Review

Reviews of gas hydrate inhibitors in gas-dominant pipelines and application of kinetic hydrate inhibitors in China

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ABSTRACT
During the development and application of natural gas, hydrate plugging the pipelines is a very important issue to solve. Currently, adding thermodynamic hydrate inhibitors (THIs) and kinetic hydrate inhibitors (KHIs) in gas-dominated pipelines is a main way to prevent hydrate plugging of flow lines. This paper mainly reviews the efforts to develop THIs and KHIs in the past 20 years, compare the role of various THIs, such as methanol, ethylene glycol and electrolyte, and give the tips in using. The direction of KHIs is toward high efficiency, low toxicity, low pollution and low cost. More than a hundred inhibitors, including polymers, natural products and ionic liquids, have been synthesized in the past decade. Some of them have better performance than the current commercial KHIs. However, there are still few problems, such as the complex synthesis process, high cost and low solubility, impeding the commercialization of these inhibitors. The review also summarized some application of KHIs in China. Research of KHIs in China began late. There are no KHIs used in gas pipelines. Only a few field tests have been carried out. In the end of this paper, the field test of self-developed KHIs by China is summarized, and the guidance is given according to the application results.

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1. Introduction

Gas hydrates are solid crystalline ice-like materials in which water molecules bond with each other by hydrogen bonds and form polyhedral water cavities, as well as gas molecules (such as CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{6}, CO\textsubscript{2} etc.) that are trapped in these cavities at low temperature and high temperature [1]. Since Hammerschmidt [2] found the hydrate in the pipeline, the threat of hydrate in pipeline became one of the biggest challenges in oil and gas flow assurance. A series of accidents caused by hydrates have drawn worldwide attentions. The oil and gas industry continuously study how to prevent hydrate forming in pipes or they will clog the lines, stop the flow of oil and gas and pose a danger.

Keeping pressure and temperature of operation system out of the hydrate formation region is the base ofhydrate inhibition [3]. Heating, using insulated pipelines, depressurization can realize the system conditions transfer from hydrate stable zone to hydrate-free zone [4–7]. But for the long distance pipes, heating and insulating pipelines become costly. Water removal is an essential method to prevent the hydrate formation. It has been used in many long distance transportation lines. But it is difficult or expensive to remove water totally from the gas and oil, especially in the production well pipes.

A practical method to prevent the hydrate formation is to inject the chemical agent into the pipes to prevent hydrate formation, which is called hydrate inhibitors. Hydrate inhibitors include thermal hydrate inhibitors (THIs), kinetic hydrate inhibitors (KHIs) and anti-agglomerant inhibitors. The last two are named low-dose inhibitors. Anti-agglomerate inhibitors must be used in the water–oil–gas system and water-cut must be in a scope [8], which means anti-agglomerant inhibitors cannot take effect in gas-dominated pipes. Fig. 1 showed a hydrate blockage process in gas-dominated pipelines, which is different with the oil-dominated pipelines [5]. In gas-dominated pipelines, there are three phases, gas, water and hydrate. As the gas and water flow, the gas and water will disperse in each other’s phase, forming hydrate particles and hydrate slurry in the pipeline. The formation of hydrate will consume the water in the pipeline. With hydrate increase, the solid–liquid ratio of hydrate slurry increased. When the solid–liquid ratio increases to a certain extent, the pipeline will be blocked due to liquid decline. Additionally, water can form a hydrate film with gas on the pipe wall, which gradually thickens over time and reduces the diameter of the pipe. Thus, pipes will clog. Therefore, preventing hydrate nuclei and growth is more important in gas-dominant pipeline than in oil-dominant pipeline, because once the hydrate starts to grow rapidly, it is hard to keep the pipes from clogging up. THIs or KHIs are necessary in natural gas pipeline, especially in high pressure and low temperature pipelines. This article reviews the hydrate inhibitors used in gas-
dominated pipelines, looks back to the efforts of researchers in the past 30 years to improve the KHI performance, and summarizes some application of KHI in Chinese gas fields.

2. Thermodynamic Hydrate Inhibitors

THIs are a kind of materials that can alter the thermodynamic conditions of hydrate by shifting the hydrate formation region to lower temperature and higher pressure. Typical THIs include methanol (MeOH), monoethylene glycols (MEG), and electrolytes. These compounds can form hydrogen bonds with water molecules to avoid the formation of ordered cages. Just because THIs act with water molecules, the usage of THI commonly is very high, which concentration used is 10 wt%–50 wt% based on water.

Alcohol is looked upon as more favorable to use in the gas field because it’s less corrosive. For MeOH, its advantage is low cost, high efficiency, especially at low concentrations. But, highly toxic and large loss of MeOH limit its usage. Comparing with MeOH, MEG has chemical stability, less poisonous and environmental effect, and low solubility in final gas products, which makes it more applied in the gas fields. Figs. 2 and 3 are methane hydrate equilibrium conditions in the presence of MeOH and MEG. Comparing Figs. 2 with 3, the temperature differences (ΔTₙ) between the two phase equilibrium curves obtained at a constant MeOH concentration difference (Δc) are almost identical, while for ethylene glycol, the temperature differences even at the same concentration difference would increase as the concentration grew. Xu et al. [10] tested the phase equilibrium conditions of natural gas hydrate with the MeOH and MEG and received the same results. So, MeOH is just an intermittent application in most cases [11], such as in restarting well [12], or removing hydrate blockage [13–16].

Electrolytes are the other kinds of THIs, shifting the hydrate dissociation conditions to lower temperature and higher pressure because the dissolved ions tightly bind to water molecules through electrostatic forces in aqueous solution [23]. Though few gas fields would like to use salts as the THIs directly because they will rot the pipeline, salts always exist in produced water and are also widely prevalent in the gas production. Different cations present a sequential inhibition effect on hydrate formation as follows: Mg²⁺ > Ca²⁺ > Na⁺ > K⁺, while Cl⁻ ion has a much stronger hydrate inhibition effect than SO₄²⁻ ion [18, 24–27]. The hydrate inhibition strength of an ion depends on the charge and the radii of ion. The higher charge and smaller radius of ions, the better inhibitory effects on hydrate. And the ionic radius plays a more important role in changing the hydrate equilibrium than the ionic charge [28,29]. Noteworthy, some electrolytes also exhibit as hydrate promoters when they are used at low concentrations [30–32]. Nguyen et al. [31] found that sodium halide has a dual effect on methane hydrate formation. At the concentration below 250 mmol·L⁻¹, sodium halide can promote the hydrate formation, especially NaI. They thought that NaI bound with water molecules and form a similar hydrophobic hydration shells to hydrate, which induce the hydrate nucleation. Choudhary et al. [33] found that a faster kinetic of methane hydrate growth was observed in 1 wt% methanol or 1 wt% NaCl system than pure water system.

