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Review Article

A Review of Kinetics of Hydrate Formation and the Mechanism of Effect of the Inhibitors on it

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ABSTRACT

The absence of high degrees below zero in most part of Iran, especially in the Persian Gulf area, provides suitable conditions for the replacement of thermodynamic inhibitors with kinetic inhibitors. Although it is possible to use kinds of LDHIs (Low Dosage Hydrate Inhibitor), especially kinetic inhibitors in most parts of Iran, it is always necessary that the limitations of these materials are checked before using. Hydrate is an aqueous network with a set of empty spaces in a small distance. If some of this space was filled by gas molecules, the hydrate could be considered as a stable solid. In other words, gas hydrates are complex crystalline molecules that are formed from the mixture of water and suitable gas molecules.

Keywords: Hydrate, Thermodynamic Inhibitors, Low Dosage Hydrate Inhibitor, Environmental Benefits.

Introduction

Hydrate is an aqueous network with a set of empty spaces in a small distance. If some of this space was filled by gas molecules, the hydrate could be considered as a stable solid. In other words, gas hydrates are complex crystalline molecules that are formed from the mixture of water and suitable gas molecules. Aqueous molecules form unstable networks due to hydrogen bonds, and gas molecules occupy the space between the network gaps. When a small number of network holes are filled, the gas hydrate molecules crystallize at temperatures even above the freezing point. The structure of the formed hydrated gas will be as follows: Structure I, structure II, and recently structure H have also been identified. Historically, done studies on the phenomenon of gas hydrate can be classified into three important periods: The first period is from its discovery in 1810 to the present, that hydrates have been studied as an unknown scientific phenomenon in which water and gas are transported into the solid network. The second period is since 1934 as yet, has studied the hydrate phenomenon in the gas transmission industry. The third period is from 1960 to the present that began with the discovery of underground resources of the hydrate in the depths of oceans and frozen areas of the earth depths [1]. In 1778, Josef Priestley had left the lab in the winter while the window was left open. When he returned to the laboratory, he found that SO₂ vapors caused the water is saturated and frozen. Whereas, this case didn't happen for HCl and SiF₄. Therefore, it is believed that Priestley had discovered hydrate more than thirty years before Davy discovered it. Hydrate discovery by Davy that done independently is considered as the first hydrate observation. Sir Humphrey Davy was the first person who notices the formation of chlorine hydrates in 1811 when the chill experiment of the saturated aqueous solution of chlorine at -40 ° F. From 1810 to 1934, the done studies in the field of hydrate were carried out on the following two main axes:

- Identification of all the compounds that can form hydrate.
- The quantitative description of compounds in terms of percentage composition and physical properties.

Since the discovery of hydrate, the number of published studies has been reported to be approximately 40 during a century, whereas this number has reached 400 in 2000 alone, and it is

indicating the peak of importance and attention to this issue in the present world. After 1934, research in the course of hydrate guided to ways to prevent the formation of hydrate on gas transmission pipelines. Because at that time, Hammersmith realized that the clogged of pipeline was due to the formation of hydrate, not freeze. The importance of hydrates after its discovery naturally has doubled in areas of Alaska, Siberia, and Canada. These mineral reserves of hydrate are recognized as an intact source of energy and have been taken consideration because of a large amount of the stored gas therein [2].

The prediction method of the hydrate formation using vapor-solid equilibrium constants

