

Determination of Induction Time of Hydrate Formation

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Abstract

The problem of hydrate formation and its attendant plugging effect on pipelines has remained a major challenge that the oil and gas industries are faced with during production. This problem is simply an issue affecting the oil and gas facilities both at drilling and production systems. As a result of this millions of dollars have been invested in remedial and preventive operations, therefore necessitating an in-depth study on the preventive methods. This study determines and validates existing postulations on favourable conditions at which hydrates form in transmission lines in a sampled Well-X, located in the Atlantic region. Measurements and experimentations were meticulously carried out on the sampled Well-X using methane gas and water at various conditions of pressure and temperature to determine the hydrate formation induction time using a stirred reactor. The result obtained in this study shows that the induction time at which hydrate starts to form in Well-X is at a pressure of 160 bar and temperature of 4°C. The obtained result confirms a pressure of 160 bar as against pressures of 120 bar and 135 bar and a temperature of 4°C as against 6°C as the induction time of hydrate formation. From the obtained result in this study, it is concluded that there is a need for a concerted effort to maintain stable pressure and temperature conditions of the flow systems. This study recommends that adequate provisions for an efficient flow assurance system with precise inhibitors in the right concentration and quality to mitigate the effects of hydrate should be made.

Keywords: Hydrate formation; Plugging; Natural gas pipeline; Corrosion; Induction time.

1. Introduction

Natural gas contains several undesired components that makes it highly corrosive, environmentally unfriendly, less combustible, hence having low British thermal units value. It is transported from wells through flowlines / pipelines till they get to their final destinations, hence the need for critical evaluation of hydrate formation effect for safe transportation.

1.2. Hydrate as a flow assurance problem

Investigations [1-2] on different flow assurance issues that affect the flow of well fluids from the reservoir to the sales point have been carried out by various researchers who identified wax deposition, hydrate formation and corrosion as flow assurance issues with emphasis on hydrate as a fundamental problem. Study [3] on hydrate formation and its influence on natural gas pipeline revealed hydrate to be a serious threat to the survival of oil and gas industry that if not quickly removed may plug the flowline/collapse the system with its attendant cost implications in terms of revenue loss annually. Tohidi *et al.* [4] in their comparative study compared hydrate plugging to other flow assurance issues such as sand deposition and concluded that hydrates are quite less dense and are accumulative when formed. In advancing this study, Singh and Krishnathasan [5] stated that at every point and condition where small deposit of sand is formed in the pipeline, is vulnerable to hydrate formation and accumulation.

1.3. Structure of gas hydrate

Rao *et al.* [6] studied the appearance of crystalline compounds of gas (clathrate) hydrate and observed that it resembles an ice plug or a snow crystal which has densities that are less than that of ice. Structurally, gas hydrates have an ice-shaped form with a crystal lattice structural molecular arrangement [7]. Laboratory study [8] shows that smaller guest molecules like CH₄ and C₂H₆ which have reduced molecular diameters improve the stability of the crystal compounds formed by the combination of water and natural gas molecules, with the formed products hidden in the micro cavities of lattices of crystals which are provided by the host component, water.

1.4. Favourable conditions for hydrate formation

Favourable conditions for hydrate formation shows that water and natural gas molecules under the condition of high pressure and low temperature is required for the formation of hydrate [7-9]. The composition of natural gas has varying effects on the pressure and temperature needed for hydrate formation in line with pressure-temperature curve, and operating outside the hydrate stability zone ensures hydrate free flow system [9-10]. For hydrates to form and be deposited in the flow system, they must occur within specified pressure and temperature conditions, especially as the gas phases of fluids from the reservoir get in contact with molecules of water [11-12].

1.5. Hydrate formation in pipeline

Talaghat *et al.* [13] from his laboratory work on favourable conditions that support hydrate formation in pipeline stated that gases that flow from the reservoir through the well to the surface pipelines combines with other non-hydrocarbon including water to form gas hydrate. Sloan *et al.* [14] in their study on hydrate formation in undersea gas pipeline stated that natural gas is best transported at high-pressure conditions with supersonic velocity and corresponding small ambient temperature, a condition that aids hydrate formation. Kvamme *et al.* [15] in their observatory study at Troll offshore of Norway stated that hydrate can occur during processing of natural gas at pressure condition of 70 bar and temperature of about -22°C though, could also form at temperature as low as -70°C mainly with a significant amount of ethane and other heavier hydrocarbons.