Because it was unusual for MEG to be used as single THIs without any mixed salts in application, accurate knowledge of synergistic effect of electrolytes and MeOH or MEG on hydrate is crucial to flow assurance. Jager et al. [34] tested methanol and sodium chloride mixture function on methane hydrate. They thought that the combined effect of mixed inhibitors surpassed the sum of the separate effects, especially at the higher concentration. Lafond et al. [35] measured methane hydrate equilibrium with NaCl and methanol and received similar results. Dholabhai et al. [36] found that MeOH mixed with electrolytes usually performed better than single methanol, while the synergistic effect of electrolytes mixed with MEG is not as significant as with methanol. For sour gas, sodium chloride has more inhibition effect on a mass basis than MEG [37].

![Fig. 1. A hydrate blockage in a gas-dominated pipelines.](image)

![Fig. 2. The experimental data of methane hydrate equilibrium conditions in the presence of methanol. Symbols represent experimental data: ](image) Javanmardi (2012) [17], pure water; (□) Jager (2001) [18], pure water; (●) Javanmardi (2012) [17], 6 mass% methanol; (△) Javanmardi (2012) [17], 10 mass% methanol; (▪) Javanmardi (2012) [17], 20 mass% methanol; (○) Haghighi (2009) [19], 10 mass% methanol; (□) Haghighi (2009) [19], 20 mass% methanol; (‖) Haghighi (2009) [19], 30 mass% methanol; (△) Haghighi (2009) [19], 40 mass% methanol; (○) Haghighi (2009) [19], 50 mass% methanol; (●) Mohammad (2010) [20], 10 mass% methanol; (□) Mohammad (2010) [20], 20 mass% methanol; (●) Mohammad (2010) [20], 30 mass% methanol; (○) Mohammad (2010) [20], 50 mass% methanol; (□) Mohammad (2010) [21], 55 mass% methanol; (●) Mohammad (2010) [21], 65 mass% methanol [21].](image)
pipelines becomes more important. Though the THIs can inhibit hydrate formation completely in the pipelines, the cost of it increases rapidly with the longer pipelines and deeper water. To decrease the hydrate inhibitors usage, Lederhos et al. [50] put forward and extend the metastable period before hydrate nucleation by inserting a crystal stabilizer between metastable hydrate crystalite. This kind of crystal stabilizer is kinetic hydrate inhibitors (KHIs). Following tests proved this kind of inhibitors was effective in prolonging the hydrate nucleation and growth time.

Kinetic hydrate inhibitors do not alter the gas hydrate phase equilibrium condition but prolong the hydrate nucleation and growth. KHIs have many advantages over THIs. Low dose of KHIs is the most outstanding advantage. So, KHIs are called low dosage hydrate inhibitors (LDHIs). Since the discovery of KHIs, it has attracted attention from the academic. Figs. 4 and 5 display the published academic articles number from 2000 in the web of science database, which showed that KHIs have always been one of the hydrate inhibition hotspots, especially in China, U.S. and Norway.

About the synergistic effect, some researchers have the opposite views. Eichholz et al. [38] tested the mixture 19.16% MEG, 15.36% MEG + 3.77% NaCl and 15.67% NaCl + 3.77% MEG, the best inhibiting effect of them on methane hydrate was 19.16% MEG. Masoudi and Tohidi [39–45] did a lot of experiments about NaCl, KCl, CaCl$_2$ mixed with MeOH and MEG at different concentrations, and summarized that the summation effect of separate effects is larger than the effect of mixed electrolytes and alcohol, especially at higher concentrations. Ranking of the inhibition effect is saturated high concentration alcohol > saturated low concentration salts > saturated high concentration salts + low concentration alcohol > saturated salts.

Salts not only affect the hydrate onset temperature and subcooling temperature, but also decrease the initial growth rate and hydrate volume. Kim et al. [46] mixed the alcohol and inorganic salts to inhibit the hydrate formation. The initial growth rate of hydrate reduced to 1/10 of pure water by increasing mixture of NaCl and MEG.

In conclusion, special attentions should be paid in using THIs, especially in the presence of electrolytes. ① How to choose methanol or ethylene glycol in cold restart well. During the well restart, the temperature of well drops down greatly due to the Joule–Thomson effect. The freezing point of MEG solution does not decrease continuously with the increase of MEG concentration. 50% MEG solution has the lowest freezing point. If the concentration of MEG solution surpasses 50%, the freezing point increases. So, it needs to pay attention whether minimum temperature after throttling exceeds the freezing point temperature of ethylene glycol. ② Consider the synergistic effect of alcohol and electrolyte mixture, which is crucial to determine the amount of THIs. ③ MeOH can enter the gas phase in the process of use. The loss of this part should be included in calculating the usage amount of MeOH. ④ The performance of MEG after recovery will be reduced and the viscosity will increase, which should be taken into account when it is recycled. Fresh MEG must be added after many cycles [47–49].

3. Kinetic Hydrate Inhibitors

With the gas and oil well transform from onshore to further offshore, the high pressure and cold deep water create suitable conditions for hydrate formation more easily. The prevention and control of hydrates in
3.1. Single function KHIs

KHIs are mainly some water soluble polymers, such as poly(vinyl pyrrolidone) (PVP), poly(vinyl caprolactam) (PVCap). These inhibitors have certain groups, adsorbing on the hydrate surface and bonded with the water molecules that form cage structure. They can play the role on the hydrate nucleation and growth process. Based on the available literature, there are two classes KHIs are commonly used or research point, synthesized KHIs and natural KHIs.

3.1.1. Synthesized KHIs

PVP and PVCap are representatives of first- and second-generation inhibitors, respectively [50]. They belong to the same family of lactam monomers, but the PVCap is much more effective than PVP on hydrate inhibition. In wide researches, their various aspects of performance are compared with each other.

