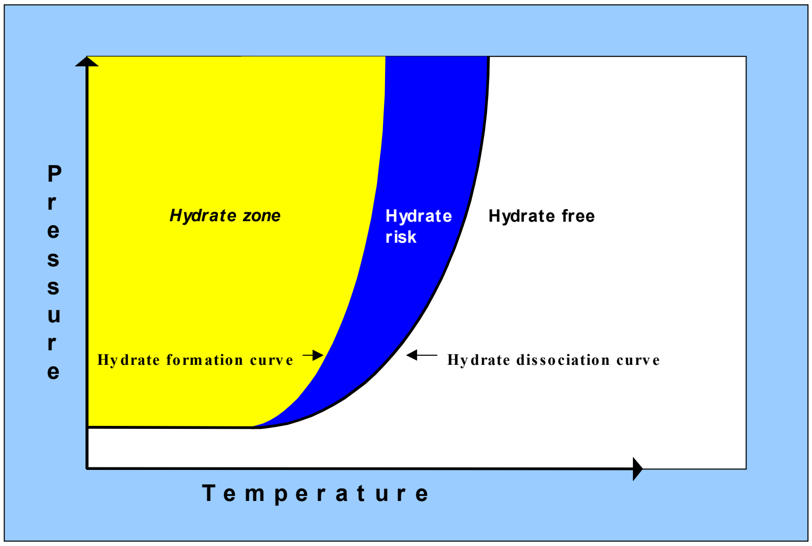
*** Requires presence of smaller 'help' molecule to stabilise structure.**

FACTORS GOVERNING HYDRATE FORMATION

For stable hydrate crystals to form in oil and gas production systems four essential elements must be present: a supply of hydrate forming guest molecules (see Table 1), access to a supply of water and conditions of low temperature and high pressure. In multiphase oil and gas production pipelines containing hydrocarbon gas and liquid phases together with a free water phase, hydrates form preferentially at the water-hydrocarbon interface having the highest availability of hydrate forming molecules. Thus in gas-condensate-water systems, hydrates tend to form at the abundant gas-water interfaces, whereas in low GOR gas-oil-water systems they tend to form at the oil-water interfaces. Although in the case of gas-oil-water systems, the distribution of the oil and water phases (i.e. water-in-oil or oil-in-water dispersions) also plays a key role in determining which interfaces govern the formation of hydrates as does the gas-oil-ratio (GOR) which determines the extent of gas-water interfaces.

Figure 2 presents a hydrate formation diagram in the pressure-temperature plane. The white region covers pressures and temperatures at which hydrates are thermodynamically unstable and is therefore 'hydrate free' as indicated. The region labeled 'hydrate risk' is where stable hydrates can exist, although in practice they may not form due to a failure to nucleate and/or slow formation kinetics. In the 'hydrate zone' the degree of subcooling[1] is sufficient such that hydrates form spontaneously.

Figure 2, Typical Hydrate Formation Diagram



The prediction of hydrate formation in the 'hydrate risk' zone is complicated by a number of factors. First, the mechanisms that govern the nucleation of hydrate crystals are essentially random in nature and poorly understood. Moreover, the kinetics of crystal growth are complex being governed by the rate at which water and guest molecules can order themselves into regular lattice structures and the rate at which hydrate formers can be transported through the surrounding phases to the hydrate reaction zone. These mechanisms lead to a time dependency which serves to impede understanding of hydrate formation. This is particularly true in black oil systems where hydrate formation can be stymied by the slow diffusion of hydrate formers and the presence of naturally occurring surface active chemicals which can hinder crystal growth.

In Figure 3 typical experimental results (Edmonds *et al.* 1998) are shown that illustrate the metastable region which defines the extent of the hydrate risk zone. The experiment commences from point A, the fluids are cooled progressively to point B where the hydrate

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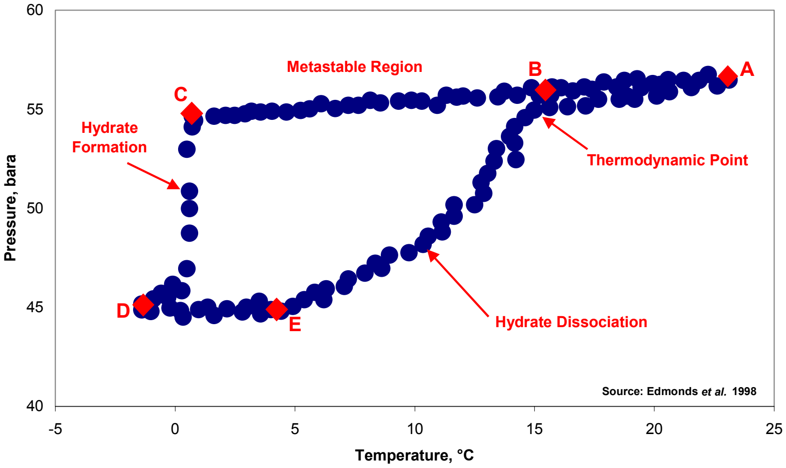
[1] The difference between the hydrate dissociation temperature and the system temperature.

dissociation locus is traversed. The system then enters the metastable region where hydrates are thermodynamically stable but may or may not form depending on kinetic considerations. The fluids are then cooled slowly to point C where hydrates are formed spontaneously and rapidly causing the system pressure to reduce (due to the abstraction of gas into the crystal structure) to point D. The system temperature is then increased slowly at almost isobaric conditions, until hydrate dissociation begins at point E. The system then follows an upwards trajectory as the temperature is increased (due to the liberation of gas) until point B is reached once more when the hydrate dissociation curve is crossed at the 'thermodynamic point'.