1.6. Methods of mitigating hydrate formation

Shuard *et al.* [16] in a simulative study on optimization approach towards reducing the risk of hydrate plugging during restarting operation obtained a genetic algorithm that minimized the restart gas velocity which ensured minimized risk of plugging. Researchers on methods of mitigating hydrate formation has shown that injecting thermodynamic hydrates inhibitors and its optimal injection point and plug remediation are key in mitigating hydrate formation [1,17].

1.7. Induction time of hydrate formation

Canale *et al.* [18] defined induction time as certain delay duration after a system composed of water and a hydrate-forming gas put under suitable thermodynamic conditions of pressure and temperature forms gas hydrate crystals. Determination of induction time according to Gambelli *et al.* [19], is to find the time between the initiation of the experiment and the formation of hydrate. Investigation by Chen *et al.* [20] on induction time of hydrate formation identified pressure range of 120bar to 160bar and temperature range of 4°C to 6°C as the most probable range of hydrate formation for wells in the temperate regions. Zheng *et al.* [21] investigated the induction time for hydrate formation in water-in-oil emulsions under varied conditions and observed that variation in viscosity has major effect on induction time in emulsion than in pure water

2. Materials and method

2.1. Equipment and raw materials

First, comprehensive lists of all the equipment, materials and procedures employed for this research were defined. Methane gas with high purity level ($\geq 99.5\%$) and distilled water with conductivity, δ of $2 \mu\text{S}/\text{cm}$ and specific gravity of 1.0 used for this research were sourced from industrial gas plant and local water respectively, all in Port Harcourt Rivers State, South South Nigeria. Measurements and experimentations were meticulously carried out on the collected samples. All experiments for this research were carried out in an industrial laboratory in Port Harcourt city Rivers State, South South Nigeria.

2.2. Method

2.2.1. Multimeter and probe

The multimeter and probe was used to determine the water sample conductivity. The electrodes in the probe were immersed in the water sample while voltage was passed through the sample between the pair of the electrodes. The drop in voltage caused by the resistance of the water is recorded from the multimeter used to calculate the conductivity of the water sample.

2.2.2. Stirred reactor

A 4568 type of stirred reactor manufactured by Deutschland Parr Instrument was used in the experiment to introduce and sustain the required turbulence necessary to perfectly replicate what happens inside pipelines in the reactor. The pressure range of its operation is between 0 and 200 bar while its temperature range is between -10 and 150°C . The stirred reactor consists of some components such as: the hollow shaft stirrer which is used when inputting gas and the temperature sensor which controls the reactor inner temperature. It has two glass windows which help in proper viewing and clear process observation during experiments. At the beginning of the experiment, the reactor was opened from the top through which one can access the reactor while the outlet (drain) valve is closed. The reactor was filled with water through the flanges after which the reactor was turned on. The reactor was closed with a metallic ring that has a hole for placing a Plexiglas of about 3cm thickness for monitoring the gas hydrate formation process. Methane gas flow was gradually introduced into the reactor by a gas compressor through the inlet valve This process initiates pressurization. Gradual increase in pressurization using gas is continued until the system got to the target condition of 160 bar. The reactor has the laboratory room temperature of 20°C as its initial.

2.2.3. Thermostat

The thermostat is a temperature regulator used to gradually cooled down the reactor system to the required experimental conditions of temperature of 6°C and pressure of 160 bar. This experimental condition is aimed at mimicking the pipeline condition for fluid flow.

2.2.4. Mass flow meter

A Coriolis brand of mass flow meter manufactured by Bronkhorst Mattig was used in measuring, monitoring and controlling of gas flow rate and setting it at the required pressure. It was initially set at pressure value of 160 bar when the corresponding temperature was at 6°C after which the pressure was maintained at 160 bar and temperature reduced to 4°C using the thermostat. The pressure was later dropped to 135 bar and 120 bar pressure conditions.

2.2.5. Stop watch

The stop watch was used to monitor and note induction time of the system, which was the point at which hydrate crystals began to form. For each of the experimental conditions conducted, a minimum of 5 values were obtained and carefully recorded in order to obtain an efficient and effective result. The experiment was also done at pressure condition of 135 bar and temperature of 4°C likewise pressure value of 125 bar and temperature of 4°C .

3. Results and discussion

3.1. Results

The results and discussions on the experimental study on induction time of hydrate formation is presented and discussed below. Table 1 shows the obtained induction time results at varied pressure and temperature conditions. Figures 1 and 2 indicates the results of the image representation of the formed hydrate as obtained using scanning electron microscope (SEM) and graphical representation of the pressure/temperature vs induction time as obtained from Table 1 respectively.