The methods that have the most successes in predicting or recognizing hydrate phases at equilibrium state in hydrocarbon- water systems are based on the coordination of ratio or size of the vapor-solid equilibrium constant (K_{vs}). Tables of the equilibrium constant for species or constituents material of the known hydrates with normal butane as the heaviest material are listed in various studies and books. With the discovery of the heaviest constituents of hydrates, their equilibrium constants must necessarily be predicted accurately in the non-hydrated phase of the hydrocarbons mixture, especially in the liquids of the reservoirs. In these investigations, by studying a closed or internal thermodynamic model against equilibrium experimental data of hydrates of four compounds, the constituent materials of the heavy hydrate HHF (Heavy Hydrate Formers), gasoline, cyclopentane, cyclohexane, and neopentane were used to prepare their K_{vs} table. The obtained K_{vs} have been used to predict the dual and triple non-hydrated phases of the HHF mixtures with methane or nitrogen and have shown more favorable results than experimental data, which this method (closed thermodynamic modeling method) will also be described in the next pages. Katz and his colleague at the University of Michigan developed a set of the equilibrium constant of the vapor-solid to predict different states of the hydrate. The prepared relationships are related to methane, ethane, propane, isobutene, carbon dioxide, and hydrogen sulfide.

A practical method for Kvs tables

The closed thermodynamic for making Kvs for each species of heavy hydrate is predictable from boundary phase of hydrate. A selected equation of each phase, the reform of Rama, is used in all liquid phases through equation to calculate the fugacity of each component. In 1963 McKay and Synagogue, a reliable detailed explanation is provided for this model. In 1996, Tahiti determined Bell coefficient between water and HHF by measuring the composition and predicting the solvability. Bell effect of dual parameters is defined as sudden effect of molecules• the initiative shapes of all components are the same. For each HHF, three data sets of hydrate equilibrium in four phases have been created: broad, aquatic zone, liquid hydrocarbon, steam and hydrates, two paired and one triple with methane or nitrogen are used as auxiliary gas. This model has been validated in the laboratory against independent data and the collection of existing data.

The effect of inhibitors on the process of hydrate formation

Lederhose and colleagues studied the effect of several kinetic inhibitors on the hydrate formation process of the natural gas in a series of experiments and showed that the formation of hydrate is slowed in the presence of salt and polyvinyl caprolactam. The ocular observations in these experiments showed that the obtained hydrate in the presence of NaCl contained larger crystals than the obtained hydrate in the presence of Pvcap. Based on the Long and Quami model can be explained the reason for the hydrate formation at low temperatures and high pressures. As the temperature decreases, the kinetic energy of the liquid phase molecules is reduced, and the greater number of hydrogen bonds are created between water molecules. The formation of these bonds increases the number of molecular aggregation at the surface. Increasing the number of these holes means that the number of the susceptible sites of the gas molecule has increased to form hydrates per surface unit, and so the chance of a gas molecule be trapped in one of these holes increases by accidental collision. Also with increasing pressure, the number of gas molecules per the unit of the water surface increased, and the probability of a gas molecule being accidentally trapped inside the appropriate cavity increases and consequently the probability of the hydrate formation increases. Based on the experiments, it can be concluded that such as NaCl by reducing the number of holes in the surface or by blocking these holes, the inhibitors can slow

or stop the hydrate formation process [3-4]. The similarity of this phenomenon to the water freezing can be used to justify the deterrence mechanism of salt in the process of hydrate formation. The pure water begins to freeze at the temperature 0 ° C. For this purpose, the first it is necessary to create suitable molecular aggregations from water molecules through the hydrogen bond. These aggregations will be the forming units of the ice crystal. The salt is rapidly ionized by dissolving in water, and its positive and negative ions are dispersed in the liquid phase. These ions generally have high charge density that can form strong attractions with polar molecules of the water.



By the establishment of the attraction between the created cations and the anions with the water molecules, each ion is rapidly surrounded by six water molecules. Thus, the presence of cations and anions keeps the water molecules out of reach for the formation of suitable molecular arrangements for ice crystal formation. On the other hand, hydration is a strongly exothermic process [5].