Figure 3, Typical Experimental Hydrate Formation/Dissociation Results

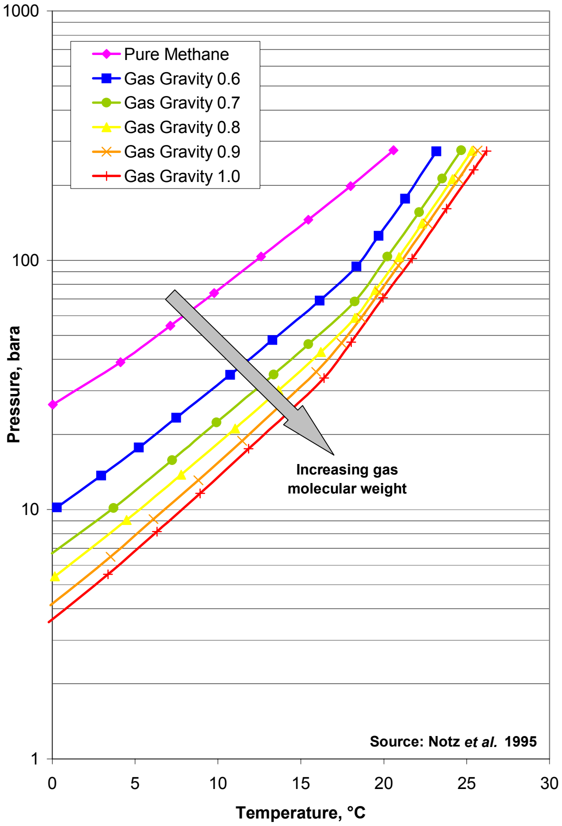


Source: Edmonds *et al.* 1998

The formation of hydrates is also dependent on the composition of the gas forming the hydrate. This point is well-known and has been reported earlier by Katz (1945). Figure 4 presents the results reported by Katz (1945) and shows that the hydrate dissociation curve is displaced towards lower pressures and higher temperatures as the gas gravity or molecular weight increases. Becke *et al.* (1992) investigated the effect on hydrate formation of adding an oil phase to a gas. They observed that the addition of oil produced a beneficial reduction in the hydrate formation temperature. This was explained as due to absorption of ethane and propane into the oil and a consequential reduction in the molecular weight of the gas; this concurs with Katz's early findings.

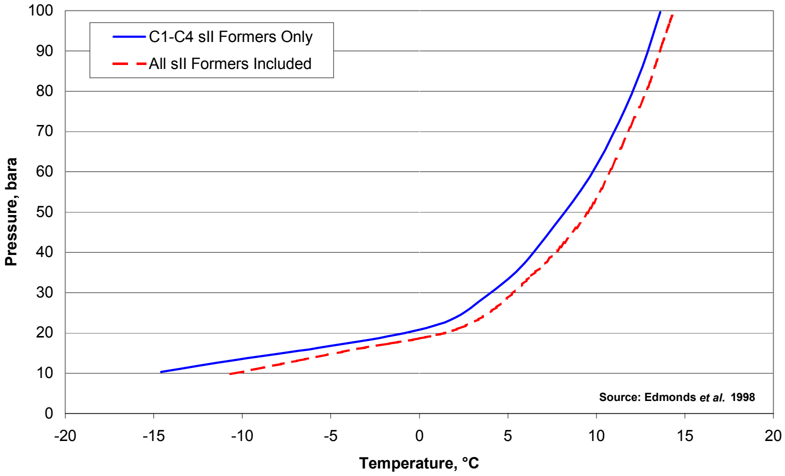
Recent work by Edmonds *et al.* (1998) also illustrates the effect of increasing gas molecular weight. They reported predictions from their hydrate dissociation model (available in the physical properties prediction software *MULTIFLASH*) which demonstrated the effect of including higher molecular weight sII formers on the position of the sII hydrate stability boundary. These predictions are reproduced in Figure 5 and show that the inclusion of the higher molecular weight sII formers shifts the stability curve towards lower pressures and higher temperatures. The impact is only circa 1-2°C for the case examined, but could be greater for different compositions. These results stress the need for accurate compositional data for the prediction of hydrate dissociation loci.

