

Hydrate Inhibition in the Niger Delta Using Plant Polymer as a Local Kinetic Hydrate Inhibitor

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Abstract: Offshore production activities have increased in the Niger Delta region of Nigeria due to available technology to produce petroleum fluids from reservoirs that lie thousands of feet below the waterbed. However, Offshore production in Nigeria is still being plagued by flow assurance challenges such as hydrate formation. In this study, the effect of Niger delta seawater salinity on hydrate prevention is evaluated. The efficiency of a locally sourced kinetic hydrate inhibitor (KHI) is also assessed. The experimental study was conducted in a 12-meter horizontal hydrate flow loop designed to model a horizontal subsea flowline. A sample of Niger delta seawater and compressed natural gas were used as the hydrate formers, and the loop was conditioned to hydrate formation conditions. Although the salinity of the seawater was 26.18ppt, hydrates still formed in the loop, as indicated by a rise in temperature and a rapid decline in loop pressure. Further experiments were conducted using the plant polymer with concentrations varying from 0.01wt% to 0.1wt%. The optimum concentration of the polymer was found to be 0.03wt%. Seawater salinity is not sufficient in preventing hydrate formation in the Niger Delta region. Operators should plan to use KHI to enhance the inhibitive property of the seawater and formation water. The optimum dosage of inhibitor should be used to minimise production cost.

Keywords: Hydrate, Flow-loop, Seawater, Kinetic Hydrate Inhibitor, Plant Polymer

1. Introduction

Methane clathrate, also known as methane or natural gas hydrate, is a solid clathrate compound in which a large amount of methane is trapped within a crystal structure of water, forming a solid similar to ice. It is formed when a gas molecule such as methane gas is entrapped inside a water molecule, forming a crystalline structure at relatively high pressure and low temperature. The trapped gas molecule is usually called the 'guest' while the water molecule is the host [1]. Hydrate is favoured by low temperature and high-pressure conditions, hydrate former (like methane, ethane, nitrogen, hydrogen sulphide and carbon dioxide), and a sufficient amount of water (not too much or too little). Natural gas (methane) hydrates are described as ice-like structures, and crystalline compounds formed when water comes in contact with the light end of petroleum crude such as methane, ethane, propane and butane gas at reduced

temperature and high pressure.

Hydrates are non-stoichiometric crystalline compounds that occur when water molecules attach themselves by hydrogen bonding and form cavities occupied by either a gas or volatile liquid molecule [2]. Formation of hydrate requires a hydrate former and sufficient water in low temperature and high-pressure conditions.

Subsea production operations are highly susceptible to hydrate formation due to harsh conditions in the offshore environment, such as reduced temperatures, the high-pressure requirement for fluid movement due to great sea depths and several other factors. Hydrate formation poses a significant challenge in the production, processing and transportation of hydrocarbon fluids and therefore needs to be prevented. When the temperature and pressure are in the hydrate formation region, light hydrocarbon forms hydrates as long as the water is available, which eventually leads to blockages. Cleaning hydrate blockages in flow lines and subsea equipment is very tedious, time-consuming and costly.

Gas hydrate is a significant problem in the Oil and Gas Industry; it can form in the reservoir during enhanced oil recovering with carbon dioxide [3]. Hydrates can also be formed because of a gas kick during wellbore drilling [4]. Hydrates can form in pipes during petroleum production [5], and during gas expansion, hydrates formed can grow due to Joule-Thomson cooling. Still, they can be managed effectively using hydrate inhibitors [6]. Stoppage of flow by blockage of the pipeline due to formation of hydrate plug can result in financial loss and several environmental and safety issues [7].

Hydrate formation can be prevented using different methods such as temperature and pressure control, dehydration, and chemical inhibition. Hydrate inhibition involves using thermodynamic hydrate inhibitors (THIs) to shift the thermodynamic equilibrium conditions from hydrate risk region to hydrate free region. However, THI have incredibly high-cost implications [8], they are toxic [9], and they are not compatible with other production chemicals [10]. Due to these shortcomings of THIs, the petroleum industry has considered alternative hydrate inhibitors that are environmental friendly and compatible with other production chemicals. These chemicals are the Low Dosage Hydrate Inhibitors (LDHI) [11-14] required in low dosages and prevent hydrate crystal growth and accumulation.

The Niger delta is the oil-rich region in Nigeria. According to the Nigerian National Petroleum Investment Management Services (NAPIMS), Nigeria currently has about 28.5 billion barrels of oil and a gas reserve of 166 trillion standard cubic feet (TCF) [15]. Although very rich in petroleum, poor environmental management has adversely affected development in this region [16]. Operators embark on many offshore petroleum exploration and production operations in Nigeria due to the frequent vandalisation of onshore facilities and larger reservoirs usually found in the offshore environment. Although there is available technology to support offshore production in Nigeria, hydrate formation is still a significant plague in offshore production in the Niger delta. Hydrate formation has caused a shutdown of production

operations and caused a massive loss in revenue from production downtime and hydrate dissociation interventions.