Table 1. Induction time at different pressure and temperature conditions.

Experimental conditions/ series of measurement	Induction time in minutes				
	1 st	2 nd	3 rd	4 th	5 th
160 bar (6°C)	248	138	150	87	107
160 bar (4°C)	158	110	139	108	105
135 bar (4°C)	278	301	2783	876	1590
120 bar (4°C)	2889	1888	641	1123	361

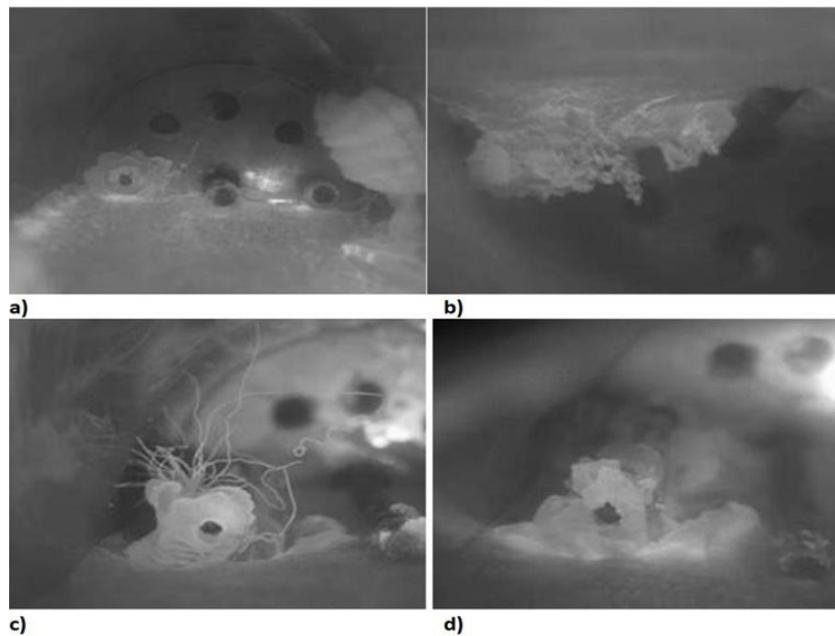


Figure 1. Formed gas hydrate in the reactor scanning electron microscope (SEM) image representation.

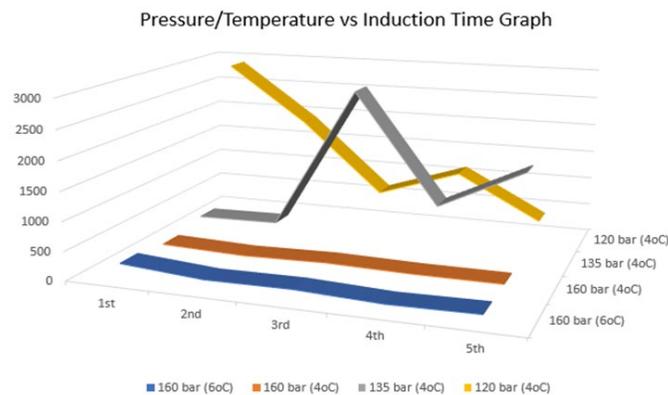


Figure 2. Pressure/temperature vs induction time.

The result of the statistical analysis of induction time are given in Table 2 while the comparison of hydrate formation induction time at 160 bar and varied temperature conditions are shown in Figure 3.

Table 2. Statistical analysis of induction time results.

Experimental Condition	Mean (Mins)	Standard deviation (Mins)	Minimum (Mins)	Median (Mins)	Maximum (Mins)	Distribution (Normal)
160 bar, 6°C	146	62	87	138	248	Yes
160 bar, 4°C	124	23	105	110	158	Yes
135 bar, 4°C	1016	1009	268	588	2783	Yes
120 bar, 4°C	1381	1023	361	1123	2889	Yes

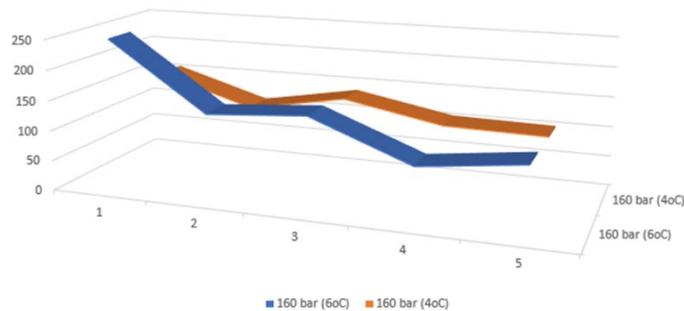


Figure 3. Comparison of hydrate formation induction time at 160 bar and temperature 4°C and 6°C.