In tolerance subcooling, PVP is effective at low subcooling conditions. When the subcooling temperature is raised above 10 K, PVP lost its effectiveness obviously and fails to prolong hydrate formation [51]. PVCap performance is better than PVP. At the same experiment conditions, PVCap cannot lost its effect until subcooling above 14.72 K [51]. At the same subcooling, the hydrate induction time of PVCap is longer than PVP. O'Reilly et al. [52,53] compared the effect of KHIs molecular weights on hydrate formation. They found that the PVP was more sensitive to molecular weight than PVCap. Below 10 K, the larger molecular weight of PVP showed more strong inhibition on the hydrate [52]. While in PVCap, the molecular weight from 2000 to 20000 was similar in performance [52]. Different types of adsorption of PVP and PVCap may be the key reason of their different performances. The adsorption of PVP is the Langmuir-type adsorption [54], which makes PVP form a loose film [55], while the PVCap adsorption on the hydrate surface is BET-type adsorption [54] and forms a more rigid and compact film [55]. Although PVP and PVCap have good inhibition effect on hydrate formation and have been commercialized, it is difficult to meet the requirements of industrial application.

The first and the most important point of KHIs development is high efficiency on hydrate nucleation and growth. Based on the structure of PVP and PVCap, lots of similar structure polymers and copolymers are used as KHIs [52,56–58], such as poly vinylpiperidone (PVPip), VIMA/VP (N-vinyl-N-methyl acrylamide and N-vinyl pyrrolidone copolymer), etc. (Fig. 6). These polymers contain one or more pendant lactam group, which is the functional group in the polymers. The oxygen atoms in the lactam can form the hydrogen bonds with the water molecules.

The relationship between the structure of the polymer and the performance of the inhibitors is very complex that is why it is unclear until now. The size of lactam ring is critical of the hydrate inhibition [59]. The strength of the interaction of the polymer with the hydrate surface increases as the number of monomer units in the polymer increases [52]. Poly(N-vinyl azacyclooctanone) (PVACO), which the lactam ring contains 8 atoms, exhibit better hydrate inhibition than that of PVP, PVAPip and PVCap [59]. The size of lactam ring should fit with the hydrate cage size at the interface [60].

Amide-based polymers is a class of KHIs, which has the N–C=O group in the chain structures. This group is particularly useful for hydrogen bonding from both the amino nitrogen atom and the carbonyl oxygen [61]. Many amide-based polymers have been proven to possess kinetic inhibition on the gas hydrate. Mainly, these polymers include acrylamide polymers [56,62–67], vinylamide polymers [68], and maleimide polymers [57,69]. Fig. 7 lists the based structures of the acrylamide, vinylamide polymers and maleimide polymers. Poly(N-isopropylacrylamide) (PNIPAM) is a representative amide-based polymer that shows strong KHI performance because of the amide functionality attached to a hydrophobic group [63,65,70,71].

Based on the lactam monomers and amide monomers, lots of copolymers were synthesized and used as KHIs, because chain structure diversifies is a method to improve the inhibition effect of KHIs, such as ter-polymer of N-vinylpyrrolidone, N-vinylcaprolactam, dimethyllimino-ethyl-methacrylate (VC-713) [72], vinyl pyrrolidone/vinyl caprolactam copolymer (VP/VCap) and copolymer (VCP/VIMA) [73], poly(N-vinyl-2-pyrrolidone-co-2-vinyl pyridine) [74], VIMA/VP, poly(N-ethyl-β-alamine)-co-N-propyl-β-alamine) [75], copolymer (N-vinyl azacyclooctanone/VIMA) (VACO/VIMA) [76], VACO/VP [76], copolymer (VACO/N-vinylacetamide) (VACO/NVA) [76], poly(2-isopropenyl-2-oxazoline-co-N-isopropylacrylamide) (iPOx-co-NIPAM) [77], poly(N-dimethylhydrazidoacrylamide-co-N-isopropylacrylamide) (DMHAM/IPAM) [78], poly(N-isopropylacrylamide-co-acrylic acid) (PNIPAM-co-AA) [66], poly(N-isopropylacrylamide-co-cyclopentylamine) (PNIPAM-co-Cp) [66], and poly(N-isopropylacrylamide-co-tetra-2-aminobutyramide) (PNIPAM-co-C4t) [66]. All of them have inhibitory effect on hydrate formation, but not all of them show a better performance than polymer with one monomeric unit. In copolymers, the ratio of monomeric units [76,78,79], the correct molecular spacing of the monomeric units in copolymer is required for the best kinetic hydrate inhibition [75].

Fig. 6. Effective KHIs structure.
Hydrophobic tails and hydrophilic groups can alter KHI performance, including solubility and inhibition. Grafting some functional groups, such as hetero-cycles, chain or cyclic amides, betaines, and amine oxides into water-soluble polymers can get better KHIIs and more functions. Roosta et al. [67] modified polyvinyl alcohols (PVA) with acrylamide, methacrylamide and acrylonitrile by graft copolymerization and functionalization techniques and got the graft copolymers that have similar performance with PVP. Zhang et al. [80] modified PVCap with carboxyl-acid and got the carboxyl-terminated polyvinyl caprolactam (PVCS)COOH, which not only improved the PVCap inhibition performance but also increased the cloud point of PVCap. Mady and Kelland [78] copolymerized the active monomers with a more hydrophilic comonomer to overcome solubility problem. Poly(fluroalkylacylamide) [81], and poly[N,N-dimethylhydrazidoacrylamides] (PDMHAMS) [78,79,82] had high cloud point and good KHI performance. Park et al. [83] modified PVCap-co-acrylic acid with imidazole (APIM) moieties, which was known as corrosion inhibitor. They got a multifunctional inhibitor with kinetic hydrate inhibition and corrosion inhibition.

Kelland [59,65,66,68,71,75,78,79,81–111] and his group at the University of Stavanger synthesized at least 50 KHIIs in the past ten years, and tested their KHI performance on synthetic natural gas (SNG). Most of these KHIIs are based on N-alkyl-N-vinylacetamide, N-alkyl-N-alkylglycines, and N-vinylcaprolactam copolymer. A similar feature among these polymers was that they all contained N-C=O group in their structures. They may be located in the backbone, branch or pendant ring. Fig. 8 lists some polymers that were synthesized by the University of Stavanger. Table 1 summarizes the performance of KHIIs that were synthesized by the University of Stavanger. They used onset temperature (T_o) and fast hydrate growth temperature (T_a) as the indicator of inhibition effects by ranking cell method [71]. These experiments were done by different researchers, with slightly different concentrations. Fortunately, they all did the PVCap performance in experiments. In order to make the results comparable between different researchers, we used T_p and T_o of the PVCap as the baseline. All the data are compared with T_p and T_o of the PVCap and obtained Fig. 9.

$$T_{p-o} = T_o^{(PVCap)} - T_p$$

$$T_{a-o} = T_o^{(PVCap)} - T_a$$

where T_o is onset temperature listed in Table 1. T_a is fast hydrate growth temperature listed in Table 1.