In this study, hydrate formation in the Niger delta is critically studied by collecting a seawater sample from an offshore field and subjecting it to hydrate formation conditions in the presence of hydrate formers. Formation water from the field of study was inaccessible. Hence, seawater was used because formation water is a mixture of originally trapped seawater modified by rock-water interaction [17]. Salts have been used to prevent hydrate formation [18]. The study investigates gas hydrate formation in an uninhibited Niger delta offshore field to ascertain if the formation water salinity is sufficient to prevent hydrate formation in the field. Also, the gas hydrate formation experiment was conducted in an experimental horizontal loop that simulates horizontal flow lines. The experiment was conducted in batches at constant volume in a gas dominated system. The efficacy of a locally-sourced polymer as a hydrate inhibitor was also studied by analysing the effect of various concentrations of the inhibitor in preventing hydrate formation in the flow loop.

2. Materials and Method

2.1. Equipment

The equipment used in this study is a flow loop fitted refrigerator, a manual pump, three electric circulation pumps, inhibitor vessel, control panel, gas cylinder with methane gas, 0.5-inch stainless steel pipe, differential pressure meter, pressure gauges, temperature gauges, electric socket. The flow loop consists of a 0.5-inch internal diameter steel tube with a length of 10.845 meters and a volume of 4.59 litres. Fiber wool is used to cover and insulate the PVC pipe from gaining heat from the surrounding. It is designed to withstand a pressure of 3500psi and is situated in a temperature-controlled room to avoid a temperature gradient between the flowing media and the surrounding.

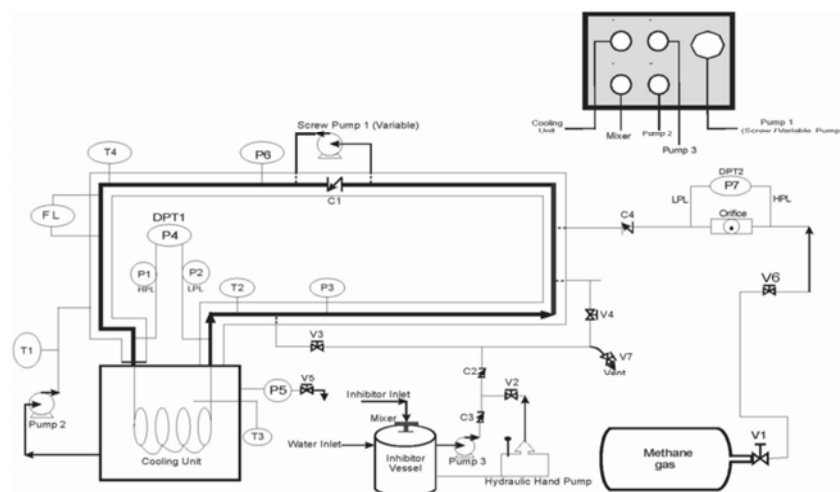


Figure 1. Schematic diagram of hydrate mini flow loop [19].

The loop is fitted with two 0.5hp pumps that operate at 220 volts, 2.5 amperes and 50 hertz with 2850 revolutions per minute, positioned to move fluid along the loop and move cooling fluid between the inner surface of PVC pipe and the outer surface of 0.5-in internal diameter stainless steel tube. The inhibitor/water pump, pump 3, is a 1.0 horsepower that pumps water and inhibitor into the 0.5in ID stainless steel tube.

The loop is fitted with four pressure gauges positioned strategically along the loop. Loop also has a differential pressure transmitter that displays the differential pressure between the inlet and outlet of the portion of the loop immersed in the refrigerator. Temperature gauges are positioned at the inlet into the refrigerator, outlet from the refrigerator and along the loop. Several hydrate inhibitors have been tested using this equipment these include: 2-(dimethylamino)ethyl methacrylate [20], N-vinyl Caprolactam [21] and Modified starch [22].

2.2. Materials

The water used in the hydrate formation is seawater from the Niger Delta. The salinity of the sea sample was measured using a refractometer to be 26.18ppt. The gas used is compressed natural gas (CNG) with a Specific gravity of 0.5, having a composition of 98.44% methane and 1.56% Carbon dioxide. Methane and carbon dioxide are hydrate formers and form the structure 1 hydrate [23]. Tap water was used as the cooling fluid. The refrigerator helped to condition the temperature of the cooling fluid.

The local inhibitor in this study is polymer extracted from a plant and administered as a low dosage kinetic inhibitor (LDHI). In this research report, the inhibitor used has not been patented and given a name, hence 'plant polymer (PP)'. The inhibitor was weighed using mass balance equipment. The masses used for each experimental runs are; 0.26, 0.52, 0.78, 1.05, 1.31, 1.57, 1.83, 2.09, 2.35 and 2.62g respectively. These were dissolved in 2616.2g (2660ml) of seawater using a measuring cylinder and beaker.

2.3. Experimental Procedures

Reactants such as 1400 ml of seawater and CNG were fed into the loop, and the loop was pressurised to about 150psi and then shut-in. While the mixture of gas and water was circulated along the length of the loop with the aid of the screw pump, the cooling water was pumped around the loop to reduce the loop temperature to hydrate formation temperature. Temperature and pressure along the loop were closely monitored and recorded every two minutes for 2 hours, after which the experiment was terminated. The experiment was conducted to ascertain if hydrate formation will occur in the seawater sample. Experiments were also conducted to study the hydrate inhibition effect of various concentrations (0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.09, and 0.1wt%) of the plant extract used as LDHI. At the

end of each experiment, the loop was depressurised by opening valve v5 (Figure 1). The initial resistance of the flow of effluent from the loop indicates a plugged flow line. Also, the effluent was physically evaluated for evidence of hydrate formation, such as whitish substances that quickly dissociate to water

Experiments conducted in this study were constant-volume batch experiments; therefore, a decline in loop pressure indicated hydrate formation reaction. The magnitude of pressure decline is an indication of how effective the inhibitor is. A rapid decrease in the pressure shows that the inhibitor is not effective. In contrast, a slight reduction in pressure is an indication that the inhibitor was effective at reducing the hydrate formation.