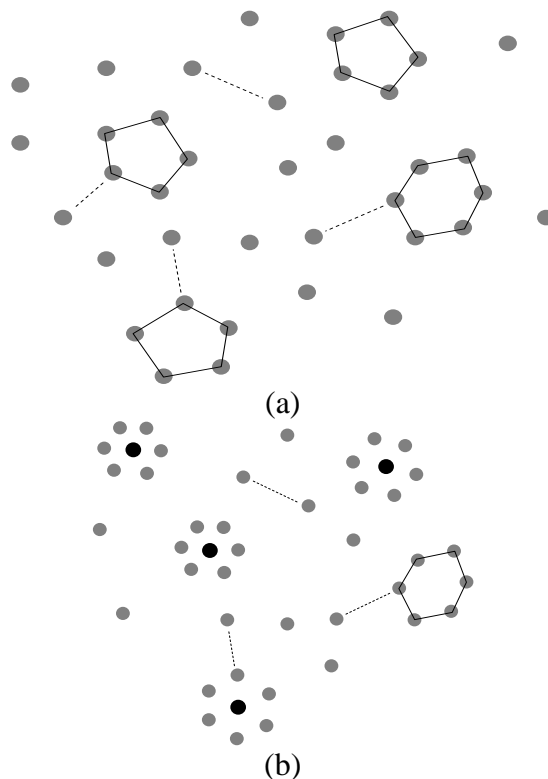


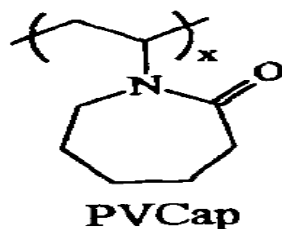
Figure 1. (a) Formation of molecular aggregations in water (b) The hydration of ions of the salt in the effect of dissolution in water

The released energy causes some of the created hydrogen bonds between the water molecules breaks down, and it destroys the pre-created molecular aggregations that the result of this two phenomena will be reducing the speed and the rate of hydrate formation. In figure 1 the Formation of molecular aggregations in water (b) the hydration of ions of the salt in the effect of dissolution in water is shown. This mechanism can be used to justify the effect of salt on the hydrate formation process. As mentioned, the existence of the holes from the water molecule in the water and gas contact surface is required to hydrate formation. In the presence of salt, water molecules are placed in the surround of the molecular forces of sodium and chlorine ions. This attraction is stronger than hydrogen bond between the water molecules and therefore causes breaks down the molecular aggregations of water. On the other hand, with the release of the heat of hydration, the liquid phase temperature raised locally and kept away it from the phase diagram of hydrate formation. Accordingly, the amount of salts deterrence depends on the amount of charge present on the ions and the radius of the released ions. Due to the lower number of hydrogen bonds in the aggregations with the lower number of the water molecules, less energy is needed to break the bonds and to adsorb toward the existent positive and negative ions, and hence the smaller holes are destroyed earlier. While the higher number of bodings in aggregations with more molecules requires more energy to break. Therefore, it is expected that in the presence of the salt with attention to disappearing small holes, the larger hydrate crystals are seen [6]. S P Kang showed that the amount of salt deterrence has a direct relation to the number of the released ions and has inverse proportional to the radius of the ions. So the best inhibitors are the ones that release the maximum number of cations with the minimum ion radius. According to the above specifications, several appropriate cations are arranged in order of reducing the amount of deterrence in the below table by S P Kang. Whatever the rate of solubility reduction of guest gas molecules by salt is high, that salt is known as the better inhibitor [14].

Table 1. The rate of solubility reduction of guest molecules by different cations [7].

AP	Ionic Radius (A)	electrical charge	Element
0.67	0.34	+2	Be
0.20	0.57	+3	Al
0.11	0.78	+2	Mg
0.05	1.06	+2	Ca
0.04	0.98	+1	Na
0.02	1.33	+1	K