Figure 4, Effect of Gas Gravity on Hydrate Formation



Source: Notz *et al.* 1995

Figure 5, Effect of sII Formers on sII Stability Boundary

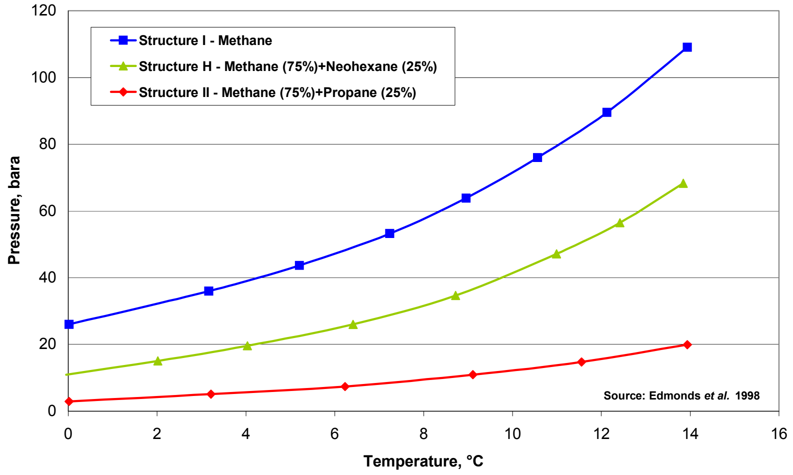


Source: Edmonds *et al.* 1998

Finally in this discussion of the factors governing hydrate formation, it is appropriate to consider the importance of hydrate structures. The existence of three structures has already been discussed, but what is their relative importance? Due to the smaller cavity sizes of sI, it is well-known that this form occurs rarely in oil and gas systems since even small amounts of heavier hydrocarbons (propane and higher) cause sII to be the more stable form.

But what is the importance of sH? Indications from laboratory experiments are that sH hydrates can form at higher temperatures and lower pressures than sI and sII. Figure 6 shows that the addition of 25% of sH former (neohexane) to methane produces an sH hydrate which is more stable than the pure methane sI hydrate. However, if the 25% neohexane is replaced with propane (a composition much more representative of a natural gas) then the sII hydrate is most stable. It is therefore likely that in the majority of oil and gas systems, sII will be the most stable and sH is unlikely to form unless all of the sII formers are consumed producing sII.

Figure 6, Relative Stability of sI, sII & sH Hydrate Structures



Source: Edmonds *et al.* 1998

IMPORTANCE OF HYDRATES DURING OIL & GAS OPERATIONS

While naturally occurring hydrates (for example in the deep oceans) may yield an abundant source of primary energy, and hydrates may also prove useful in the long-distance transportation of stranded natural gas, in conventional oil and gas drilling and production operations the occurrence of hydrates presents serious operational and safety problems together with substantial potential losses of revenue.

Hydrates can form at pressures and temperatures found in natural gas and oil pipelines causing blockages, especially when temperatures fall significantly such as when closing in a well or flowing gas through a choke. Together with other potential solid depositions, such as waxes, asphaltenes and scales, hydrates pose a serious potential problem for the offshore industry. In addition, the remediation of hydrate blockages can also present significant technical difficulties (Mehta *et al.* 2001) with major cost implications.

The presence of hydrates can also have serious safety implications for drilling operations. At the conditions which prevail during drilling, hydrates can form in drilling risers, chokes, kill lines and blowout preventers (Edmonds *et al.* 2001). In addition, the occurrence of naturally occurring hydrates close to the surface can also present a serious hazard during drilling by releasing gas into the borehole leading to well control difficulties and the potential for blowouts. Furthermore, operations such as fraccing[2] can also suffer from hydrate formation (Nelson *et al.* 2000) requiring special fluid and inhibitor formulations to prevent blockages.

Finally, as the offshore industry advances in to the new deepwater provinces, the difficulties associated with hydrate formation are becoming more significant. The fluids from deepwater reservoirs tend to be at relatively low temperatures, and this coupled with the low ambient temperatures that prevail in deepwaters and the higher flowline pressures required to propel fluids up the very tall production risers, means that hydrates are more likely to form in these systems. Moreover, the difficulties associated with depressurisation of deepwater flowline-riser systems and the high cost of interventions also serve to frustrate traditional hydrate remediation strategies.

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[2] Forcing fluid into the well under pressure to fracture the formation thus promoting flow.

HYDRATE MITIGATION & REMEDIATION

As mentioned earlier, the formation of hydrates requires four essential elements to be present: a supply of hydrate forming guest molecules, a supply of water and a combination of high pressures and/or low temperatures. Strategies for hydrate mitigation and remediation often modify one or more of these elements to destabilise the hydrate and thus remove the problem.