3.2. Result discussion

3.2.1. Induction time

The induction time of hydrate formation as presented in Table 1 shows the obtained induction time results at varied pressure and temperature conditions. About five (5) different series of experimental result on induction time were obtained. The quest for higher certainty in statistical analysis orchestrated by high level of variance in the series of measurement actually necessitated the need for higher number of experiment.

3.2.2. Statistical analysis of induction time

The result of the statistical analysis of induction time are given in Table 2 while the comparison of hydrate formation induction time at 160 bar and varied temperature conditions are shown in Figure 3. The statistical analysis of the obtained induction time result from Table 1 as shown in Table 2 is a clear evident to the degree to which temperature and pressure conditions affect hydrate formation. The results from Table 2 shows that at increased pressure of 160 bar and corresponding temperature of 4°C and 6°C, the mean induction time values are 124 minutes and 146 minutes. The induction time deviation values were quite small, as low as 23 and 62, They are minimal enough to easily support hydrate formation unlike pressure values of 120 bar and 135 bar with corresponding temperature of 4°C. Their mean induction time values are 1381 minutes and 1016 minutes respectively. The calculated deviations from the induction time at 120 bar and 135 bar pressures are 1023 and 1009 respectively and these later conditions does not support hydrate formation. It is clearly seen from the statistical analysis of the obtained results from Table 2, that the least mean value which is the easiest condition at which hydrates can form is 124 minutes and was obtained at pressure of 160 bar and temperature of 4°C. This mean value as shown in Table 2 normalized the pseudo-effect that gave 87 minutes at pressure of 160 bar and temperature of 6°C according to Table 1. Figure 3 shows the result of the comparisons of hydrate induction time at pressure of 160 bar and temperatures of 4°C and 6°C to determine the most accurate temperature value. The

results as obtained shows that 4°C has the least deviation, hence the most favourable condition for hydrate formation. The obtained results from this study are a confirmation to studies by [7-9] on required conditions for hydrate formation.

3.2.3. Formed hydrate

The result of the formed hydrate image using scanning electron microscope (SEM) is presented in Fig. 1. The obtained pictorial image of the formed hydrate according to Fig.1 shows crystals of hydrates formed around the steel pipe during methane gas flow in the system. Because of the varied test conditions of pressure and temperature, the hydrate that was formed at different induction times have different structural shape and appearance.

4. Conclusion

Based on the obtained results and discussions, there is higher probability of hydrate formation at pressure condition of 160 bar and 4°C. The above conclusion is in consonance with the principles of hydrate formation where increase in pressure and decrease in temperature favours hydrate formation. Presence of hydrate in flow system obstructs fluid flow which reduces the quantity of recovered flow. Again, it poses some level of risk to the entire facility and lives of personnel working in the facility in eventuality of accident caused by hydrate plugging.

Recommendation

Wells with high concentration of formation water has an increased risk of hydrate formation and internal corrosion hence, adequate mitigation plan against such occurrence such as good hydrate inhibition plan should be put in place. Dehydrators and absorbents are used in removing water from fluid flow. Therefore, further studies are recommended to unravel their corrosive effects on metallic pipelines.

Conflict of interest: on behalf of all authors, the corresponding author states that there is no conflict of interest.