In addition to the ionic radius and the electric charge, the price and the solubility of salt is also important. Among anions, chlorides, nitrates, and sulfates are most commonly used. An important factor to consider when choosing salt used as an inhibitor is its corrosion. The other weakness of salts is that these materials become more concentrated at the effect of heat and after they reach the colder areas, they precipitate in the downstream of pipe. In other words, these inhibitors are entered with lower concentration exactly where the possibility of the hydrate formation is more. Mohammadi et al.'s experiments in the presence of PVC polymer showed that the presence of only 1 weight percent of it in the solution completely stopped the hydrate formation process. This polymer is composed of a large monomer molecule (Figure 2). Because of the existence of the oxygen and nitrogen electron-withdrawing groups on the benzene ring, the ring electron cloud is drawn towards these atoms and some positive charge is applied to the ring hydrogen's. In the effect of the created charge, the molecules of this polymer could establish the attraction with the negative charge of the oxygen atoms of the water molecule and blocked inside of their absorbed surface holes. Thus, the number of existent active points for nucleation in the surface is reduced, and the chance of the gas molecule being trapped in these holes reduced. These molecules can only be absorbed into large holes due to their large size and left small holes to hydrate formation. For this reason, the formed hydrate in the presence of macromolecular polymeric inhibitors will be composed of smaller crystals relative to the pure solution state [7].

**Figure 2.** The molecule of Pvcap polymer

Zhang presented the following empirical equation for how the effect of the inhibitors on the hydrate formation process.

$$\Delta T = \frac{k \cdot x}{M (100 - x)} \quad (2)$$

In above equation ΔT is the rate of temperature decrease in the of the hydrate formation, k is the especial constant to inhibitors, M is the molecular mass of the inhibitor, and x is the mass concentration of the inhibitor. The amount of K is shown for several inhibitors in table 2.

Table 2. The amounts of constant of K for several inhibitors

Inhibitor	K values
Methanol, Ethanol, cymene, ammonia	1228
Sodium chloride	1220
Glycol, propyl	2195
Sulphur	2425

Peargon has presented the following equation for temperature reducing of the hydrate formation in the effect of the inhibitor presence:

$$\Delta T = \frac{nRT_0^2}{\Delta H} X_3 \quad (3)$$

Where in X_3 is the concentration of the non-electrolyte solution, T_0 is the formation temperature of hydrate without inhibitor, ΔH is the heat of the hydrate formation, and R is the universal gas constant [8]. Hashemi-fard et al; presented the following thermodynamic equations for how the influence of inhibitors in 1998:

$$f_i = x_i f_i^0 \left[1 - \sum_j \theta_j \right]^\alpha \quad (4)$$

$$\sum_i x_i = 1.0 \quad (5)$$

$$\sum_j \theta_j = \frac{\sum_j f_j C_j}{1 + \sum_j f_j C_j} \quad (6)$$

Where in the α is equal to 1.3 for the structure of one hydrate and is equal to 2 for the structure of two hydrates. The f_i is the fugacity of the constitutive gas of the hydrate. The x is the concentration of the participant components in the hydrate formation process, and z is the number of the together connected holes in the effect of the presence of a component of i from the gas within the liquid phase. By obtaining C_j from the above relationship and placing it in the below relationship, the temperature of the hydrate formation in the presence of the inhibitor is calculated:

$$C_j = X_j \exp \left[\frac{Y_j}{T - Z_j} \right] \quad (7)$$

In the above equation x , y , z are the constants related to the inhibitor [9]. The model results are presented in Table 3.