3. Results and Discussion

A plot of pressure against time for the experiment conducted with the seawater sample without inhibitor (Figure 2) showed a rapid decrease in loop pressure from 150psi to about 96psi. This implies that the formation water salinity of this Niger delta field measured as 26.18ppt was insufficient to prevent hydrate formation. At the termination of the 2-hour experiment, valve v5 was plugged, indicating that hydrate was formed, and the seawater salinity was inadequate to prevent hydrate formation. Therefore, it is imperative to add some low dosage hydrate inhibitors to improve the inhibitive properties of the formation water.

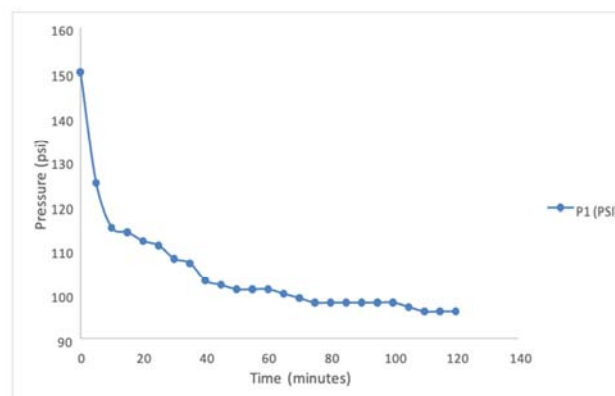


Figure 2 Plot of pressure against time for the experiment conducted without inhibitor.

3.1. Effect on Pressure

To study the effect of PP used as a KHI, the polymer was applied in varying concentrations in ten different experimental runs. The plots of pressure against temperature for the experiments conducted using 0.01wt%, 0.02wt%, 0.03wt%, 0.04wt%, 0.05wt%, 0.06wt%, 0.07wt%, 0.08wt%, 0.09wt%, and 0.1wt% of the PP shown in figure 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12 respectively.

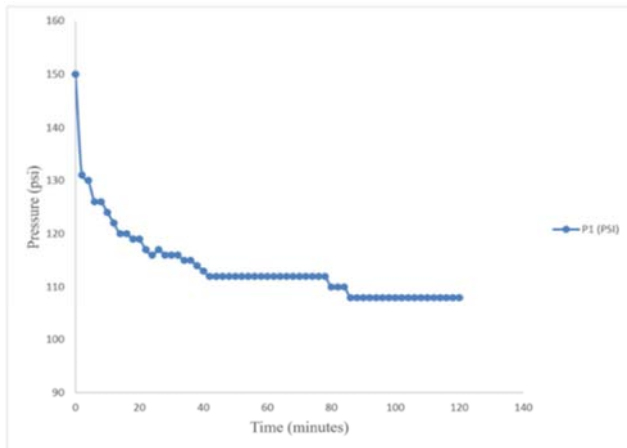


Figure 3. Plot of pressure against time for 0.01wt% PP.

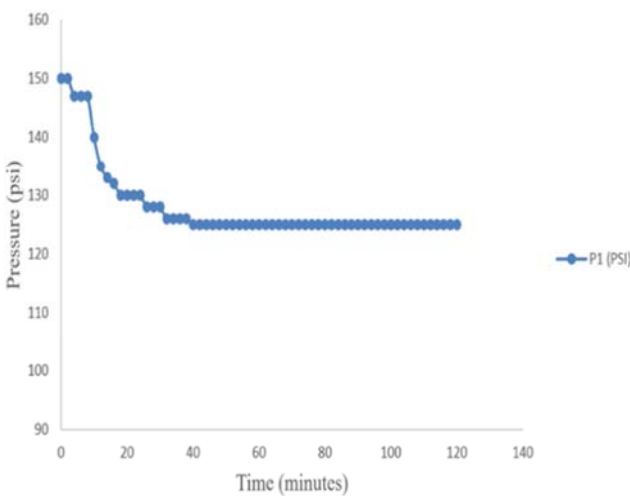


Figure 4. Plot of pressure against time for 0.02wt% PP.

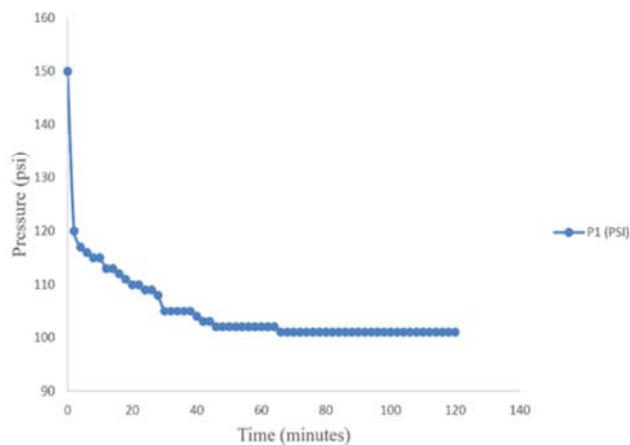


Figure 5. Plot of pressure against time for 0.03wt% PP.