References

- [1] Theyab MA. Fluid flow assurance issues: literature review. SF J Petroleum, 2018; 2:1.
- [2] Sloan ED, Koh C, Sum A, Ballard A, Shoup G, McMullen N, Creek J, Palermo T. Hydrates: state of the art inside and outside flowlines. Journal of Petroleum Technology, 2009; 6(12): 89-94.
- [3] Obanijesu EO, Pareek V, Gubner R, Tade OM. Hydrate formation and its influence on natural gas pipeline internal corrosion. NAFTA, 2011; 62: 164-173.
- [4] Tohidi B, Danesh A, Burgess RW. Measurement and prediction of hydrate-phase equilibria for reservoir fluids. SPE Production and Operation, 1996; 11 (2): 69-76. <https://www.sciencedirect.com/science/article/pii/S0360544218325106>.
- [5] Singh B, and Krishnathasan K. Pragmatic effects of flow on corrosion prediction. Corrosion Conference & Expo, NACE International, Atlanta, GA, 2009.
- [6] Rao I, Koh CA, Sloan ED, Sum AK. Gas hydrate deposition on a cold surface in water-saturated gas systems. Ind. Eng. Chem. Res., 2013; 52(18):6262-6269. <https://doi.org/10.4043/24099-MS>
- [7] Abdel-Aal HK, Aggour M, Fahim MA. Petroleum and gas field processing. Marcel Dekker Inc., New York, USA, 2003. <https://doi.org/10.1201/9780203911099>.
- [8] Sloan ED. Fundamental principles and applications of natural gas hydrates. Nature, 2003; 426(6964): 353.
- [9] Rajnauth J, Barrufet M, Falcone G. Hydrate formation: considering the effects of pressure, temperature, composition, and water. Energy Science and Technology Journal, 2012; 4(1): 60-67. <http://doi.org/10.3968/j.est.1923847920120401.397>.
- [10] Bunaev A, Dolganov I, Dolganov I, Vladescu A. Mathematical simulation of low-temperature gas separation. Petroleum and Coal, 2016; 58(2): 210-219.
- [11] Olabisi O, John C, Udim M. Experimental investigation of modified starch from white corn as a kinetic inhibitor of gas hydrate. Petroleum and Coal, 2019; 61(6) 1487-1493.

- [12] Pickarts MA, Ravichandran S, Ismail NA, Stoner HM, Delgado-Linares J, Sloan ED, Koh CA. Perspective on the oil-dominated gas hydrate plugging conceptual picture as applied to transient shut-in/restart. *Fuel*, 2022; 324(B). <https://doi.org/10.1016/j.fuel.2022.124606>.
- [13] Talaghat MR, Esmaeilzadeh F, Fathikaljahi J. Experimental and theoretical investigation of simple gas hydrate formation with or without presence of kinetic inhibitors in a flow mini-loop apparatus. *Fluid Phase Equilibria*, 2009; 279(1):28-40. <https://doi.org/10.1002/ceat.200800601>.
- [14] Sloan ED, Koh CA, Sum AK. Natural gas hydrates in flow assurance. Gulf Professional Publishing, Boston, 2011; 1–11. <https://doi.org/10.1146/annurev-chembioeng-061010-114152>.
- [15] Kvamme B, Aromada SA, Saeidi NN, Hustache-Marmou G. Hydrate nucleation, growth, and induction. *ACS Omega Journal*, 2020; 2603-2619. <https://doi.org/10.1021/acsomega.9b02865>.
- [16] Shuard AM, Mahmud HB, King AJ. An optimization approach to reduce the risk of hydrate plugging during gas-dominated restart operations. *Journal of Petroleum Science and Engineering*, 2017; 156: 220-234. <https://doi.org/10.4043/24099-MS>.
- [17] Sloan ED, and Koh CA. Hydrates in production, processing, and transportation, In clathrate hydrates of natural gases, 3rd Edition, CRC Press, Boca Raton, 2008; Chapter 8; 643-683. <https://doi.org/10.1201/9781420008494>.
- [18] Canale V, Antonella F, Siani G, Di-Profio P. Hydrate induction time with temperature steps: A novel method for the determination of kinetic parameters. *Energy & amp Fuels Journal*, 2019; 7: 6113-611. <https://doi.org/10.1021/acs.energyfuels.9b00875>.
- [19] Gambelli AM, Filioooni M, Rossi F. Determination of induction time of hydrates. *Journal of Physics: ATI Annual Congress Conference Series*, 2022; Vol. 2385. <https://doi.org/10.1088/1742-6596/2385/1/012110>.
- [20] Chen J, Guang-Jin C, Yuan Q, Deng B, Tao L, Li C, Xiao S, Jiang J, Li X, Li J. Insights into induction time and agglomeration of methane hydrate formation in diesel oil dominated dispersed systems. *Energy*, 2019; 170: 604-610. <https://doi.org/10.1016/j.energy.2018.12.138>.
- [21] Zhang H, Orcid QH, Wang W, Long Z, Kusalik PG. Induction time of hydrate formation in water-in-oil emulsions. *Ind. Eng. Chem. Res.*, 2017; 56: 8330-8339. <https://doi.org/10.1021/acs.iecr.7b01332>.

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