In Fig. 9, there are four quadrants. In the first quadrant, T_p and T_o are lower than that of PVCap, meaning this KHI performance was better than PVCap. In the second and forth quadrants, T_p (T_o) is higher than PVCap’s but T_o (T_p) is lower than that of PVCap, which means that the nucleation inhibition (growth inhibition) is worse than PVCap. The point in the third quadrant means this KHI is worse in both nucleation and growth inhibition. As seen from Fig. 9, most of the new developed KHIIs has similar KHI performance to PVCap. Just VACO/VP, polyNPMA, and PNPAM were apparently better than PVCap. But they are still inferior to Luvicap, which is a commercial KHI, and its main composition is poly(VP/VC).

Though the above polymers have great inhibitory performance in hydrate formation, they need some synergists to strengthen their inhibition effect and decrease their costs. Various series polymers, organic salts can be used as a synergist of PVCap, including anionic carboxylate [116], tetraalkylammonium salts [117], hexaalkylguanidinium salts [108], tris(dialkylamino) cyclopropenium chlorides [118], fluorinated quaternary ammonium bromides [119], tetraalkyl phosphonium bromide salts [120], tris(tert-heptyl)-N-alkyl-1-ammonium bromides [121], and tert-Heptylated quaternary ammonium salts [122]. But, most of them proved ultimately unsuccessful. Just tri-n-pentylamine oxide (TPAO) [123], tetra(n-hexyl)ammonium bromide (TheXAB) [117], monofluoro ammonium salt [119], tris(t-heptyl)(n-pentyl)
ammonium bromide (tris(t-heptyl)PeAB) [121], Bu(6)GuanCl [99], and tris(tert-heptyl)PeAB [122] have some synergistic effect with PVCap on hydrate formation.

Xu et al. [124] tested synergism of glycine with PVCap. Glycine cannot inhibit CH₄ hydrate formation alone but it can enhance the inhibitory performance of PVCap apparently. The subcooling temperature of PVCap increased by 4.1 K and the induction time also increased by 16-fold after blending the glycine with PVCap. The biggest difference between glycine and common synergists was that 1.0% mass fraction glycine can equivalently replace PVCap in the same amount, leading 40.8% lower cost and 23.4% higher biodegradability.

Although hundreds of polymers have been proven to inhibit hydrate formation well, especially PVCap, VC-713, VP/VIM, PVCSCOOH, VACO/VP, poly(N-(pyrrolidin-1-yl))-methacrylamide), and PNIPMA, several challenges and uncertainties prevent their widespread use in the industry (lack of compatibility with other types of production chemicals, relative low cloud point/fouling issues, poor repeatability of test results, performance concern under shut-in conditions, potential risk of hydrate formation at the top of pipelines, etc.) [125]. While the performance of KHIs is influenced by chemical structure (active group, mass weight, arrangement of monomeric), subcooling, salinity, gas composition, etc., and the inhibition mechanism are still not clear. A lot of experiments and simulations are still needed for further study.

### 3.1.2. Natural KHIs

With the improvement of environmental protection requirements, offshore field application has more and more limitations to inhibitors’ biodegradability. Many researches are focus on the green inhibitors, which are usually extracted from biology, such as antifreeze protein, polysaccharides. So, they have good biodegradability.

Antifreeze proteins (AFPs) exist in some deep ocean fish, such as pufferfish, redfish, and marine macroinvertebrates, such as crabs, etc., which can bind to the surface of hydrate crystals at low temperature, which can bind to the surface of hydrate crystals at low temperature. They can prevent the formation of ice crystals at low temperature, which is particularly important in offshore field applications. Many researches focus on the green inhibitors, which are usually extracted from biology, such as antifreeze protein, polysaccharides. So, they have good biodegradability.

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on hydrate inhibition were Type I AFP, Type III AFP, Maxi AFP and RmAFP. Type I AFP is from winter flounder [127,128], which is a small alanine rich, α-helical monomer with an 11-residue periodicity [129]. Maxi is five times as long as Type I AFP [129]. Type III AFP is from recombinant Saccharomyces cerevisiae yeast cells [130] or ocean pout fish [131]. RmAFP is from the bark beetle Rhagium mordax. AFPs from different species have different inhibition effect on the hydrate. Type I AFP can inhibit hydrate formation [127,128], especially at lower hydrate formation driving force [132] and eliminate memory effect [128], but it is not resistant to salt. Saline will reduce the induction time of Type I AFP [133]. Compared to Type I AFP, Type III AFP displays more active in the present of saline [133]. Type III AFP can selectively inhibit the sl hydrate appearance and allow the growth of sl hydrate [134]. RmAFP shows more activity in both hydrate nucleation and formation [131, 135]. MixAFP can slow hydrate growth rates up to an order of magnitude compared to pure water [136]. The hydrate formed with AFPs requires higher temperature to melt [137], but it is easier to decompose than hydrate formed with PVP [130,134,138]. AFPs can change the morphology of growing hydrate crystal, which keeps the hydrate particles small and well dispersed [139]. Though AFPs have good effect on hydrate formation, it is not practical to use in the field due to its high cost and low production.

Other green inhibitors are polysaccharides, such as starch, chitosan and pectin. They have similar molecular structure, as in Fig. 10. In these structures, there are lots of OH—, NH₂—, COOH—, which the group can form the hydrogen bonds with water molecules and fixed the water molecules.

Starch is a polysaccharide, which from different sources has different effects on the hydrate. Lee et al. [140] tested seven stashes as KHI in methane and methane/ethane mixture hydrate and found that starches except for tapioca starch exhibit a very weak inhibition effect in hydrate formation. Fakharian et al. [141] even found that potato starch can promote the hydrate nucleation and formation in all tested concentrations. Starch modified is a common method to change their function as additive because it can change in several ways. Talaghat tested oxidized starch in a mini-loop. The induction time for SNG hydrate formation in the presence of oxidized starch is longer than that of PVP. Roosta et al. [142] thought that the inhibition and promotion effects may be altered with the modification of starch. He found that the native starch synthesized by ceric ammonium nitrate and ammonium persulfate and ammonium persulfate showed inhibition effects. Xu et al. [143] introduced chitosans as a good KHI. They found that the induction time of gas hydrate formation evidently increased with the degree of deacetylation (DD). However, when DD was higher than 80%, the effect of DD on the induction time was negligible.