Table 3. The model results

Gas phase	Concentration of Inhibitor in Aqueous Phase (wt %)	Pressure-range (Mpa)	Temperature-range (K)	Average absolute deviation on temperature (1) (%)	Average absolute deviation on temperature (2) (%)
CH ₄	10% CH ₃ OH	2.14-18.82	266.23-286.40	0.140	0.698
	20% CH ₃ OH	2.83-18.75	263.34-280.17	0.146	1.326
	35% CH ₃ OH	2.38-20.51	250.90-270.10	0.468	0.508
	15% C ₂ H ₅ OH	3.83-13.67	273.30-284.70	0.113	0.256
CH ₄ +C ₃ H ₈	10% CH ₃ OH	0.53-13.83	265.51-291.23	0.442	0.150
	20% CH ₃ OH	0.94-14.10	265.17-286.47	0.423	0.521
	35% CH ₃ OH	0.62-20.11	253.10-276.60	0.437	0.539
	50% CH ₃ OH	0.69-20.42	241.20-262.60	0.484	0.521
C ₂ H ₆	10% CH ₃ OH	0.42-2.82	268.28-281.89	0.085	0.474
	20% CH ₃ OH	0.55-2.06	263.53-274.07	0.094	1.322
	35% CH ₃ OH	0.50-1.47	252.6-262.2	0.588	0.386
	50% CH ₃ OH	0.42-1.01	237.5-249.8	1.281	0.380
C ₃ H ₈	5% CH ₃ OH	0.23-0.47	272.12-274.79	0.149	0.138
	10.39% CH ₃ OH	0.19-0.43	268.30-271.82	0.053	0.443
	35% CH ₃ OH	0.14-0.21	248.00-250.20	0.132	0.807
CO ₂	10% CH ₃ OH	1.59-3.48	272.12-274.79	0.149	1.264
	20.02% CH ₃ OH	1.59-2.94	268.30-271.82	0.053	2.039
	10.04% EG	1.15-3.20	248.00-250.20	0.132	0.278
	10% CH ₃ OH	1.74-2.35			0.272
H ₂ S	10% CH ₃ OH	0.07-1.08	265.69-291.77	0.255	0.604
	16.5% CH ₃ OH	0.28-1.50	273.20-290.10	0.625	1.810

	20%CH ₃ OH	0.22-0.59	271.79-281.15	0.115	1.218
	35%CH ₃ OH	0.22-0.58	263.20-274.20	0.410	0.670
	16.5%C ₂ H ₅ OH	0.39-1.48	280.70-291.80	0.890	0.745
CO ₂ +CH ₄	10%EG	1.14-3.22	268.70-278.00	0.384	0.646
CO ₂ +C ₂ H ₆	10.6%EG	0.85-2.31	269.10-276.40	0.173	0.199
CO ₂ +N ₂	13.01%EG	0.93-3.39	267.20-276.90	0.143	0.637
NG1	10%CH ₃ OH	1.04-19.03	268.27-288.34	0.653	1.550
	20%CH ₃ OH	1.41-19.15	264.41-280.97	1.062	2.617
NG2	42.9% TEG	2.31-8.59	275.15-285.25	0.201	0.209

Yu et al; were able to improve the function of the inhibitor by adding polyethylene oxide. For example, the delay time of hydrate formation from methane reached to 150 hours in the presence of polyethylene oxide, while this time was about 29 hours in the presence of the inhibitor alone [15-18].

Table 4. The effect of adding polyethylene oxide on the formation of the methane hydrate

No.	System	Pressure (kPa)	Temperature (K)	Induction time (min)
1	No inhibitor	6000	273.7	0.5
4	INH1	6000	273.7	1253
5	INH1+P	6000	273.7	9006
6	INH2	6000	273.7	40
7	INH2+P	6000	273.7	27
8	INH3	6000	273.7	86
9	INH3+P	6000	273.7	148
10	INH4	6000	273.7	8.6
11	INH4+P	6000	273.7	15.6
12	INH5	6000	273.7	6.5
13	INH5+P	6000	273.7	82.3
14	INH6	6000	273.7	1.3
15	INH6+P	6000	273.7	16.6
16	INH7	6000	273.7	6.6
17	INH7+P	6000	273.7	7.3
19	INH8	6000	273.7	30
20	INH8+P	6000	273.7	21.3

How to eliminate and Prevention of hydrate formation in Gas Pipelines Theoretically

