International Journal of Innovation and Applied Studies
ISSN 2028-9324 Vol. 1 No. 2 Dec. 2012, pp. 226-231

http://www.issr-journals.org/ijias/

Offer a New Model to Prevent Formation of Hydrate in Gas Pipeline in Gas Refinery

Amir Samimi

Department of Chemical Engineering,
Mahshahr Branch, Islamic Azad University,
Mahshahr, Iran

ABSTRACT: Water molecules by making hydrogen joint with its molecules creates holes in which quest molecules will be trapped and by creating van deer Waals joint with water molecules, hydrates crystals will be produced. Natural gas and crude oil in natural exist in underground reservoirs are in contact with water. Hydration needs condition which consists of having water in pipe line, high pressure (pressure always is high because of reinforcing gas pressure in gas transportation pipe lines), low temperature (temperature is always low in cold seasons of year), and presence of hydrate-making substances like methane, carbon dioxide, and... There are four methods to prevent hydration. This article will focus on analyzing synthetic inhibitors, and their function the task orders are as followed: 1. Synthetic investigation of hydrate formation with and without presence of inhibitor. 2. Using Kashchiev- Firozabad model and experimental data of gas transporting pipe lines for drawing synthetic graphs of gas hydrates formation with presence of synthetic inhibitors.

KEYWORDS: Water Molecule, Hydrogen, Hydrate-Making Substances, Kashchiev- Firozabad model.

1 INTRODUCTION

Understanding the phenomenon of hydrate formation goes back to the early nineteenth century. Humphrey Davy the first person was in 1810 AD, when tested by cooling an aqueous solution saturated with chlorine at temperature 9the formation of chlorine hydrate gas was. After Dewey, researchers found that between 1850 and 1890 Hydrates also discovered. Hydrates double ingredient which has a definite melting point and a simple Hydrates are different, because the double hydrate degradation temperature may vary with temperature degradation of Hydrates simple. Forkrond in 1897 AD found that carbon tetrachloride and acetylene are formed of a double hydrate. They also double Hydrates of acetylene, ethylene, sulfur dioxide, and carbon dioxide with ethylene chloride, ethylene bromide, methyl iodide, methyl bromide, ethylene chloride, and ethylene iodide reported. And similar compounds such as carbon dioxide and ether reported. Methyl *MERCAPTAN* and water will form a crystalline hydrate. Many studies in the field of hydrate formation by several people, including Frost and Dayton, Kobayashi, Katz, Pelatiand Van deer waltz, Davidson and Makogon done. Water molecules by making hydrogen joint with its molecules creates holes in which quest molecules will be trapped and by creating van deer Waals joint with water molecules, hydrates crystals will be produced. Hydration needs condition which consists of having water in pipe line, high pressure (pressure always is high because of reinforcing gas pressure in gas transportation pipe lines), low temperature (temperature is always low in cold seasons of year), and presence of hydrate-making substances like methane, carbon dioxide, and... There are four methods to prevent hydration:

1- Controlling pressure (the lower pressure the less hydration but in gas transporting lines it's impossible because of reinforcing gas pressure for transporting it).
2- Controlling temperature (heating the system by electrical heating so as to prevent from reaching hydrate formation point).
3- Removing water (water in pipe lines should be removed. In spite of this, there is always some water along with gas).
4- Injecting chemical inhibitors (these inhibitors prevent.

Corresponding Author: Amir Samimi (amirsamimi1161@gmail.com)

Hydrate formation and are prior to other methods).there are two important groups of chemical inhibitors; thermodynamic and synthetic inhibitors, Thermodynamic inhibitors affect on thermodynamic balance of aquatic phase [1] and they consist of methanol, de ethylene glycol, some salt (salt is not used because of its corrosion effect on transporting pipe lines). These inhibitors are very expensive, poisonous and harmful for environment. They also have high volatility. Synthetic inhibitor induces crystal growth and trapping hydrocarbons in ice crystal net, they affect by being adsorbed on water molecules and prevent making chemical connection between gas and water molecules. These inhibitors are added with low density to gas lines. Analyzing amount of gas hydrate formation (using methane) along the time and also induction time in gas hydrate formation in different pressures because of synthetic effect of these inhibitors is the most important event to do. In this article All efforts has been done to draw the methane diagram along with passing of time using modeling for hydrate formation synthetic with and without inhibitors for gas hydrate. Also induction time in gas hydrates is analyzed with and without inhibitors. Synthetic analysis of hydrate formation with and without inhibitor: for synthetic analysis of gas hydrate formation, suppose one current line of gas in high pressure and low temperature in which gas hydrate is formed. While forming hydrate, pressure falls a little and temperature raises a little.gas hydrate formation using methane gas molecules is according to follows crystallization reaction along with water:

$$H_2O + \lambda 2G \rightarrow G_{\lambda 2}\, H_2O \qquad (1)$$

In which λ_2 are gas molecules? Current line consider as below:

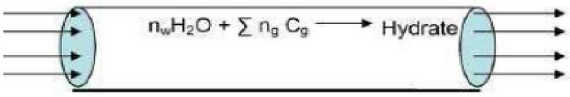

Fig. 1. Current Line Consider

A. Hydrate Formation in Respect of Synthetic is Two Stages

1. Nucleation in holes is a stage in which hydrate forming molecules reach holes and reach stability.

2. Growth stage after nucleation stage, hydrate crystals gradually grow .in this stage there are experimental equations which are as fallow.

2 MODEL

There are different models for synthetic analysis of hydrates formation. Two models are mentioned as follow:

ESBERGON MODEL: This model introduces velocity of used methane mol in stable pressure during hydrate growth, In this equation V_{1*} is dissolvent volume, ρ_W is water density, MW_W is water molecular weight, $X^i_{G\text{-}L}$ is formed hydrate partial molar in shared surface between gas and liquid, and $X^i_{H\text{-}L}$ is formed hydrate partial molar in shared surface between hydrate and liquid. K^* in this equation is calculated as follows:

$$(1/K) = (1/K_1A_i) + (1/K_rA_P) \qquad (2)$$

$(1/K_1A_i)$: surface resistance of gas molecules when their sediment in liquid surface starts K_1: velocity constant of influence in liquid.A_{i1}: gas-liquid shared surface area, $(1/K_rA_P)$: surface resistance of gas molecules when they react with each other and hydrate particles are formed. K_r: velocity constant of hydrate film, A_P: surface area of hydrate particle. In this model hydrate formation with inhibitor is divided into three areas: A: related to nucleation and no mechanism is analyzed for it. Area B: it is hydrate growth area and is not linear because inhibitors are absorbed to hydrate surface and available surface for hydrate growth is reduced by them then A_P will be reduced consequently $K^*= K_r.\ A_P$ that K_r is a constant amount because is dependent on temperature and tem. During growth area is nearly constant. But A_P changes with time in square.

Area C: hydrates have been formed after area C and hydrate growth is not possible by this inhibitors then their function is dependent on time. This model analyzes the process of hydrate formation with inhibitor like increase and decrease process; there is no consequence in respect of amount.

Kashchiev and Firozabad: This modeling is based on theories as followed:

1. Constant temperature.

2. Disturbed gas current.

3. Clogging pipe lines by gas hydrate because of growth and joint of crystals together.

4. Sudden fall of pressure which is a sign for gas hydrate formation.

5. Gas compounds will dissolve in water then hydrate crystals will be formed.

2.1 APPLYING KASHCHIEV AND FIROZABAD'S MODEL

Experimental Data of Gas Transporting Pipe Lines for Drawing Synthetic Diagram of Gas Hydrate Formation with Synthetic Inhibitors: velocity diagram of hydrate formation is very important for synthetic inhibitors against time. Then this diagram using above equation will be achieved for different inhibitors. They are considered for calculations of north-south roomier line because hydrate formation has been reported several times in this area. Growth rate is different dependent on kind of inhibitors. For example in this calculation tow inhibitors have been Chosen in which growth rate in L_ Tyrosine is more than PVP. Density of inhibitor also affect son growth rate. For example in this diagram two densities, 100ppm and 200ppm have been chosen for two inhibitors which shows that whatever density increases, growth will decrease. Of course this amount of density has an optimum rate.