In the experiment conducted with 0.01wt% of PP, the final loop pressure after the 2 hours batch experiment was 108psi. Compared with the uninhibited system, which had a final loop pressure of 96psi, it implies that less gas was used up in forming hydrates in this system containing hydrate inhibitor.

Hence, the loop pressure didn't decline as much as it did during the uninhibited experiment. This implies that 0.01wt% of PP prevented hydrate formation in the loop to an extent. It was also noticed that valve v4 (Figure 1), which was plugged during the uninhibited experiment, was unplugged with 0.01wt% of the PP.

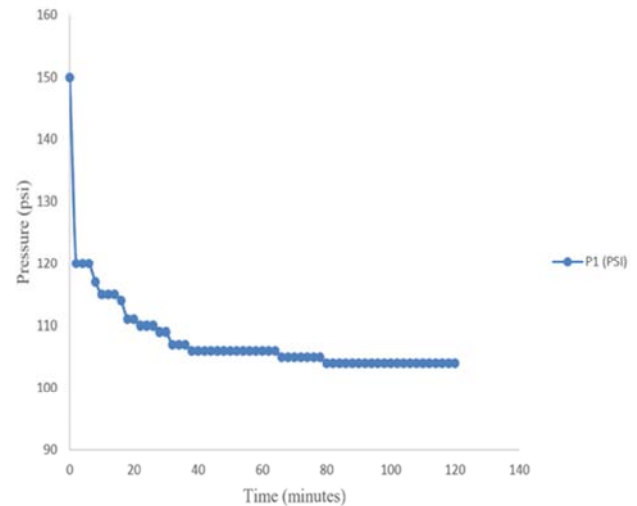


Figure 6. Plot of pressure against time for 0.04wt% PP.

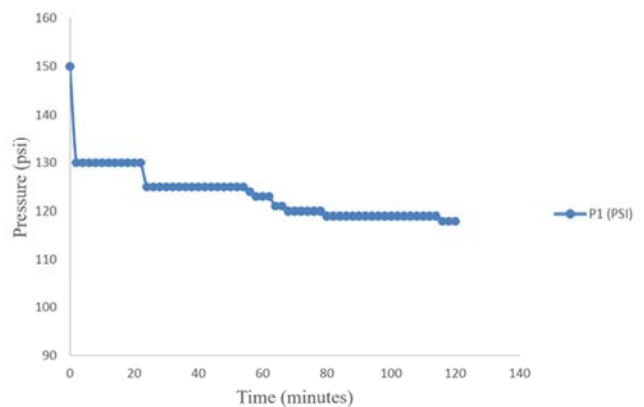


Figure 7. Plot of pressure against time for 0.05wt% PP.

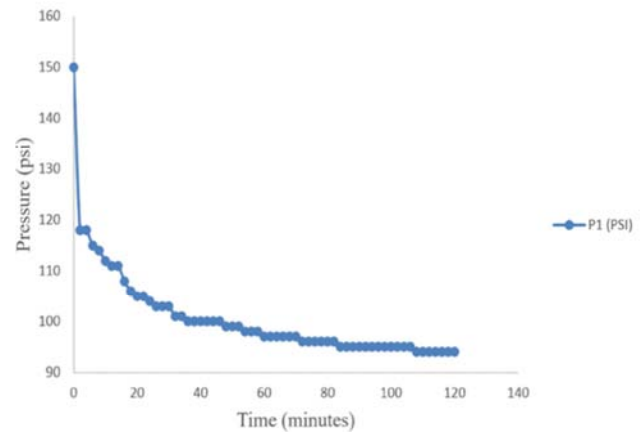


Figure 8. Plot of pressure against time for 0.06wt% PP.

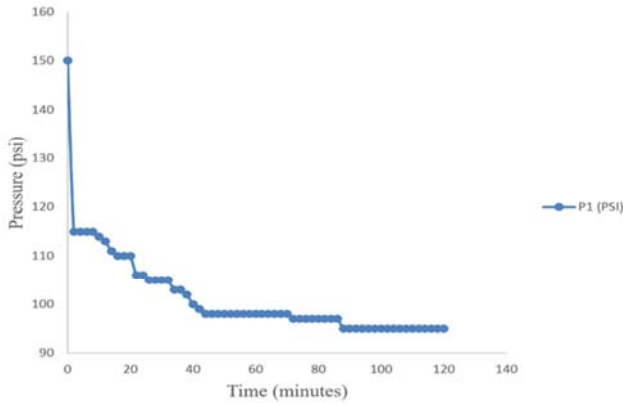


Figure 9. Plot of pressure against time for 0.07wt% PP.

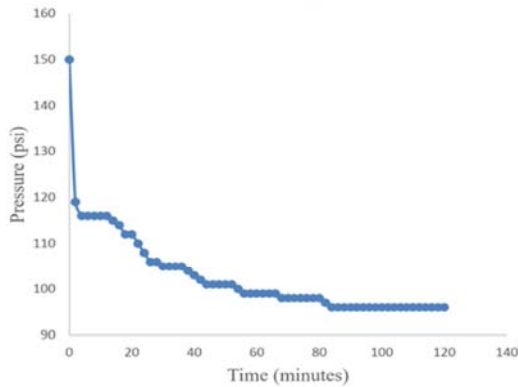


Figure 10. Plot of pressure against time for 0.08wt% PP.