Glycol and alcohol may be used to decrease (prevention) the hydrate formation. This is one of the fundamental phenomena that the solute compound may be lower than the freezing point of the solvent. The appropriate equation is as follows:

$$d = \frac{k_i \times X}{100M - X \times M} \quad (8)$$

d = depression of hydrate point

w = weight percent inhibitor in the liquid water phase

M = mol wt of inhibitor

The pressure drop (d) should be reduced from the point of the determined hydrate and by the linear methods mentioned above. Ethylene glycol (DEG) is the most common used glycol in this work. Because it is a good intermediate state between vapor pressure and solubility in hydrocarbons. This is a suggested value, so the liquid flow in the pipeline involves between 50-60% of the DEG volume percent [10-11]. The recent suggestion is about concentration. The solubility will usually be lower than 0.1 to 0.3 gallons of DEG per 100 barrels of the extracted hydrocarbon that, it depends on the aromatic content. The total of losses includes evaporation, abscission, pump leakage, solubility, and so on, which is usually the average of 1 gallon per 100 barrels of the transferred compressed amount from a factory. (Or the compressed amount of the injected into a unit). In a specified unit, it is possible to operate at temperatures of 50-60 °F lower than the hydrate point. The appropriate amount of methanol or glycol for adding may be determined [19-22]. The sequence of calculations is as follows:

The determination of the hydrate formation temperature from a gas

Defining the lowest expected temperature in the system (If the fixed data isn't available, 40°F is a good guess in underground pipes). The calculation the amount of present liquid water in

temperature of step(2), the use of the dew point of water at that temperature and related corrections of the along water. The use of the equation to solve w. In equation, the temperature of step (1) is the minus of step (2).

$$W(\text{wt}\%) = \frac{\text{Lbs(Losses)}}{\text{Lbs(Losses)} + \text{Lbs(liquid-water)}} \quad (9)$$

The following constants are used to calculate the inhibitor losses in the above equation:

DEG = 9.33 lbs/gal

TEG = 9.41 lbs/gal

If the methanol is used, correction must be done for the wasted values in the vapor phase. The horizontal reading of the lowest temperature and coming down till the axis of length vertically.

Decomposition of hydrates in the pipeline

Blockage doesn't cause much trouble during the normal pipeline's operation. However, unforeseen problems such as pump failure or deterrent problems in the course of transmission cause hydrate formation and consequently blockage of pipelines. The eliminate of this contraction takes a few weeks. The purpose of this work is the investigation of the phenomenon of hydrate decomposition in pipelines.

The Computational Model

The system of the created equation requires a numerical solution. The hydrate appears to be porous in this method. The recent experiments have shown that hydrate pores vary between 33% to 84%. Subsequent experiments confirmed that the existing hydrates in the pipelines were also porous. Because the hydrate is porous, it is capable of transmitting the pressure and, this is while acting as a barrier to the normal flow of pipelines. The hydrate temperature remains constant during decomposition and will be identical to the ambient temperature. If the system pressure is approximately less than 2.5 mpa, the identical temperature of the hydrate gets lower than the

freezing point, and there will be a possibility of freezing. Any water drop that results from hydrate decomposition immediately frozen when the temperature is lower than the freezing point. The hydrate appears to decompose radially, and its axial decomposition should be ignored. In this method, the hydrate dimensions are changed to reduce pressure. The existing equilibrant pressure is lower than the ambient pressure which causes the heat flow radially, and to melt the hydrate [11-15].

Empirical Proceedings

Empirical tools include a stainless steel activator. The activator has 0.2m long, and 0.048m internal diameter. The activator is present in the ethylene glycol- water reservoir with the controlled temperature. The temperature of the reservoir is controlled by resistive thermometer from platinum type. The hydrate temperature is controlled through five different axial positions with the J-type thermocouple thermometer. The temperature of the existent gas at the two ends of the thermometer is also measured through a J-type thermocouple. The system pressure is measured through the converter pressure. All of these temperatures and pressures are placed in the information program and stored on the specific computer. The method of producing hydrate was the Stern method. In this method, the 850m of ice study are stored in a stainless steel activator. When the activator gets filled with ice, it is contracted by methane gas to 21mpa. Then the activator temperature reaches above the freezing point to start the hydrate formation. The amount of hydrate change is controlled by measuring the pressure of the system. All the ice studies converted to hydrates when the pressure decreasing is stopped. Those who use the evolution of gas as hydrate decomposition also confirm the amount of the created hydrate. The hydrate decomposition begins by decreasing the pressure at the two ends of the pipe, the initial temperature of the hydrate in reservoir three is 40°C. When the pressure gets lower than the equilibrant pressure at the reservoir temperature, the hydrate begins to decompose. When hydrate decomposes, two things must be measured: the amount of the diffuse methane gas from the hydrate decomposition, and the hydrate temperature at the center of the rod at 5 different axial positions. In this decomposition method, there is the possibility of keeping the decomposition pressure constant during the experiment at atmospheric pressure or the pressure about 2.4-5.2 (MPa). This pressure is maintained by the valve [12]. The experimental formation results show