However, hydrates can also be prevented by the injection of chemical inhibitors which seek to modify the chemistry of hydrate formation such that the system is operated outside the hydrate envelope or the kinetics of hydrate formation do not allow hydrates to form blockages during transit through the production system. The various methods of hydrate control can be summarised as follows:

a) **Pressure Control**

Design and operate the system with pressures low enough to maintain the fluids outside the hydrate envelope. This approach is often impractical for normal operation since the pressures required for transportation of production fluids would usually exceed the hydrate formation pressure at the ambient temperature. However, for the removal of hydrates following unplanned shutdowns, depressurisation outside the hydrate envelope is normal practice.

b) **Temperature Control**

Maintain the temperature of the production fluids by either passive insulation or active heating (e.g. direct electrical heating) in order to prevent the system entering the hydrate envelope. The use of insulation to maintain the temperatures of production fluids outside the hydrate envelope at system operating pressures is an established approach to hydrate prevention during normal operation, particularly in black oil systems where hydrate prevention may often be a ‘byproduct’ of wax prevention.

However, temperature control by passive insulation only offers hydrate control during normal operation when the system is being continually heated by hot production fluids. Following a shutdown the production fluids will cool down and can enter the hydrate envelope. Under these circumstances the traditional approach has been to depressure the system as discussed above, although recently active heating has been installed to prevent cooldown into the hydrate region by maintaining temperatures (Mehta *et al.* 2001).

c) **Remove Supply of Water**

Prevent the formation of hydrates by removing the supply of water using separation and dehydration. This approach has proved popular for the export of sales gas but is impractical for subsea applications.

d) **Remove Supply of Hydrate Formers**

Prevent the formation of hydrates by removing the supply of hydrate forming molecules perhaps by gas-liquid separation. This approach has been proposed for subsea operation where gas and liquids are separated subsea and are transported to the processing facilities in separate pipelines. The gas pipeline still requires hydrate inhibition (through chemical inhibitors) but the liquids line (containing oil and water) is able to operate satisfactorily without forming hydrates due to the absence of hydrate formers. It is not known whether such a system has yet been installed and operated in this way.

e) **Inject Chemical Inhibitors**

Inject chemical inhibitors into the system which modify the hydrate phase diagram or the kinetics/morphology of hydrate formation. Along with the use of insulation for temperature control (see above), the injection of chemical inhibitors has also found widespread application. The use of chemical inhibitors is a main focus of this paper and is discussed in more detail in the next section.

HYDRATE MITIGATION WITH CHEMICAL INHIBITORS

The various chemicals available for hydrate prevention fall into three classes: traditional thermodynamic inhibitors, novel kinetic inhibitors and novel anti-agglomeration inhibitors. The salient features are summarised below. For more detailed discussions, Kelland *et al.* (1995a & 1995b) present good reviews.

Thermodynamic Hydrate Inhibitors (THIs) – These chemicals work by altering the chemical potential of the aqueous phase such that the equilibrium dissociation curve is displaced to lower temperatures and higher pressures. They are added at relatively high concentrations (10-60 wt% in the aqueous phase) and examples include methanol and monoethylene glycol (MEG). In addition, the naturally occurring inorganic salts which exist in both sea water and formation water[3] also act as thermodynamic inhibitors.

Kinetic Hydrate Inhibitors (KHIs) – This class of chemicals does not alter the thermodynamics of hydrate formation but instead modifies the kinetics of hydrate formation. They achieve this both by prevention of nucleation and by hindering crystal growth. Their effect is time dependent and ultimately hydrates will form and block the pipeline but only if the transit time through the pipeline is sufficiently long, for example following a shutdown. KHIs are added at low concentrations (typically less than 1 wt% in the aqueous phase) and examples include poly[N-vinyl pyrrolidone] or poly[vinylmethylacetamide / vinylcaprolactam].

Anti-Agglomerants (AAs) – These chemicals do not seek to prevent hydrate formation but rather to prevent the crystals from agglomerating and forming a blockage. They are surface active chemicals which adhere to hydrate crystals helping to stabilise the crystal in a continuous oil phase. Their main limitation is that they require a continuous oil phase and are therefore only applicable at lower watercuts. AAs are added in low doses (typically less than 1 wt% in the aqueous phase) and examples include alkyl aromatic sulphonates or alkylphenylethoxylates. AAs can also display a kinetic inhibition effect and are sometimes included in the class of KHIs.

Kinetic Hydrate Inhibitors (KHIs)

The search for novel Kinetic Hydrate Inhibitors was driven by the need to reduce chemical costs, especially those associated with traditional thermodynamic inhibitors. Some of the early inspiration came from the occurrence of natural inhibitors in the plant and animal world. In particular, it is known that some fish produce so-called anti-freeze proteins (AFPs) which allow them to function at low temperatures and high pressures without freezing solid! The work in the area of KHIs began in earnest in the early 1990s and the first article to be published describing true kinetic inhibitors was the BP patent in 1993 (Duncum *et al.* 1993) on tyrosine and selected derivatives. This was followed by a Shell patent covering tests on many kinds of polymers (Anselme *et al.* 1993).

Throughout the 1990s extensive research was carried out into the effectiveness of KHIs leading to successful field trials. The recent paper by Fu *et al.* (2001) describes the successful application of the copolymer of vinylmethylacetamide and vinylcaprolactam (poly[VIMA/VCAP]) to four field locations. In all cases the KHI provided a workable and cost-effective alternative to traditional inhibitors. However, all systems were gas based and none of the cases were representative of black oil systems.