Xu et al. [144] first reported the pectin as an extraordinary natural KHI. The dosage of pectin decreased by 66% and effectivity time extended 10 times than PVCap. Besides, its maximum growth rate was no more than 2.0%/h, which was far less than 5.5%/h of growth rate for PVCap at the same dosage. Xu et al. [145] used the molecular dynamics simulations to examine the effect of pectin on the methane hydrate growth. They verified that the double-bonded oxygen atoms of pectin combine with hydrogen atoms of water, and the hydrogen atoms of hydroxyl in pectin combine with oxygen atoms of water through hydrogen bonds, which disturbed the further growth of the methane hydrate. The role of the pectin’s active groups in hydrogen bonds with water both as a proton donor and as an electron acceptor makes pectin have a better inhibitory effect on the growth of methane hydrate.

Carboxymethylcellulose sodium salt as a kind of polysaccharide only possesses dual functional natural inhibitor in published articles. It was reported that carboxymethylcellulose sodium salt can slow down the rate and change the conditions of gas hydrate formation, showing the properties of the thermodynamic and kinetic inhibitor. Its efficiency exceeds 300 times of methanol when used in the same dosages.

![Fig. 9. KHI performance of different KHIs compared with PVCap.](https://doi.org/10.1016/j.cjche.2019.02.023)

Fig. 9. Structure of starch, chitosan and pectin.

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Magnusson et al. [146] reported a development of green KHI based on a cheap, abundantly available natural product that is readily biodegradable and low in toxicity. They called this KHI530, but they did not introduce the components of this green KHI. They just introduced that the KHI530 is a polymer blend containing the classic features of KHI polymers, pendant hydrophobic groups, and hydrophilic groups including amide groups. The performance of KHI530 was better than a low molecular PVP.

Natural KHIs have good degradability, no pollution and good inhibitory performance, but they still cannot be applied in the industry due to some defects. AFPs extracted from living organisms have high cost and low yield, which limit the AFP application. Polysaccharides are cheap and easy to obtain, but they are usually poorly soluble in water or have a high viscosity after dissolving in water, so it is difficult to inject them into the pipeline during use. It is necessary to improve its water solubility or to develop new injection processes. The breakthrough of production with low cost or injection processes may promote the application of natural KHIs in the industry.

### 3.2. Dual functional inhibitor

The main shortage of KHI is the limitation of subcooling temperature. Commonly, the durable subcooling temperature of KHI is no more than 10 °C. Below the 10 °C, KHI has a very good performance. But surpass the 10 °C, KHIs will lose their inhibition effects quickly. To avoid KHI from losing inhibition, the common method is compounded inhibitors. The compounded inhibitor is usually a mixture of KHI and THI. Besides compounded inhibitors, researchers found that the ionic liquids (ILs) are hydride inhibitor, which have a dual effect of THI and KHI.

ILs are organic salts with a low melting point (<100 °C), which are the focus of many investigations because of their chemical stability, low flammability, negligible vapor pressure, high ionic conductivity and wide electrochemical window [147]. There are thousands kinds of ILs. Most of ionic liquids used for gas hydrate inhibition studies in the literatures belong to the imidazolium family and a few ILs belong to the pyrrolidinium, ammonium, phosphonium, and morpholinium families. The highest efficiency of ILs in thermodynamic CH4 hydrate inhibition is [C2C1im][Cl]. However, the effect of IL inhibition is much lower, compared to the conventional thermal dynamic inhibitor methanol in the same amount. Just 30 wt% [C2C1im][Cl] is exhibiting a similar inhibition effect as 10% methanol. Li et al. [148] tested methane hydrate equilibrium conditions with 0.1 mass fraction dialkylimidazolium-based ILs and tetraalkylammonium-based ILs. For dialkylimidazolium-based ionic liquids studied, the hydroxyl-functionalization of the cation (1-hydroxyethyl-3-methylimidazolium chloride ([OH-C2MIM]-Cl)) exhibits the enhancement on the inhibition effectiveness. The ones with the shorter alkyl substituents of the cations perform better on inhibiting hydrate formation than the ones with longer alkyl substituents of cations. For tetraalkylammonium-based ionic liquids studied, it was found that the ionic liquids with the shorter alkyl substituents of the cations perform better thermodynamic inhibition effects than the ones with the hydroxylated longer alkyl substituents of the cations. Among all of the ionic liquids studied, tetramethylammonium chloride ([N1.1.1.1]-Cl) is the most effective thermodynamic inhibitor, which is comparable with EG.

Tariq et al. [149] reviewed the ILs as hydrate inhibitors literature and analyzed the experimental data before 2014. They found that the more the concentration of ILs added to the system, the more effective was the shift of the equilibrium toward lower temperatures, thus leading to efficient thermodynamic inhibition. Commonly, the longer the alkyl chain of the cation of ILs, the less effective they are as inhibitors. The presence of suitable hydrogen-bond-forming functional groups (e.g., OH, NH2, NHCO, SO3H) in an IL structure would provide more-efficient gas hydrate inhibitors, compared to unsubstituted ILs. Later, Chu et al. [150] proved Tariq’s conclusion about the effect of alkyl chain through testing the dissociation temperature of methane hydrate in the presence of ionic liquid 1-alkyl-3-methylimidazolium chloride. They found that the shorter the alkyl chain length is, the stronger the thermodynamic inhibition effect is.

The kinetic effect of ILs on the hydrate formation is more complicated than their thermodynamic effects; and there exist controversies. Xiao et al. [151,152] tested a series of ILs including dialkylimidazolium halides ILs of varying cations and anions. They found that 1-butyl-3-methylimidazolium iodide ([BMIM][I]) is the most effective KHI and better than the commercial kinetic inhibitors. Given at 0.01 mass fraction concentration, it exhibits the longest induction time. They attributed this inhibition effect to strong electrostatic charges and hydrogen bonding with water. Kim et al. [153] studied the inhibition effect of pyrrolidinium-based ILs on methane hydrate formation and showed that these ILs exhibit longer induction time than PVP and PVPc at 7 MPa and 15 K subcooling. They thought that a function group such as OH enhances the hydrate inhibition as there is an increase in hydrophilicity of IL and intermolecular hydrogen bonding with water molecules. In contrast, Villano and Kelland [154] measured the kinetic performance of [EMIM][BF4] and [BMIM][BF4] solutions on standard natural gas (SNG). They showed that these ILs are very poor KHIs when used alone at 0.5 wt%–1.0 wt%.