that there is up to 90% the possibility of changing ice to hydrate. This developed method shows that, as far as possible, the reduction of pressure causes the optimal decomposition of the hydrate. When the pressure decreased, the final decomposition time, the disappeared time of ice and hydrate will also decrease. These results show that the formation of ice helps the deletion of the hydrate and create more ice. This is for two reasons: 1) With the existence of ice, heat diffusion is more important than water. 2) There is more heat drop with the existence of ice. This shows that, when the hydrate is cleaned from the pipelines, it is best to contract the pipelines quickly and reduce the pressure. When the pressure decreases rapidly, causing the gas getting cold, which this is related to Joule-Thomson's law, then cools the hydrate and leads to create the ice. The obtained important result of the empirical decomposition method is the change of the radial decomposition hypothesis. The benefit of radial decomposition method is that the length of the pipe isn't important only the radius of the pipe is considered. Each hydrated pipe decomposed in a certain time, and then the activator stopped till the rest of the hydrates are controlled. There is also the equilibrant pressure with the average of the decomposition temperature during the experiment. However, when the decomposition pressure is in the temperature lower than the freezing point, and ice is created in the system, the hydrate temperature remains constant at the freezing point. The formation of ice from hydrate decomposition caused the absorption of the decomposition heat and hydrate temperature regulation. As a result, the ice adjusts a solid temperature between 0 °C and 1 °C. This process can be performed both at the decomposition time with the help of the model and at the measured time of the empirical experiment through the comparison. This model can predict the movement time of the ice/ limit of the hydrate. This prediction will reverse in the amount of the created gas and will be compared to the full-fledged gas. The model and the experiment, both of them predict the identical decomposition curve. It is also mentionable that the predictable decomposition time is approximately 5% of the experimental decomposition time.

The safety cares related to hydrate decomposition

The important result is that when hydrate is decomposed in the pipelines, this is done radially. This shows that when the hydrate decomposed, it first spreads from the wall of the pipe and then dragged toward the internal cortex. The only concern about the decomposition mechanism is that

the pressure decreasing at the end of the rod causes the hydrate moves, of course, as soon as the hydrate is spread from the wall of the pipe. If there is enough pressure, it has the required ability for damaging when there is an obstruction in the pipelines. The multiple cases have been reported that the rod has contracted from its two ends and the rod is slowly broken that create millions of dollars in damage [9]. There is another possibility that there may be some rod in the pipelines. When the pipelines contract from self-two ends, there may be too much pressure between several pipes, so there isn't possible to reduce the pressure rapidly, instead, the pressure must be reduced slowly. A method has been discovered that doesn't have constant parameters and predicts the time of hydrate decomposition in pipelines. This method changed the experimental results [12]. The hydrate decomposes radially. However, due to the adjustment of the ice capacity, it is difficult to reach temperatures lower than 1°C. But the results of this work are unlike to two previous beliefs: 1) the formation of ice in pipelines is detrimental when decomposing hydrate. 2) The hydrate decomposes longitudinally. The results of this work are a valuable aid to techniques of the hydrate in the future [13]. There is the possibility of creation hydrate decomposition with the existence of these results. The model and experiment show that ice formation is useful and helps to eliminate hydrate. This proves that the pressure must be rapidly reduced to the amount of barley pressure at both ends of the rod. However, for safety reasons, such as the presence of different rods, the pressure should be reduced slowly at both ends of the rod, but be in the limit of barley pressure. It should be paid attention which should be prevented pressure decreasing in the rod. When the rod wall starts to decompose, the blocking operator (for example, methanol) may be placed in the rod to increase the rate of decomposition. This method can predict the radius of hydrate in the time. By using the prediction method, it will be possible to the determination of the blocker flow time in the hydrate. The results of this work exist only in bilateral contraction. Recent research has been useful for the development of model and experience, which is similar to unilateral contraction [16]. Gas hydrates are ice-like compounds from water and gas that are usually formed at high pressures and at low temperatures such that one gas molecule is enclosed in a cage of water molecules in each of their constituent units. Gas hydrate was introduced in 1934 by Hammersmith as one of the problems of the gas industry in the transmission pipelines because the decreasing the internal cross-section of the pipe caused to increase the pressure drop and sometimes leading to complete blockage of the pipe. Hydrate formation can also lead to the destruction of the existent tools in the process such