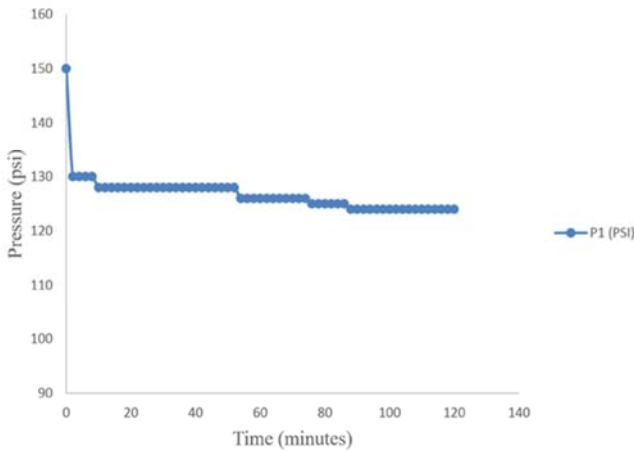


Figure 11. Plot of pressure against time for 0.09wt% PP.

The plugging of valve v5 (Figure 11) was an indication that hydrates formed in the system. All experiments conducted with the PP inhibitor recorded an unplugged valve v5. This implies that the PP is an effective KHI. However, to obtain the optimum inhibitor dosage, the amount of gas consumed in the experiment, which is indicated by the loop pressure decrease, is analysed for each experiment (Figure 13). Since constant volume batch experiments were conducted, the change in loop pressure is a vital indication of how much gas was used up in

forming hydrates. The experiment with the least pressure change signifies a lower gas consumption and implies the optimum inhibitor dosage. From figure 13, the best hydrate inhibitor as indicated by pressure decline will be 0.03wt% of the PP. Notice that the inhibitor efficiency declined at 0.04wt%, as indicated by an increase in gas consumption shown by a significant loop pressure decline. It is observed that the inhibitor efficiency improved at 0.05wt% but still declined again at 0.06wt%, 0.07wt% and 0.08wt% of the PP. An improved inhibitor performance is observed at 0.09wt% and a decline at 0.1wt% (Figure 13). However, the optimum dosage is still 0.03wt% of the PP because it effected the least pressure change at a smaller dosage, which will help reduce production costs.

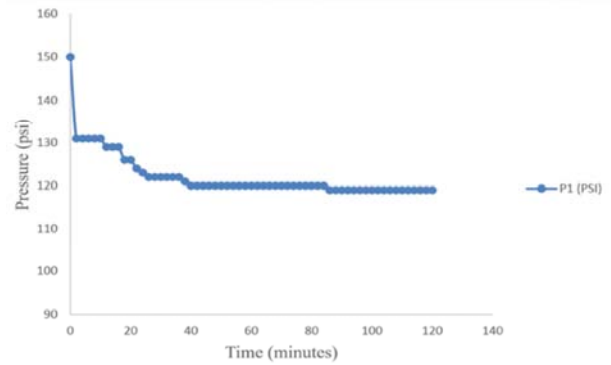


Figure 12. Plot of pressure against time for 0.1wt% PP.

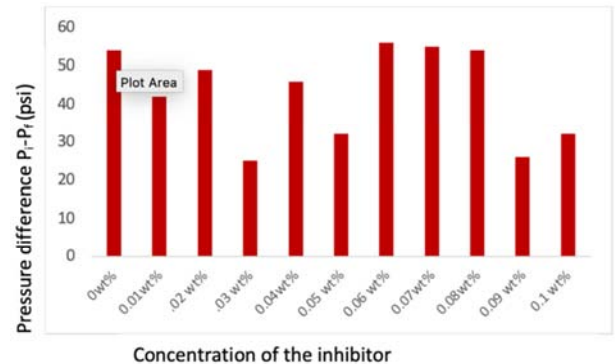


Figure 13. Plot of Change in Pressure against inhibitor concentration.

3.2. Effect on Temperature

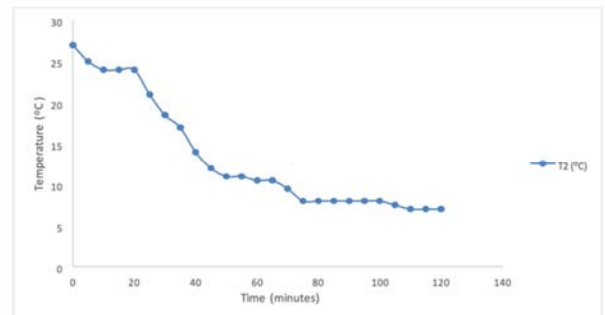


Figure 14. Temperature against time for the experiment conducted without inhibitor.

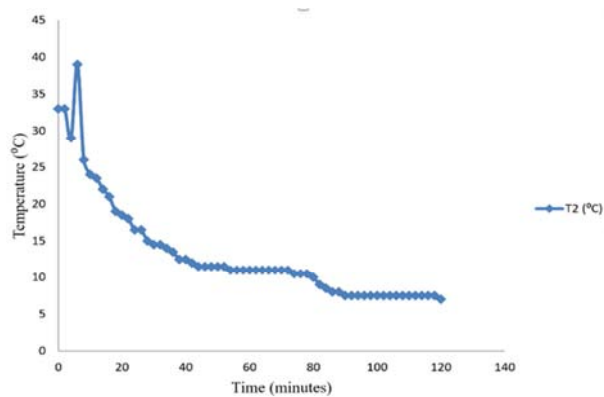


Figure 15. Plot of temperature against time for 0.01wt% PP.