The kinetic performance of ILs is dependent on many factors, such as cations, anions, concentration, subcooling, guest sorts and hydrate structure. Lee et al. [155] investigated the different effects of anions in ILs of 1-hydroxyethyl-1-methylmorpholinium chloride ([HMIM][Cl]) and 1-hydroxyethyl-1-methylmorpholinium tetrafluoroborate ([HMIM][BF4]) on the methane hydrate formation kinetics. [HMIM][Cl] and [HEMM][BF4] acted as the kinetic hydrate promoter and inhibitor, respectively. They believed that [HMIM][Cl] might distort the rigid hydrate host framework at the surface by the hydrogen bonds of the ions with water molecules, which can promote the methane penetration or inclusion into the growing clathrate hydrate structures. In contrast, the kinetic hydrate inhibition behavior of [HEMM][BF4] might be attributed to the hypothesis that BF4− can act as a mobile pseudo guest because the anion cannot be the guest of the hydrate cage owing to the charge imbalance even though it can fit into the structure I hydrate cages.

Nashed et al. [156] studied nine ILs as KHI for methane gas hydrate with 0.01 mass fraction, nine ILs including BMI- based ILs and OH-EMI-based ILs. It is found that [BMIM][CF3SO3], [BMIM][CH3SO4], and [OH-EMIM][Br] can delay hydrate formation at this concentration. The other ILs exhibit promotional effect. There is a strong correlation between molar mass of [BMIM]+-based ILs and induction time.

Tetramethylammonium chloride (TMACl) has similar ionic structure to ILs and has been proven to be a good dual functional inhibitor [157]. TMACl possessed similar thermal dynamic and kinetic inhibition effect compared to most of imidazolium-based ILs. Four weakest hydrophobic methyl cation ([CH3]+) makes tetramethyl ammonium [TMA+] cation more hydrophilic. Chloride anion ([Cl]−) can bind with water by hydrogen bond [158,159]. Thus, TMACl adsors on the interface of gas-water and prevent hydrate nucleation and sterically block the hydrate formation [157]. Interestingly, TMACl does not form semi-hydrate with water.

Though the kinetic inhibition of ILs has conflict, all researchers proved that the ILs have good synergetic performance with PVP or PVPc. Researchers studied 1-hexyl-1-methylpyrrolidinium tetrafluoroborate ([HMP][BF4]) [160], 1-methyl-1-propylpyrrolidinium chloride [PMPy] [Cl] and 1-methyl-1-propylpyrrolidinium triflate [PMPy] [triflate] [161], 1-hydroxyethyl-1-methylpyrrolidinium chloride ([HMP][Cl]) [162], 1-hydroxyethyl-1-methylpyrrolidinium tetrafluoroborate ([HMP][BF4]) [162,163], 1-butyl-1-methylpyrrolidinium bromide ([BMP][Br]) [162], 1-butyl-1-methylpyrrolidinium tetrafluoroborate ([BMP][BF4]) [162] etc. mixed with PVPc and these ILs exhibited enhanced kinetic inhibition effects for CH4 hydrate formation.
3.3. Mechanism of KHIs

Since the appearance of KHIs, researchers denoted to understand how the KHIs affect the hydrate nucleation and growth. With the development of research theories and methods, more and more researches on the KHI mechanism have been carried out, but it is still not clear. It is generally accepted that the adsorption of inhibitors is the fundamental of inhibition mechanism. Generally, macromolecules can adsorb on surface at some extent, but difference of adsorption type and adsorption strength affect the kinetic inhibition of nucleation, growth and re-nucleation of hydrate [128].

Makogon and Sloan proposed that KHIs hinder hydrate formation by adsorbing and sterically blocking [164]. King et al. and Hutter et al. [165, 166] proved KHI’s surface adsorption on hydrate growing crystal by small angle neutron scattering studying the KHIs adsorbed on the hydrate.

The hydrate formation is a process of nucleation and growth [167, 168]. So, the inhibition of hydrate includes two stages, nucleation inhibition and growth inhibition. In the nucleation process, inhibitor molecules disrupt the local organization of the water and guest molecules, increasing the barrier to nucleation and nuclei propagation [30,73, 169]. Once nucleation occurs, the inhibitor binds to the surface of the hydrate nanocrystal through hydrogen bonds [170] and retards further growth along the bound growth plane [73]. The adsorbed KHI molecules sterically block gas molecules entering and completing hydrate cavities, and force the hydrate to grow around and between KHI molecules [164, 170]. Additionally, un-adsorbed KHI molecules are easy to enrich on the water surface due to hydrophilic amide groups in polymers, which decrease the host water molecules concentration on the interface of gas and water [170]. The KHI film on the interface increases the mass resistance and retards the hydrate nucleation and growth. The key feature of this mechanism was an inhibitor molecule bound to the surface of an ensuing hydrate crystal interrupting the growth and crystallization. KHI molecules adsorbed on the nucleation sites (hydrate nuclei) and growth sites (minute hydrate particles) can delay nucleation and growth. When the clump spacing is less than the critical nucleation radius [181], the adsorbed KHI molecules cannot stably adsorb on the hydrate surface due to their amide that tends to bind with liquid water at the liquid–solid interface, which can destroy the hydrate around PVCap. This phenomenon was also observed in Chen et al.’s study [173].

Insight of KHI mechanism is very important for new inhibitor development. However, it is still unclear. Various structure of polymers and molecules can be used as KHIs, they all contain hydrophilic parts and hydrophobic parts, but their structures are dissimilar to each other, for example, the size and the shape of pendant groups [53,87,183,184], the length of hydrophobic side chain [185,186], the spacing between hydrophobic groups [63,98,169], degree of polymerization [187,188], and versatile monomer of copolymers [170,189,190], which the relationship was proven with the inhibition effects by experiments. But how it works and its mechanism is unclear. Further research and MD simulations are required to settle these problems.

3.4. Coating technology

Regardless of the amount of low-dosage inhibitor (KHIs), adding the chemical to the pipelines can cause more or less environmental pollution, and the cost of inhibitors for a long time is very high. The best way to keep the hydrates from blocking the pipeline is not to add inhibitors. Pipeline coating technology is a potential method to prevent the hydrate in pipelines.