as taps and sensors or caused increasing the laborer cost for clean through the accumulating in the maintenance reservoirs. One of the thermal, mechanical, thermodynamic, and kinetic methods usually is used to prevent hydrate formation or it's eliminate in the industry [17]. The effort is that the gas is kept away from hydrate formation terms by insulating the pipe, using the spin of water or hot oil, or electrically heating the pipe. Using the PIG is a mechanical way to eliminate pipe clogged due to hydrate formation. The phase diagram of the gas mixture can also be changed by adding the third material, and the possibility of formation of hydrate can be eliminated at the working temperature and pressure of the system [18]. Kinetic methods help the improvement of the working conditions of the gas transmission system by increasing the delay time or decreasing the amount of growth or adhesion of the hydrate crystals. These methods due to less use of the inhibitor (less than 1% of weight percent) are usually preferred to thermodynamic methods in which is required a large amount of additive (more than 25 % of weight percent).

Conclusion

The absence of high degrees below zero in most part of Iran, especially in the Persian Gulf area, provides suitable conditions for the replacement of thermodynamic inhibitors with kinetic inhibitors. Although it is possible to use kinds of LDHIs (Low Dosage Hydrate Inhibitor), especially kinetic inhibitors in most parts of Iran, it is always necessary that the limitations of these materials are checked before using. However, the use of these materials can have economic and environmental benefits.

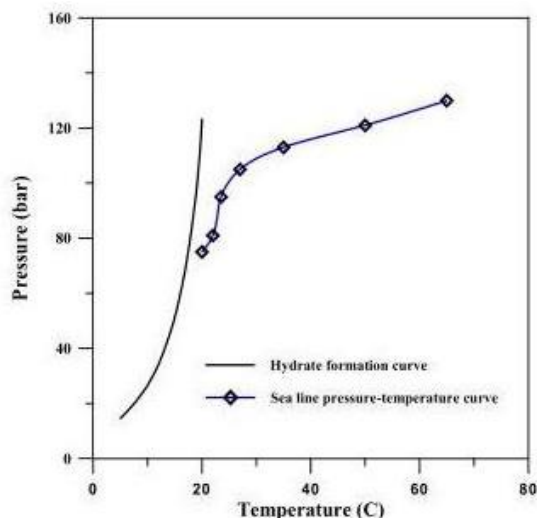


Figure 3. Comparison of thermodynamic curve of hydrate formation and the curve of temperature-pressure of pipeline, for gas and gas condensate transmission line of the South Pars

These are shown in figure 2 and 3. In this suggested method, the related "k" of n-butane is considered to like ethane which has low concentration. "K" is considered freely for nitrogen and heavier components. Because they are in the hydrate form at the various states or they aren't such generally never. This method, like the dew point calculation, has already been discussed, which the vapor-liquid values simply displaced with the vapor-solid values by the figures of the next pages. This simulation is useful for encountering with higher pressures. It should be noticed that manual calculations are relatively onerous in this method.

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