In addition, Argo *et al.* (2000) report on extensive field trials of the KHI 'Hytreat', developed through collaborative research between BP and Shell and marketed by TR Oil Services. The chemical was tested initially in the Ravenspurn-Cleeton pipeline in May 1995 before application in the West Sole to Easington pipeline. The pipeline is a 24-inch wet gas pipeline carrying 50-180 MMscfd of gas. The pipeline was converted from glycol inhibition to Hytreat late in 1996 and has been operating successfully since then with the low dose inhibitor.

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[3] Liquid or 'free' water produced from the underground reservoir along with oil and gas production.

Mitchell and Talley (1999) report on the application of the KHI poly[VIMA/VCAP] to a crude oil system. They note that the test is the first commercial application of their KHI to a crude oil system. The field application was a 1.5 mile flowline at the West Pembina field in Alberta Canada. The operator Imperial Oil had been experiencing persistent problems when using batch treatment with methanol. After switching to the KHI in February 1999 downtime due to hydrates was eliminated. However, while the paper states that the crude oil pipeline has a high GOR, the value is not provided.

Pakulski and others (Pakulski *et al.* 1998 and Pakulski 1997) describe work carried out on nonpolymeric KHIs developed by Unichem. In the earlier paper, laboratory investigations are reported which compare the effectiveness of their nonpolymeric KHI with selected polymeric types. In the later paper, the successful application of the KHI to a gas injection system operated by Trinmar Ltd in the Gulf of Paria off the West coast of Trinidad is reported.

Finally Notz *et al.* (1995) report on successful field trials of polyvinylpyrrolidone (PVP) in gas wells and pipelines in Wyoming. They report that PVP was used as a replacement for methanol giving beneficial reductions in chemical costs and improved hydrate control.

Anti-Agglomerants (AAs)

Anti-Agglomerants are surface active chemicals (surfactants) which do not attempt to prevent hydrate crystals from forming but rather prevent them from agglomerating to form hydrate plugs. Thus they do not display the same pressure-temperature limitations as KHIs. However, AAs known to date only work in systems with a continuous hydrocarbon liquid phase and their effectiveness is dependent on the type of oil/condensate, the salinity of the formation water and the watercut. In addition, the operation of the pipeline can also be important since dispersions of small hydrate crystals will be favoured by higher velocities, whereas at low flow rates crystals may settle-out and agglomerate provided that the oil-hydrate density difference is sufficient. This is analogous to the behaviour of water-oil dispersions in wet crude oil pipelines.

The Institut Français du Pétrole (IFP) has carried out extensive research into the application of AAs in oil and gas pipelines, including many tests in a specially designed test loop (see for example Palermo *et al.* 1997). As a result the IFP has numerous patents related to specific anti-agglomerant chemicals. In addition, Shell has also conducted extensive research in this area and has numerous patents. However, in contrast to the literature associated with KHIs, that related to AAs seems somewhat limited. Indeed, it is understood that there are to date no commercial applications of AAs (Fu *et al.* 2001).

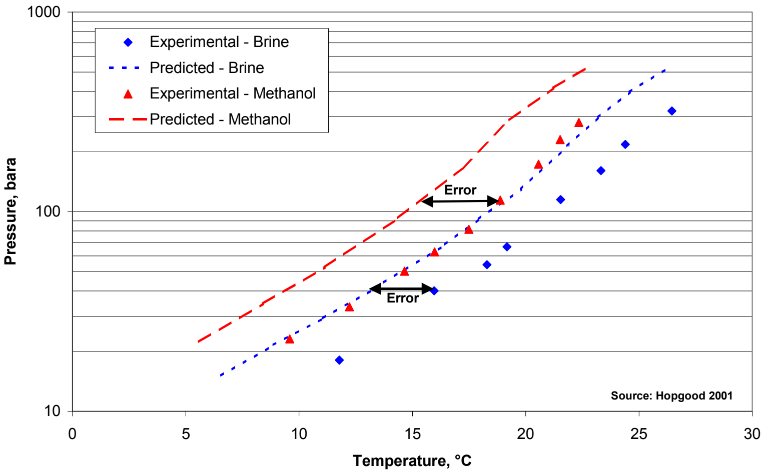
PREDICTING HYDRATE FORMATION

For the optimal design of oil and gas production systems, it is imperative that hydrate formation can be adequately predicted. Moreover, it is essential that the impact of various inhibitors can also be evaluated quantitatively. Some examples of hydrate predictions were given earlier during the discussion of hydrate structures and stability. This section provides a more detailed review of the status of hydrate modelling identifying the areas where further work is required.