Pipeline coating technology for hydrate inhibition is a novel technology in recent years. The pipeline coating usually has anti-corrosion and adsorbing and sterically blocking [164]. King et al. and Hutter et al. [165, 166] proved KHI’s surface adsorption on hydrate growing crystal by small angle neutron scattering studying the KHIs adsorbed on the hydrate.

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Pipeline coating technology for hydrate inhibition is a novel technology in recent years. The pipeline coating usually has anti-corrosion and

Fig. 11. The process of hydrate growth on the pipe wall.
flow-resistance reducer, which the effect on the hydrate deposition is not known. In gas-dominant pipelines, water will add moisture to the wall and form a water film or droplets on the wall. Due to the large gas–liquid interface and low temperature of the wall, this water film is more easy to form hydrate. After the hydrate film is formed, water will continue to form a film cover, the hydrate and hydrate film will continue to grow thicker and gradually develop into clogging, as Fig. 11 shows. The first step of the solution is to avoid the formation of water film in the pipe wall.

Aman et al. [191] deal the steel by five physical and chemical modifications, including oleamide, graphite, citric acid ester, nonanedithiol, and Rain-X anti-wetting agent. They measured the adhesive force between hydrate particles and the steel using a micromechanical force apparatus. The results showed that graphite coating reduced hydrate–steel adhesion force by 79%, due to an increase in the water wetting angle from 42 ± 81° to 154 ± 71°. Two chemical surface coatings (nonanedithiol and the citric acid ester) induced rapid hydrate growth in the hydrate particles; nonanedithiol increased hydrate adhesive force by 49% from the baseline, while the citric acid ester coating reduced hydrate adhesion force by 98%.

Hall et al. [192] conjugated glycerol to glass test tube surfaces employing two different silane spacers, covalent attachment to glycerol at either the 1- or the 2-position, and with a succinic acid spacer. The resulting surfaces were tested to inhibit the nucleation of tetrahydrofuran hydrate (THF hydrate) in comparison with polyvinylpyrrolidone (PVP). The results showed that coating with (3-amino propyl) triethoxysilane (APTES) and glycerol coupled at the 1-position (leaving a free 1,2-diol) displayed significant inhibition of the formation of THF hydrate.

Zhang et al. [193] modified the steel sheet with polydimethylsiloxane coating and tested the contact angles and hydrate inhibition performance. The coating can increase the water contact angle and decrease the hydrate particle adhesion force, as well as inhibit the THF or methane hydrate growth on the wall. They believed that hydrate-phobic coating will be one of the most promising methods of hydrate prevention in the future without more actions.

Now, the hydrate coating technology is just emerging, there are many problems to be solved. For example, coating needs good hydrophobicity, good oleophobicity and good hydrate-phobicity. At same time, coating can inhibit the growth of hydrate. Additionally, fastness, wear-resistance, and good compatibility with other coating materials are also required.

### 4. Application of KHIs in China

Research of gas hydrate in China began relatively late, but it has developed rapidly in recent years. As seen from Fig. 5, the number of articles published on KHIs of China is No. 1 among all countries since 2000. In China, institutions that conduct research on hydrate inhibitors are China University Petroleum (Beijing), Guangzhou Inst Energy Conver of Chinese Acad Sci, South China University of Technology, Southwest Petroleum University, Natural Gas Research Institute, China National Offshore Oil Corporation (CNOOC) and China National Petroleum Corporation (CNPC).

The natural gas of China is mainly produced in Sichuan Province, Xinjiang Province, Shaanxi Province, and offshore area. The high latitude or altitude of these gas-producing areas makes hydrate formation very easy, so there is a great demand for hydrate inhibitors. With the development of natural gas, research on kinetic hydrate inhibitors has developed greatly. But, in Chinese gas field and gas pipelines, methanol and MEG are the main inhibitors. Kinetic hydrate inhibitors are still predominantly laboratory studies. Only a few inhibitors that evaluated reliably in the laboratory have been tested in the field with the support of the Chinese government, China National Offshore Oil Corporation (CNOOC) and China National Petroleum Corporation (CNPC). Table 2 lists the field application of KHIs in China. The following part will introduce the field application cases in details.

Field tests were carried out in Sichuan, Shaanxi and offshore gas fields. Table 3 lists some tested field gas components and conditions. In Luojaizhai gas fields, the high content of acid gas, especially the high content of hydrogen sulfide (7.34%), brought great challenge to hydrate inhibition. Before GHI-1 was tested in Luojaizhai gas field, the tested pipeline was filled with MEG about 50 kg every day. Shifting to the kinetic inhibitor GHI-1, which the main component was PVP [203], the daily dosage was controlled at 15 kg. According to field-tested results [194], during the test period of GHI inhibitor, the production pipeline was running smoothly and no hydrate blocking occurred. The pigging cycle was prolonged from 5 days with MEG injection to more than 15 days with GHI-1 injection. The shortage of GHI-1 was a high cost, which makes it difficult to replace MEG applied in gas field.

The features of Changqing gas field are low content of condensate oil, high water yield, and high subcooling temperature. The surrounding temperature was below 0°C in winter. So, combined inhibitor needs to be used in controlling the hydrate. HY-10 was synthesized by NVP through one-step methods. Synergists include glycol ether, methanol and TBAB. During the field application, although there is no blockage, the pressure difference would increase when the dosage of HY-10 is lower than 2% [196].

### Table 2

<table>
<thead>
<tr>
<th>Name</th>
<th>Developer</th>
<th>Field test</th>
<th>Field test time</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>GHI</td>
<td>Natural Gas Research Institute</td>
<td>Luojaizhai</td>
<td>2005 [194]</td>
<td></td>
</tr>
<tr>
<td>CTS-54</td>
<td>Natural Gas Research Institute</td>
<td>Wenhuang</td>
<td>2006 [195]</td>
<td></td>
</tr>
<tr>
<td>HY10</td>
<td>SCUT</td>
<td>Changqing,</td>
<td>2010–2011 [196]</td>
<td></td>
</tr>
<tr>
<td>Z-3</td>
<td>PetroChina</td>
<td>Jinbian</td>
<td>2008 [199]</td>
<td></td>
</tr>
<tr>
<td>Z-7</td>
<td>PetroChina</td>
<td>Jinbian</td>
<td>2008 [199,200]</td>
<td></td>
</tr>
<tr>
<td>Z-6</td>
<td>PetroChina</td>
<td>Yan’an</td>
<td>2013–2014 [199,200]</td>
<td></td>
</tr>
<tr>
<td>KHI-6033</td>
<td>PetroChina</td>
<td>Dongsheng</td>
<td>2015 [201]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SPU</td>
<td>Dongfeng</td>
<td>2014 [202]</td>
<td></td>
</tr>
</tbody>
</table>

SCUT—South China University of Technology, CUP(B)—China University Petroleum (Beijing), SPU—Southwest Petroleum University.