3 APPLICATIONS OF GAS HYDRATE

Hydrates is the first time as a factor in understanding the gas tubes are blocked, but now many studies done on these compounds and has found many applications. Absorb carbon dioxide from the air Separation of mixed gases Storage and transmission of natural gas 64% increase in CO_2 emissions of the greenhouse phenomenon. One method of reduce of CO_2 is separation from the environment and sent them in the depths of the seas and oceans. At depth below 400 m, CO_2 gas is injected and trapped by dissolving in water. Between 100-2000 m, CO_2 is liquid and the water will penetrate. CO_2 hydrate at 500 -900 meters of sea water is formed. With the Injection of cold sea water, hydrate crystals are formed. After their separation, and warm, fresh water is achieved. Because of the high cost of this method still has not found industrial application. Another application is the separation of carbon dioxide from the mixtures of combustion gas. Another separation process that called separation hydrate method, is tetra hydro jet used as a propellant of formed hydrate. Equilibrium pressure of hydrate formation lowers and the hydrate stability zone will expand. Gas hydrates capability to storage natural gas, which creates attractive about using it for storage and transportation of natural gas and other gases as a rival for the liquefy and condensation will be. At 1960 gas hydrate that as a factor interfering in a gas pipeline, the idea of using natural gas hydrate formed in the minds of many scientists. Because the temperature of formed hydrate is more than temperature of transport liquid natural gas (LNG), the gas hydrate can be moved easily, hence making it hydrate vessels, much less complexity than LNG vessels. Hydrate production facility can be designed much easier than LNG sites. But the basic problem, the gas volume is less. Studies in this case show each cubic hydrate, 175 cubic meters of gas in their place offers. If the LNG technology, the reduced to a six hundredth size and economic issue in the design of gas transmission, especially over long distances is important, however, there is still hope to use hydrate as a very economic safe solution for the transport gas. British Petroleum Company in collaboration with other scientific centers such as University Godson building a small plant that can produce 100 kg per day to hydrate. Gas hydrates can be used in the separation processes. Gas hydrate formation has only a limited number of materials.

If want separate the material of the mixture that can be form the hydrate, use hydrate is seen as an opportunity. For example, you can thicken the rich streams of water, providing drinking water from sea water or gas flow separation point. The discovery of large amounts of gas hydrates in northern Alaska Range and down the East Bay, United States of America, gives strength to the idea that gas hydrates, a very important source of energy in the future are considered. However, the important technical and technical issues must be resolved to possible gas hydrate as an energy source in the world, was introduced. Hydrate in natural gas to form a crystalline material composed of water and gas are. In the hydrate, a solid network of water, keep molecules of the gas in a cage-like structure. Hydrates usually in the polar and sea ice and sedimentary layers are present. However, methane, propane and other gases can be trapped in the cage-like, but the probability is much higher methane hydrate. The amount of methane trapped in gas hydrates is very high and the estimate is more guesswork and assumption. The amount of gas hydrate deposits in the world is much more than the volume of other sources of energy. Although the access to and production of gas hydrate research has been done by many [1].

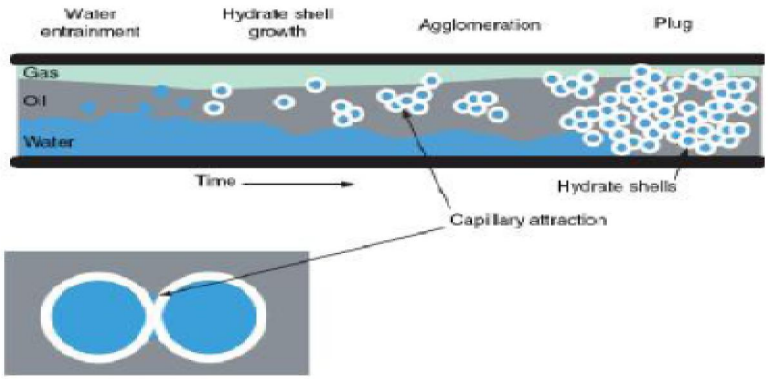

Fig. 2. Eclipse Pipes in Oil Pipes

4 PRODUCING GAS FROM GAS HYDRATE

Proposed methods of gas recovery from hydrates usually involve separation or melting of gas hydrates has the following methods:

Heating tank, the temperature of hydrate

Reducing the pressure below the equilibrium Hydrate

Injection inhibitors such as methanol or glycol into a reservoir to decrease hydrate stability conditions.

Currently, the recovery of gas hydrates to be postponed because it hydrates rough areas usually polar and deep-sea areas have been expanded. Recently, a series of simple thermal model for stimulating the production of gas hydrate and streams of water heater use has shown that gas hydrate can be produced is enough to allow gas hydrates to become technically a renewable resource, although the high cost of advanced recycling techniques, cause recycling not use. The gas hydrate inhibitors for the production of gas hydrate is physically possible, however, the use of large volumes of chemicals such as methanol, economic and environmental costs are high. Among the various techniques of produce natural gas hydrate, the best economic and most economical plan is to de-stress.