Black Oil Systems

The recent paper by Hopgood (2001) considers the accuracy of hydrate dissociation predictions (using an Unocal internal model) and the possible implications for field development. Hopgood points out that the accuracy of predictions in gas-condensate systems is generally very good with predictions agreeing with experimental data to within typically ±1°C. However, for black oil systems the accuracy of predictions is estimated to be ±6°C. Figure 7 reproduces Hopgood's original figure and compares the predictions of two systems (containing brine and methanol) with the experimental data reported by Notz *et al.* (1991). The results show that the predictions systematically underpredict the experimental data by a significant margin and if used in design could have very serious ramifications.

Figure 7, Accuracy of Dissociation Predictions in Black Oil Systems



Hopgood points out that the errors associated with hydrate dissociation curves in black oil systems could have significant cost implications. For example, in a number of the recent deepwater developments the prevention of hydrate formation during shutdown has forced designers to select costly subsea configurations. The principal difficulty with these deepwater fields arises because of the inability to depressure the systems outside the hydrate envelope at seabed temperatures following an unplanned shutdown.

Design decisions have been based on the prediction of hydrate dissociation in black oil systems and could err in either direction by a considerable margin. Based on this uncertain information, designers have either selected very costly insulation systems such as pipe-in-pipe (which offer very low overall heat transfer coefficients) or even electrically heated systems (for example Statoil's Asgard development or Shell's Serrano and Oregano).

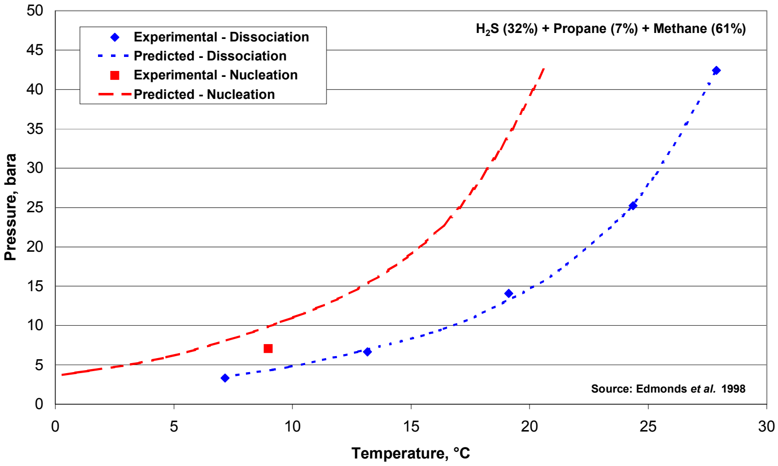
However even with such provisions in place, hydrates may not be entirely avoided and if formed may be difficult to remedy. In particular, the occurrence of a hydrate blockage in a pipe-in-pipe system has been likened to an ice-cube in a thermos flask (Mehta *et al.* 2001) – once formed it will prove very difficult to disperse. Moreover, even in electrically heated systems, concerns exist about the possibility of over-pressuring the pipeline or launching a high-velocity hydrate projectile inside the pipeline! It seems clear that better predictions of hydrate dissociation are required for black oil systems if costly design errors are to be avoided.

Hydrate Nucleation & Formation

In the early part of the paper, discussion of hydrate kinetics was provided and the difference between hydrate formation and dissociation was explained. Current design practice is to design to the hydrate dissociation curve, which in many cases could be an extremely conservative approximation with costly implications. Thus work is required to develop reliable kinetics models able to predict the extent of subcooling possible before spontaneous hydrate formation is initiated.

Edmonds *et al.* (1998) describe their work implementing the BP nucleation model (developed during the Eucharis JIP) into the *MULTIFLASH* software. The model is based on a statistical theory of nucleation in multicomponent systems and provides estimates of the location of the nucleation boundary and the extent of the metastable region (see Figure 2). Unfortunately most comparisons between the model and experimental nucleation measurements are proprietary, but Edmonds *et al.* (1998) do report a public domain example which is presented in Figure 8 below. Based on this and other unpublished results, they state that predictions are usually within the experimental error of hydrate nucleation measurements of ±2°C.

Figure 8, Accuracy of Hydrate Dissociation & Nucleation Predictions



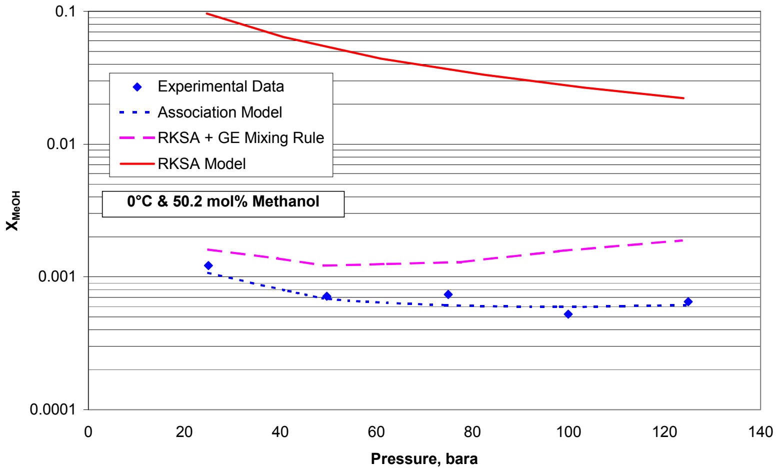
Effect of Thermodynamic Inhibitors

Good progress has been made in incorporating the effect of thermodynamic inhibitors into prediction models for hydrate dissociation curves. However, a particular difficulty encountered when predicting the effect of inhibition with methanol is being able to predict the partitioning of methanol.

