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Preventing Hydrate Formation in Gas Transporting Pipe Lines with Synthetic Inhibitors

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***Abstract*:** Gas hydrates are ice like crystals, but they are different in structure. gas hydrates formation in gas transporting pipe lines causes clogging the pipe lines, and prevents transporting gas .therefore gas hydrates formation should be prevented because clogging price is high and it's time- consuming. To stop gas hydrate formation in gas transporting pipe lines, chemical inhibitors are used. These inhibitors are divided into thermodynamic and synthetic inhibitors. Synthetic inhibitors are used with low density and prevents making and growing of crystal hydrates. 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: *Gas Hydrates, Synthetic Inhibitor, Modeling, Gas Transporting Pipe Lines.*

I. INTRODUCTION

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-controling pressure (the lower pressure the less hydration but in gas transporting lines it's impossible because of reinforcing gas pressure for transporting it)

2-controling 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

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:

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

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

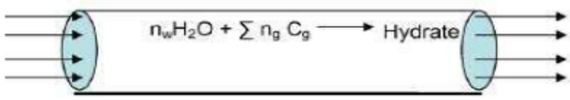

Figure 1: Current Line Consider

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. Synthetic diagram of hydrate has been drawn in figure 2.

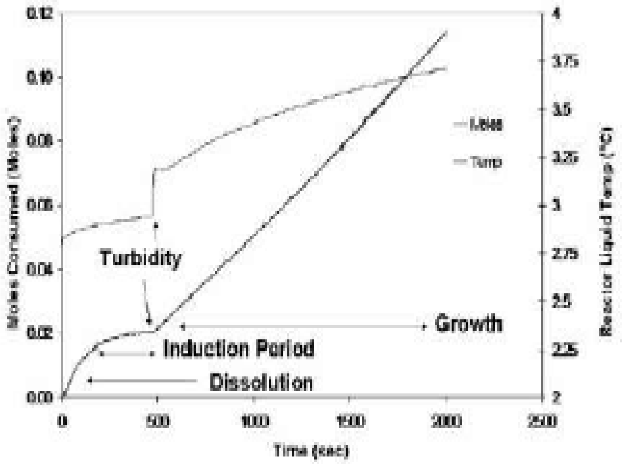

Figure 2: Synthetic Diagram of Hydrate Has Been Drawn

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-L} is formed hydrate partial molar in shared surface between gas and liquid, and X^i_{H-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. [2, 4]

II. MODEL

A. 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.

B. 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. The most amount of passing current intensity is 2 million cubic meter in a day. Percentage of passing natural gas compounds through pipe lines on the average in January and February in 2009 are in 1 Table.

Table 1: Operational Temperature and Pressure Average on Several Days of this Two Month. Reported from Roomier CGS

T ^{0}C	5	7	7	8	9	10	12	14	15	17
P (BAR)	61	54	63	60	53	56	57	59	54	63

Two synthetic inhibitors, PVP and L_ Tyrosine, have been chosen with different density. Velocity diagram without inhibitor is in fig.4

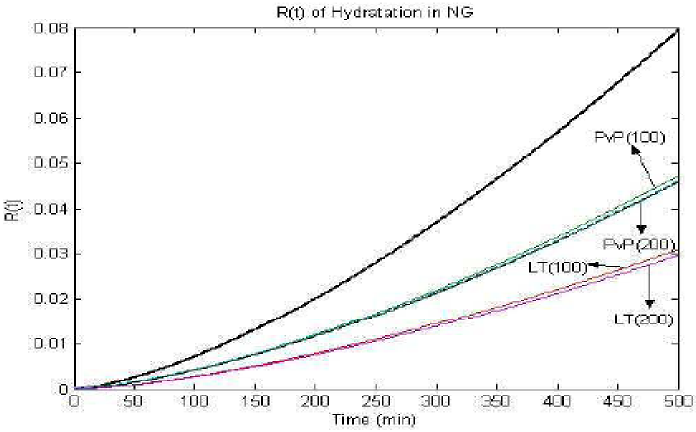

Figure 3: Growth Rate of Hydrate Formation without Inhibitor Goes up and has Rising Growth with Time Increase

III. DISCUSSION

Figure 3 shows that growth rate of hydrate formation without inhibitor goes up and has rising growth with time increase, but rate of this growth with inhibitor will be decreased .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.

IV. 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.

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