5 CONCLUSION

In this article first synthetic analysis of hydrate formation which consists of two stages was considered. It was also said that from these two stages, controlling growth stage is necessary and possible. then two common models in synthetic hydrate formation were considered an it was determined that the first model explains qualitative and relative velocity of hydrate formation and second model considers velocity of hydrate formation .at the end growth velocity with and without inhibitor was calculated using second model and experimental data in one part of district 8 gas transporting pipe line that in which hydrate formation had been reported and based on them it was concluded that hydrate growth velocity with inhibitor decreases and this decrease is different based on kind and density of inhibitor.

Because gas hydrate layers are present in the Polar Regions and marine sediments, can be considered as a potential energy source, the predictions for the amount of natural gas from gas hydrate layers in the 5.1020 to 1.1062 trillion cubic feet for the Polar Regions and 1.1051 to 2.1087 trillion cubic feet for the sedimentary layers of the ocean. Estimation about the gas hydrate resource is showing considerable fluctuations. Recent predictions of the amount of methane gas hydrate in global accumulated about 1,057 trillion cubic feet, but it seems that the sedimentary layers of the ocean has more resources and larger natural gas to continental sedimentary layers. The job evaluation and estimation of the Research Institute for Earth Cognitive America, estimating the gas hydrate resource in America's coastal and marine areas. Assessment of gas hydrates on the basis of an analysis, the state by state. We all gas hydrate regardless of their technical issues, define, describe and evaluate. We, therefore, this evaluation, only the volume of the gas hydrate resource concerned, the amount of gas within the gas hydrate, regardless of its recycling there. In one method of analysis, potential hydrocarbon accumulation, are grouped according to their geological characteristics of the geological conditions of occurrence of hydrocarbons in the modeling. In this evaluation, the geologists, the geological factors necessary for the formation and accumulation of hydrocarbons and geological factors determining their size, are discussed. In an assessment of 11 areas of gas hydrate, offshore and onshore oil discovery in four states and the amount of gas hydrate was estimated. Predictions made for each of

these 11 areas collected from gas hydrate resources in the United States of America is estimated. The gas hydrate resources in the United States of America between 112.765 trillion cubic feet of gas to the 676.110 level course with 0.05-0.95. Although these statistics, along with a high percentage of the doubt, but it represents a very large amount of gas stored in gas hydrates. The total value of the gas hydrate was in America for about 222 to 320 trillion cubic feet of gas. Necessary Naval Research, noted that recent excavations within the Special Economic Zone along the eastern area of this country is America, there are significant amounts of methane stored as solid gas hydrate and free gas, gas hydrates under arrest, confirms . In the past few years, government agencies in Japan, India and South Korea began to develop research programs to recover gas from oceanic hydrates have. One of the most important gas hydrate projects is underway in Japan, a 5-year project to assess the internal resources Potential natural gas hydrates. The articles have been published: Institute executive, has announced that methane hydrates can be integrated to produce the next generation energy source

In 1996, geological and seismological research programs on the continent of North and Southeast regions of Japan have been conducted. According to the research, has discovered that about 1,800 trillion cubic feet of gas within the gas hydrate zone is stored Nankay. Studies show that between India and Myanmar, the Andaman Sea, a huge source of gas hydrates, which is conjectured, with 211 trillion cubic feet of gas. The government of India has announced that it's important to answer for needs energy in this Country. Although our information about the underground gas hydrate is very low, but can expect with the development of new technologies in order to hydrate as an energy source for future generations to see. The output lines that move of the sweet gas from refineries to consumers in major cities and industrial plants to move, despite all the measures foreseen in the design and implementation of the pension regulations, such as leak detection and measurement of the voltage period and ... that it applies during the operation, which is due to a large extent and distribution can't ignore the possibility of leakage. In fact, due to high pressure pipelines operating any minor leaks can be quickly learned and their surroundings in the wake of the explosion and fire are burning. If the water drops already formed crystals and destroyed the company is, I will re-hydrate formation induction time is less; seen that if a drop in the presence of the hydrate memory is added to water droplets, the hydrate formation time for a new water droplets time, the water droplets time memory effect is the phenomenon called Paul. Methods to prevent formation of gas hydrate Although Hydra hay high pressure gas and low temperature, but this situation occurs for each line pipe for oil and gas used may arise. To avoid blocking pipes hydrate formation should be prevented. Different methods to prevent hydrate formation include:

A) Maintenance of low pressure gas flow in the hydrate formation pressure, temperature and composition at a specified percentage of vapor phases.