Most thermophysical property prediction packages are based on cubic equations of state (generally Redlich-Kwong-Soave of Peng-Robinson) which are well-known to give poor results for molecules with strong specific interactions such as water and methanol (Assael *et al.* 1996). Hence with these packages the correct prediction of the effect of methanol inhibition is obfuscated by inaccurate prediction of the methanol distribution among the phases. However, application of an association model for predicting the methanol partitioning greatly improves the partitioning predictions and hence the accuracy of hydrate dissociation predictions.

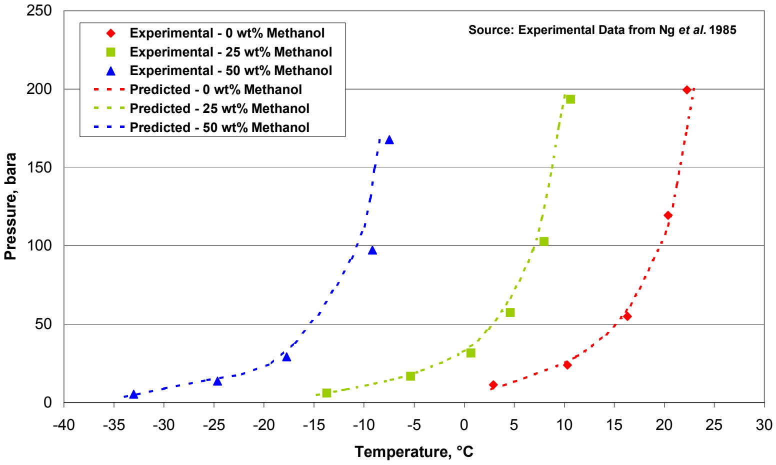
Figure 9 presents predicted mole fractions of methanol in the vapour phase compared to experimental data. The predictions were generated using Infochem's *MULTIFLASH* property prediction software. Noting the logarithmic ordinate axis, it is clear that the RKSA model with the standard van der Waals mixing rules gives very bad predictions. The predictions with RKSA and the GE (NRTL style) mixing rules are better but still give significant over-predictions of methanol in the vapour phase. The association model, however, gives excellent predictions.

Figure 9, Methanol Partitioning into the Vapour Phase



With accurate predictions of methanol partitioning, it is then possible to accurately predict the displacement of the hydrate dissociation curve with increasing methanol concentration. In addition, calculating the losses to the vapour phase (and hence the operating cost associated with make-up methanol if regeneration facilities are available) is also greatly improved. Figure 10 presents the results of comparisons between *MULTIFLASH* predictions with the experimental data of Ng *et al.* (1985).

Figure 10, Hydrate Dissociation with Increasing Methanol



Infochem's software *MULTIFLASH* is also able to reliably predict the inhibitive effect of inorganic salts in the free water, and for more details including comparisons with experimental data, the Reader is referred to Edmonds *et al.* 1996. However, one complicating factor encountered when modelling the effect of salt, is the interaction that occurs with other inhibitors. For example, if methanol is added to formation water then depending on the salt concentration, salt precipitation will occur at a given concentration of methanol in the aqueous phase.

Effect of Kinetic Hydrate Inhibitors

To our knowledge, there are no established methods for predicting the effect of kinetic hydrate inhibitors on the onset of hydrate formation. It seems unlikely that such models will be available in the foreseeable future since the fundamental interactions between kinetic inhibitors and hydrate crystals are poorly understood. Moreover, an additional complication is the impact of hydrate crystal structure on kinetic inhibitor effectiveness (Subramanian *et al.* 2000). Indications are that predictive models for kinetic inhibitors would also need to take account of the potential for separate and coexistent crystal structures.

At this time the only practical way to confirm the effectiveness of a particular inhibitor is to test the chemical with representative fluid samples.

SELECTION OF HYDRATE MITIGATION & REMEDIATION STRATEGIES

The selection of hydrate mitigation and remediation strategies is based on technical and economic considerations and the decision is not always clear-cut. For example, in a deepwater development where the recoverable reserves and required capital expenditure mean that the development is struggling to meet economic hurdles, a low-cost hydrate strategy may be adopted which incurs a small risk of disruption due to hydrates formation. However, in a similar development with a significantly higher reserves base, the operator may elect for a higher cost strategy (e.g. electrical heating) in order to minimise risks.

In addition, the selection of a hydrate strategy is often swayed by other considerations, such as the requirement to avoid wax deposition which naturally leads developers towards insulated pipelines.

Table 2 provides a summary of the applications, benefits and limitations of the three classes of chemical inhibitors.