### Table 3

<table>
<thead>
<tr>
<th>Component</th>
<th>Luojaizhai</th>
<th>Wenhuang</th>
<th>Changqing</th>
<th>Dongfeng</th>
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</thead>
<tbody>
<tr>
<td>CH4</td>
<td>90.38</td>
<td>95.79</td>
<td>93.84</td>
<td>91.87</td>
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<tr>
<td>C2H6</td>
<td>0.07</td>
<td>0.15</td>
<td>3.43</td>
<td>3.24</td>
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<tr>
<td>C2H3</td>
<td>0</td>
<td>0</td>
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<tr>
<td>C3H8</td>
<td>0.006</td>
<td>0.002</td>
<td>0.46</td>
<td>0.81</td>
</tr>
<tr>
<td>i-C3H8</td>
<td>0</td>
<td>0</td>
<td>0.08</td>
<td>0.12</td>
</tr>
<tr>
<td>n-C2H3</td>
<td>0</td>
<td>0</td>
<td>0.10</td>
<td>0.17</td>
</tr>
<tr>
<td>i-C3H12</td>
<td>0</td>
<td>0</td>
<td>0.05</td>
<td>0</td>
</tr>
<tr>
<td>n-C5H12</td>
<td>0</td>
<td>0</td>
<td>0.00</td>
<td>0.04</td>
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<tr>
<td>CO2</td>
<td>1.65</td>
<td>2.67</td>
<td>1.73</td>
<td>0.08</td>
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<tr>
<td>O2</td>
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<td>0</td>
<td>0.31</td>
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<tr>
<td>He</td>
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<td>0.028</td>
<td>0</td>
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<tr>
<td>HS</td>
<td>7.34</td>
<td>0.87</td>
<td>0</td>
<td>0.00</td>
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<tr>
<td>Total</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
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</table>

### Table 4

<table>
<thead>
<tr>
<th>Name</th>
<th>pH</th>
<th>Density/g·cm⁻³</th>
<th>Frozen temperature/°C</th>
</tr>
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<tbody>
<tr>
<td>Z-3</td>
<td>7.0</td>
<td>1.1</td>
<td>−15</td>
</tr>
<tr>
<td>Z-6</td>
<td>6.8</td>
<td>1.02</td>
<td>−35</td>
</tr>
<tr>
<td>Z-7</td>
<td>7.0</td>
<td>1.06</td>
<td>−35</td>
</tr>
</tbody>
</table>

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The largest field tests were Z-x series inhibitors, which were developed by PetroChina. Z-x series has three types, Z-3, Z-6 and Z-7. Their properties were listed in Table 4 [199–201]. Three field tests were proceeded at 2008, 2013, and 2015. KHIs Z-3 and Z-7 were tested at 13 wells. Z-6 were tested at 8 wells. The most efficient KHI was Z-6.

Z-6 is the newest type of inhibitor of the Z-x series inhibitors, which are a kind of water-soluble combing polymer block copolymer formed by acrylic monomer, epoxypropane, alkyl butyl ester monomer, cyclopentadiene and amide monomer. Table 5 lists the results of the Z-6 applied in gas wells. From the results, Z-6 decreased the block numbers and increased the product time rate of wells, while the usage is 30% of methanol year on year. But the inhibition effect was inconsistent for different wells.

Summarizing the results of several field tests, the KHIs can reduce the dosage of THIs and the number of blockages. But, the test time was too short. The longest field test was carried out in Luojiazhai gas field for two months in winter. Other field tests were carried out in one to four weeks. The sustainable effect of KHIs needs longer field testing. The applicability of inhibitors is poor. The inhibition effects were greatly affected by gas composition and environmental conditions. In addition, cost was still a major problem affecting the field application of KHIs.

In the development of hydrate inhibitors, it is necessary to adapt to the specific conditions of gas fields in China, such as high subcooling, acidic gas. In most of Chinese gas field, KHIs must be used together with THIs in application. Therefore, the influence of KHIs on THIs must be considered to ensure that it cannot affect the recovery process of THIs. In addition, the recovery of kinetic inhibitors should also be considered in order to reduce costs.

In the development of hydrate inhibitors, the development time of new inhibitors. Studying the compatibility of KHIs with other production agents in the pipeline is important. The cost can be reduced by recycling and utilization of KHIs.

2. The main problems of natural KHIs are poor water solubility. Solubility of natural products can be crafted by hydrophobic group improvement or the use of microporcelain technology to encapsulate natural KHIs in the fluid and injected into pipelines.

3. Targeted kinetic inhibitors, in no hydrate areas, kinetic inhibitors do not release or are not working. When KHIs enter into the hydrate formation stage, it takes effect. It can be triggered by temperature or pressure.

4. No action. The final goal of hydrate management is no action. Nothing needs to be added into the pipeline to inhibit hydrate. Coating technology is a good choice. But, this technology is just used in hydrate inhibition, and its performance cannot inhibit hydrate completely. Additionally, pipeline coating has the effect on anticorrosion, antigradation, paraffin inhibition. The interaction between these agents is coating technology future studies.

5. The theory of hydrate nucleation and growth, and inhibition mechanism provides the base of KHIs developed, and theory of pipeline safety management. Further insight of inhibition mechanism must be continued.

5. Conclusions

Hydrate inhibition and management is very important to gas industry, relating to the safety and efficiency of production. This issue involves complicated theories, such as thermodynamic, heat and mass transfer, multiphase flow, chemical reaction, phase transfer. Although the studies on hydrate inhibition make a great progress, several challenges and limitations in experiments and application still exist. The main purpose of this paper is to give a review of hydrate inhibition technology in gas-dominant pipelines. The currently open data led some conclusions and future advices.

1. The development of hydrate inhibitors should be based on the requirement of engineering. The basic requirements are high efficiency, low cost, low pollution and low toxicity. At present, the issues of KHIs are that of low tolerance of subcooling, low cloud point, and uncertain compatibility with other types of production chemicals. Therefore, in the future, solving these issues are still the key of KHI research. Using molecular design and group modification technology as well as molecular simulation technology can shorten the development time of new inhibitors. Studying the compatibility of KHIs with other production agents in the pipeline is important. The cost can be reduced by recycling and utilization of KHIs.

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