B) Keeping the temperature higher than the flowed gas hydrate form and pressure in a combined percentage steam.

C) To prevent water in liquid phase by reducing the amount of water pipelines in the system.

D) Injection inhibitors that are divided into two categories: thermodynamic inhibitors and specific inhibitors.

REFERENCES

[1] V.S. Sastri, "Corrosion Inhibitors Principles and Application," *Wiley Pub, New York.*

[2] T.C. Chevro and M. Bonis, "Use of pH Stablization of Corrosion Control of Long Multiphase Pipelines", TOTAL FINA ELF, *Second Congress of Corrosion in Oil Industries*, Iran, Oil Industry University.

[3] A. Nazarboland and S. Java poor, "Application of corrosion technology into gas and oil pipe," *Second National Conference Conference of Technology in Oil Craft / Challenges and Strategies*.

[4] Samimi, Amir and Zarinabadi, Soroush, "Reduction of greenhouse gases emission and effect on environment," *Australian Journal of Basic and Applied Science*, pp. 752-756, 2011.

[5] Zarinabadi, Soroush and Samimi, Amir, "Problems of hydrate formation in oil and gas pipes deal," *Australian Journal of Basic and Applied Science*, 2011.

[6] Zarinabadi, Soroush, Samimi, Amir, Erfan Ziarifar, and Mohammad Sadegh Marouf, "Modeling and Simulation for Olefin Production in Amir Kabir Petrochemical," *Proceedings of the World Congress on Engineering and Computer Science*, 2010, Vol II, WCECS, San Francisco, USA, 2010.

[7] Samimi, Amir and Zarinabadi, Soroush, "Application Polyurethane as Coating in Oil and Gas Pipelines," *International Journal of Science and Investigations*, France, pp. 43-45, 2012.

[8] Samimi, Amir, Zarinabadi, Soroush, and Samimi, Marzieh, "Solar Energy Application on Environmental Protection," *International Journal of Science and Investigations*, France, pp. 21-24, 2012.

[9] Setoudeh, Mehrdad, Samimi, Amir, Zarinabadi, Soroush, Almasinia, Babak, Nazem, Esmaeil, Rezaei, Rohollah, and hedayati, Abbas, "Experimental Study of Factors Affecting Corrosion in Gas Wells Using Potantio Acetate and Galvan Acetate Tests," *International Journal of Science and Investigations*, pp. 13-16, 2012.
[10] Samimi, Amir, "Preventing Hydrate Formation in Gas Transporting Pipe Lines with Synthetic Inhibitors," *International Journal of Science and Investigations*, France, pp. 48-50, 2012.
[11] Samimi, Amir, Zarinabadi, Soroush, Setoudeh, Mehrdad, and Safavian, Amir, "Review Applications to Prevent Corrosion Reducing Gas Pipe Line," *International Journal of Basic and Applied science,* Indonesia, pp. 423-428, 2012.
[12] Samimi, Amir, Zarinabadi, Soroush, and Setoudeh, Mehrdad, "Safety and Inspection for Preventing Fouling in Oil Exchangers," *International Journal of Basic and Applied science*, Indonesia, pp. 429-434, 2012.
[13] Samimi, Amir and Zarinabadi, Soroush, "The Comparison of Increasing Method for Petroleum Pits Output (Fluids Dynamic)," International *Journal of Basic and Applied science*, Indonesia, pp. 435-439, 2012.

Amir Samimi

(16/05/1983, Isfahan City, Isfahan Province, Iran)

Studied M.SC Chemical Engineering, Master at Islamic Azad University, The Member of IAENG, Have 2 Years Experience in Oil Refinery Company, Member of Young Research, and Have 17 Articles in the International Journal, Conference (U.S.A, France, Italy, Indonesia, India, Australia, Europe Chemical Engineering Conference) and More than 45 Articles in the National Journal, Conference in Iran.
Email: amirsamimi1161@gmail.com