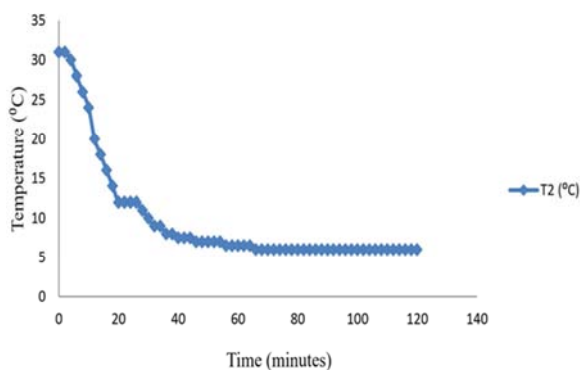


Figure 16. Plot of temperature against time for 0.02wt% PP.

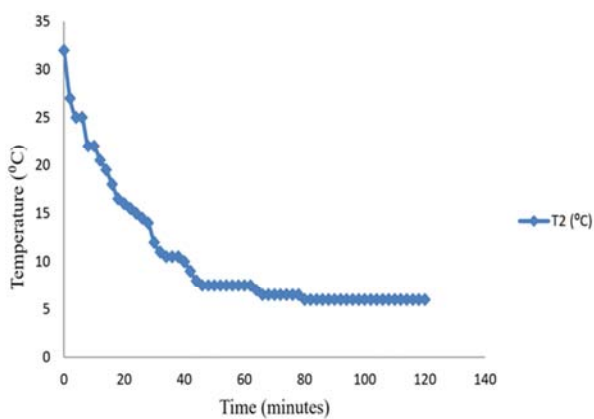


Figure 17. Plot of Temperature against time for 0.03wt% PP.

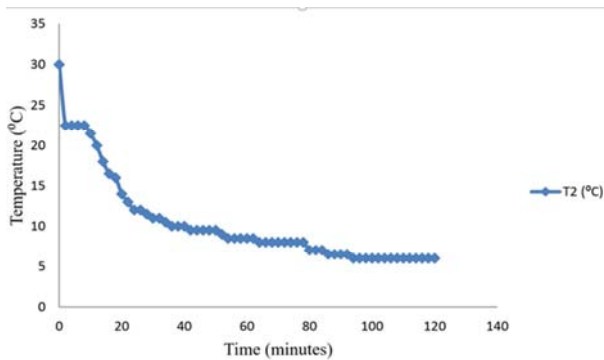


Figure 18. Plot of Temperature against time for 0.04wt% PP.

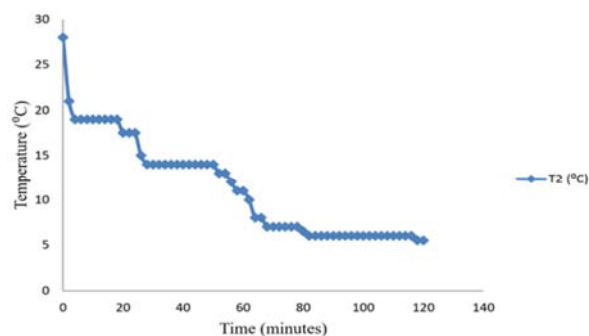


Figure 19. Plot of Temperature against time for 0.05wt% PP.

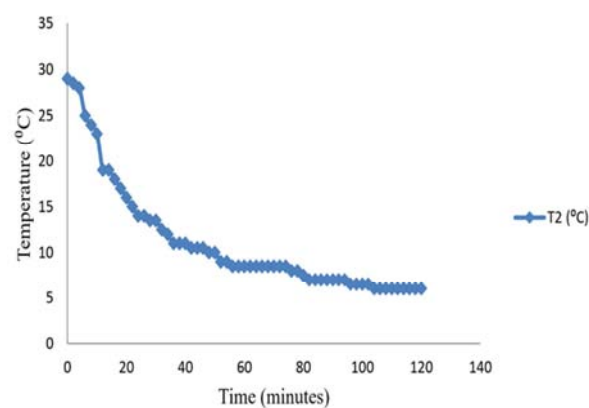


Figure 20. Plot of Temperature against time for 0.06wt% PP.

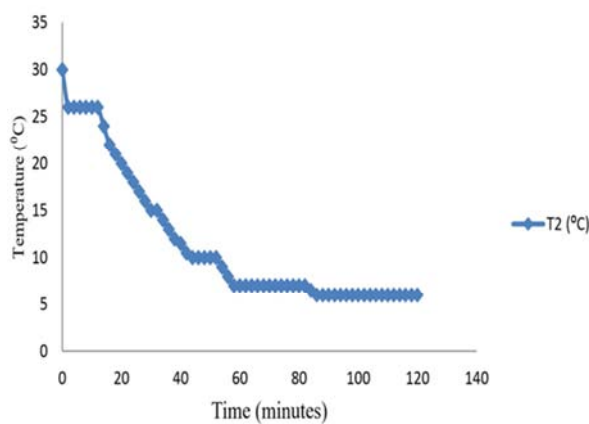


Figure 21. Plot of Temperature against time for 0.07wt% PP.