Table 2, Summary of Applications, Benefits & Limitations of Chemical Inhibitors

Thermodynamic Hydrate Inhibitors	Kinetic Hydrate Inhibitors	Anti-Agglomerant Inhibitors
Applications		
1. Multiphase	1. Multiphase	1. Multiphase
2. Gas & Condensate	2. Gas & Condensate	2. Condensate
3. Crude Oil	3. Crude Oil?	3. Crude Oil
Benefits		
1. Robust & effective	1. Lower OPEX/CAPEX	1. Lower OPEX/CAPEX
2. Well understood	2. Low volumes (< 1wt%)	2. Low volumes (< 1wt%)
3. Predictable	3. Environmentally friendly	3. Environmentally friendly
4. Proven track-record	4. Non-toxic	4. Non-toxic
	5. Tested in gas systems	5. Wide range of subcooling
Limitations		
1. Higher OPEX/CAPEX	1. Limited subcoolings (<10°C)	1. Time dependency?
2. High volumes (10-60 wt%)	2. Time dependency	2. Shutdowns?
3. Toxic / hazardous	3. Shutdowns	3. Restricted to lower watercuts
4. Environmentally harmful	4. System specific – testing	4. System specific – testing
5. Volatile – losses to vapour	5. Compatibility	5. Compatibility
6. ‘Salting out’	6. Precipitation at higher temps	6. Limited experience
	7. Limited exp. in oil systems	7. No predictive models
	8. No predictive models	

The main benefits of the traditional thermodynamic hydrate inhibitors (THIs) are their effectiveness, reliability (provided sufficient quantities are injected) and proven track-records. However, these benefits are outweighed by significant limitations, including the high volumes, high associated costs (both CAPEX and OPEX), toxicity and flammability. In addition, they are harmful to the environment and significant disposal into the environment is prohibited.

Kinetic hydrate inhibitors are injected in much smaller quantities compared to thermodynamic inhibitors and therefore offer significant potential costs savings, depending on the pricing policies of major chemical suppliers. They are also typically non-toxic and environmentally friendly. Moreover, considerable field experience is now available following a number of successful trials. However, they have some important limitations, including restrictions on the degree of subcooling (typically only guaranteed for less than 10°C) and problems associated with residence times (implications for shutdowns). In addition, the effectiveness of KHIs appears to be system specific meaning that testing programmes are required prior to implementation. Unfortunately adequate testing can require appreciable quantities of production fluids which may not be available, particularly for new field developments. Furthermore, KHIs can interact with other chemical inhibitors (e.g. corrosion inhibitors) and testing programmes need to account for this also (Graham *et al.*, 2001). Finally, there are no established models for predicting the effectiveness of KHIs which presents difficulties for field developers considering the application of these chemicals.

The benefits and limitations of Anti-Agglomerants are largely similar to those for KHIs, although AAs do not have the same subcooling limitations. However, there is uncertainty about the effectiveness of AAs under shutdown or low flow rate conditions and it is postulated that agglomeration may still proceed. In addition, the one major limitation of AAs compared to KHIs or THIs is that they are limited to lower watercuts due the requirement for a continuous hydrocarbon liquid phase. Finally, compared to both THIs and KHIs, field experience with Anti-Agglomerants appears to be lacking which is reflected by the relatively small number of publications available in the open literature.

CONCLUSIONS

The paper presents a review of strategies for hydrate mitigation and remediation focusing on novel chemical inhibitors and the prediction of hydrate formation and dissociation. The factors governing hydrate formation are also discussed, including the necessary precursors and the effects of parameters such as gas molecular weight and hydrate crystal structure.

The different methods of hydrate mitigation and remediation are summarised before concentrating on the relative merits and demerits of the three main classes of chemical inhibitors: Thermodynamic Hydrate Inhibitors (THIs), Kinetic Hydrate Inhibitors (KHIs) and Anti-Agglomerants (AAs).

For chemical inhibitors, the review concludes that KHIs are finding favour in gas-condensate systems as a cost-effective alternative to traditional thermodynamic inhibitors. Although the gas-condensate systems where KHIs have found application are generally those where moderate subcoolings prevail (e.g. less than 10°C), pipeline residence times are short and depressurisation is available following an unplanned shutdown. For gas-oil systems, the application of KHIs remains limited.

Anti-agglomerants on the other hand, have not found widespread application in the field to date, and while these chemicals offer certain benefits compared to KHIs (e.g. less stringent limitations on subcooling and residence times) they are restricted to lower watercut systems typically less than 40%.

However notwithstanding the limitations of the novel low dosage hydrate inhibitors, they do offer very significant cost and environmental advantages and current research and development activities promise to yield substantial future benefits.

The paper also addresses the inadequacies of current predictive tools, particularly concerning black oil systems and the effectiveness of novel inhibitors. The need for more work in this area is highlighted.

Finally, the paper presents a qualitative summary of the relative advantages and disadvantages of chemical inhibitors which offers some limited guidance to designers in the selection of hydration mitigation and remediation strategies.

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