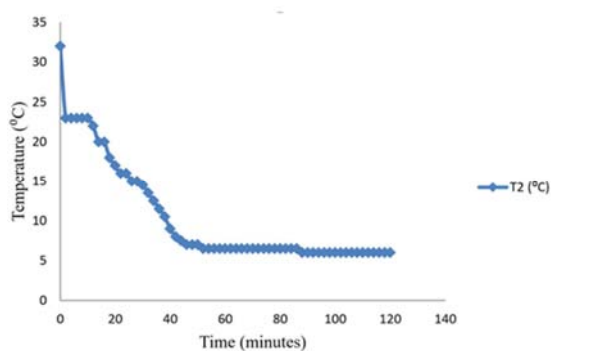


Figure 22. Plot of Temperature against time for 0.08wt% PP.

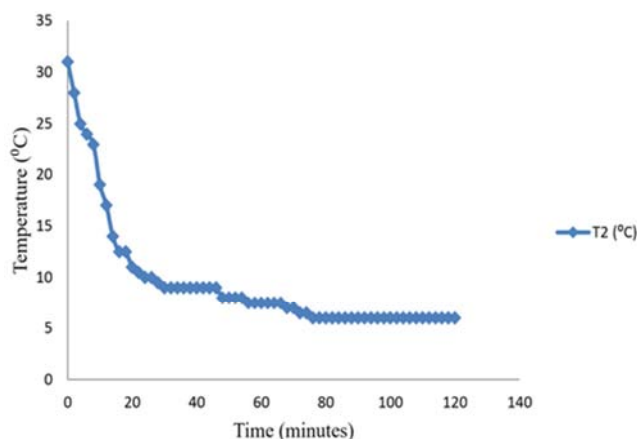


Figure 23. Plot of Temperature against time for 0.09wt% PP.

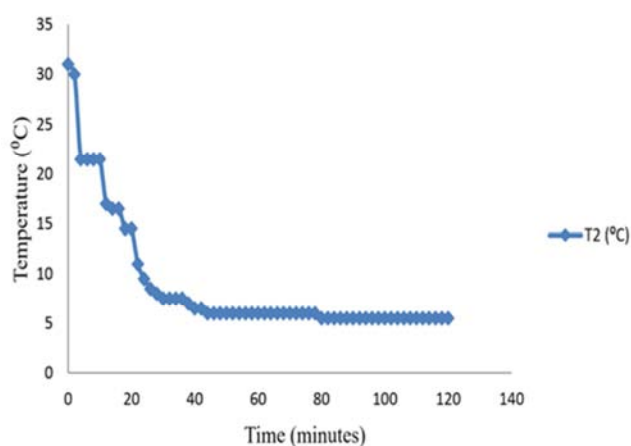


Figure 24. Plot of Temperature against time for 0.1wt% PP.

Hydrate formation is an exothermic reaction, and heat is released during hydrate formation. Notice that in Figure 14, the fluid temperature increased at about 20 minutes, indicating the onset of hydrate formation. This is also observed in the experiment conducted with 0.01wt% PP as Inhibitor (Figure 15). Subsequent experiments conducted with 0.02wt% to 0.1wt% PP inhibitor did observe a distinct rise in Temperature (Figures 15, 16, 17, 18, 19, 20, 21, 22, 23 and 24). This is because the PP effectively reduced the hydrate formation, and the heat of reaction evolved was relatively small and was quickly cooled off by the circulating cooling fluid circulating. Notice that although some hydrates formed when inhibited with the PP, they did not block valve v5. This is because the PP inhibited the growth of the hydrate crystals and prevented the crystal agglomeration.

4. Conclusion

The experimental investigation on the effect of seawater on hydrate formation indicated that hydrate formed with seawater and the seawater salinity was not sufficient to prevent hydrate formation in the loop. It is imperative to check for hydrate formation even when producing from a

saline environment. Although salts can act as ionic hydrate inhibitors, they may not be sufficient to prevent hydrate formation. The addition of PP was efficient in preventing hydrate formation in the loop with an optimum dosage of 0.03wt% PP. The combined effect of the seawater salinity and the kinetic inhibitive property of the PP prevented hydrate formation in the experiments conducted in the loop. The PP is a viable alternative to current commercial KHIs, especially when used in a saline environment.

Ethical Statement

The authors declare that they have no competing interests.

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List of Abbreviations

PP: Plant Polymer

THI: Thermodynamic Hydrate Inhibitor

KHI: Kinetic Hydrate Inhibitor

References

- [1] Sloan, E. D, Koh, C. A., Sum, A. K., Ballard, A. L., Shoup, G. J., McMullen, N., Creek, J. L., Palermo, T., (2009). Hydrate; state of the art inside and outside flowlines. JPT distinguished lecture series.
- [2] Gbaruko, B. C, Igwe, J. C, Gbaruko, P. N., Nwokeoma, R. G, (2005). Gas hydrates and Clathrates: flow assurance, environmental and economic perspectives and the Nigerian Liquefied natural gas project. J. Pet. Sci. Eng. 56, 192-198.
- [3] Gbaruko, B. C., (2004). Asphaltenes Oil Recovery and Down-hole Upgrading in Nigerian Petroleum Industry. 228 ACS National meeting, Philadelphia, USA.
- [4] Barker, J. W., Gomez, R. K, (1989). Formation of Hydrates during Deep water Drilling Operations, SPE/ADC 16130, presented at the 1987 SPE/LADC Drilling Conference in New Orleans, LA.
- [5] Dorstewitz, F. Mewes, D., (1995). Hydrate Formation in Pipelines. !SOPE-1-95-038. Presented at the Fifth International Offshore and Polar Engineering Conference. The Hague. The Netherlands.
- [6] Odutola T. O., Ikiensikimama S. S., Ajenka J. A (2015): Effective Hydrate Management during Gas Expansion Conference paper at Nigeria Annual International Conference and Exhibition (2015) Society of Petroleum Engineers/2015/ SPE 178342.
- [7] Argo, C. B., Blaine, R. A., Osborne, C. G, (1997). Commercial Deployment of Low Dosage Hydrate Inhibitors in a Southern North Sea 69km West – Gas Subsea Pipeline. SPE 37255. Presented at SPE Intl. Symposium on Oilfield Chemistry in Houston, TX.

- [8] Kelland, M. A., Svaftaas, T. M., Dybvik, L. (1995). A New Generation of Gas Hydrate Inhibitors. Paper SPE 30695. Presented at SPE Annual Technical Conference and Exhibition, Dallas, Texas.
- [9] Kruppa K., Aarti P., (2009). Low Dosage, Efficient and Environment Friendly Inhibitors: A New Horizon in Gas Hydrate Mitigation in Production Systems. SPE 120905. Presented at SPE International Symposium on Oilfield Chemistry. The Woodlands. Texas.
- [10] Williams H., Herrmann T., Jordan M., and Catriona M. (2016): "The Impact of Thermodynamic Hydrate Inhibitors (MEG and Methanol) on Scale Dissolver Performance." Paper presented at the SPE International Oilfield Scale Conference and Exhibition, Aberdeen, Scotland, UK, May 2016. doi: <https://doi.org/10.2118/179864-MS>.
- [11] Lederhos, J. P.; Long, J. P.; Sum, A.; Christiansen, R. L. and Sloan, E. D., Jr., (1996): Effective Kinetic Inhibitors for Natural Gas Hydrates, *Chemical Engineering Science*, 51 (8), (1996) 1221.
- [12] Kelland, M. A., (2006). History of the development of low dosage hydrate inhibitors. *Energy and Fuels* 20 (3), 825–847.
- [13] Notz, K.; Bumgartner, S. B.; Schaneman, B. D. and Todd, J. L. (1995): "The Application of Kinetic Inhibitors to Gas Hydrate Problems," 27th Annual Offshore Technology Conference, Houston, Tx, 1-4 May 1995, 719.
- [14] Pakulski, M., Pukop. G and Mitchell, C. (1998): "Field Testing and Commercial Application of High-Efficiency Non Polymeric Gas Hydrate Inhibitor in Offshore Platforms". Presented at the SPE Annual Technical Conference and Exhibition, New Orleans, Louisiana, 27-30 September 1998. SPE-49210-MS; <http://dx.doi.org/10.2118/49210-MS>.
- [15] National Petroleum Investment Management Services. NAPIMS (2021): Crude Oil Reserves/ Production: <http://www.napims.com/crudeoil.html>.
- [16] Odotola, T. O (2020): "Effect of Environmental Pollution on Sustainable Development in Nigeria" *International Journal of Latest Technology in Engineering, Management & Applied Science (IJLTEMAS)* Volume IX, Issue 1, January 2020 | ISSN 2278-2540.
- [17] Robert T. G. (2003): *Encyclopedia of Physical Science and Technology* (Third Edition), Academic Press, 2003, Pages 695-714, ISBN 9780122274107, <https://doi.org/10.1016/B012-227410-5/00723-7>.
- [18] Odotola, T. O., Ikensikimama, S. S., Dulu, A., (2014). Chemical Compromise; a Thermodynamic and Ionic Solution to Hydrate Inhibition. Paper SPE 172410 presented at SPE Nigeria Annual International Conference and Exhibition, Lagos, Nigeria.
- [19] Odotola T. O., Ajenka J. A., Onyekonwu M. O., Ikiensikimama S. S. (2017): Design, Fabrication and Validation of a Laboratory Flow Loop for Hydrate Studies. *American Journal of Chemical Engineering. Special Issue: Oil Field Chemicals and Petrochemicals*. Vol. 5, No. 3-1, 2017, pp. 28-41. doi: 10.11648/j.ajche.s.2017050301.14.
- [20] Odotola T. O., Ajenka J. A., Onyekonwu M. O. and Ikiensikimama S. S. (2016): "Hydrate Inhibition in laboratory flowloop using polyvinylpyrrolidone, N-Vinylcaprolactam and 2-(Dimethylamino) ethylmethacrylate" *Journal of Natural Gas Science and Engineering*, Volume 36, Part A, pp54–61.
- [21] Odotola T. O., Onyekonwu M. O. and Ikiensikimama S. S. (2016): "Effect of N-Vinylcaprolactam on Hydrate Inhibition in Gas Dominated System" Paper SPE 184354 Presented at SPE Nigeria Annual International Conference and Exhibition, Lagos, Nigeria.
- [22] Odotola T. O, Chukwu U. J. and Monday C. U. (2019): Experimental Investigation of Modified Starch from White Corn as a Kinetic Hydrate Inhibitor of Gas Hydrate, *PetCoal* (2019); 61 (6) 1487-1493.
- [23] Carroll J. (2009): *Natural Gas Hydrates, A Guide for Engineers*, Gulf Professional Publishing is an imprint of Elsevier, 30 Corporate Drive, Suite 400, Burlington, MA 01803, USA, pp 22.