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A Review of Hydrate Formation and its Influence on Transmission Lines

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Abstract

Hydrate formation which is a mixture of water and gas forms at high pressure, low temperature, and the presence of water. Problems associated with hydrate formation in pipelines include corrosion, leakages, explosion, pollution, and huge economic consequences. This paper reviewed different methods of predicting hydrate formation. The Katz gravity method, though a manual method, is the most widely used method because of its simplicity in application. Hydrate inhibitors are very necessary for mitigating the formation of hydrate but have corrosive consequences, hence, the need for more study to determine the best inhibitor with no detrimental consequences.

Keywords*: Hydrate; Inhibitor; Transmission line; Corrosion; van der Waal force.*

1. Introduction

Hydrates are solid crystals formed when natural gas and water mix with each other under favourable conditions of low temperature and high pressure. Hydrate can as well mean a trap or storage system of gas molecules which are facilitated by water molecules energized by hydrogen bonds [1-3]. The later definition of hydrate is not the type of hydrate under review, but rather, the former. Generally, hydrate has many undesirable consequences when formed in transmission lines. The challenges include erosion, corrosion, and leaking of transmission lines, partial or total blockage of transmission lines, and bursting or explosion of transmission lines and processing equipment.

Hydrate formation and its corrosive effects have been a threat and bane in the oil and gas industry [4-6]. It is a major flow assurance challenge and has become a perennial challenge that is more peculiar to the oil and gas sector [7-8]. The blockage of pipelines and equipment due to hydrate formation imposes a potential safety hazard. To ensure continuous functionality of the production system and minimize production losses, many approaches are currently being adopted by the industry where probabilistic estimation of hydrate formation is considered a critical step of safety evaluation [9-10]. Several methods of predicting hydrate formation [11-15] were reviewed in this study likewise the relationship between hydrate formation and corrosion of natural gas pipelines under different conditions. Solutions to mitigating the hydrate occurrence and corrosion of natural gas pipelines were discussed in detail [16].

2. Types and structures of hydrates

Hydrate takes different forms for structural formation. In the formation process, water molecules serve as the host while hydrate formers serve as a guest to form a cage. The hydrate structure takes a polyhedral shape of strong hydrogen-bonded water molecules. This formed hydrate structure is held in position by strong Van der Waals forces which ensure the stability of the cages formed by the hydrate formers and water molecules [17-18]. Water molecule is the major content of hydrate crystal with about 85% content [19]. The trapped gas molecules have no bond holding them whereas the water molecules are tightly bonded by a hydrogen bond.

Hydrate structure is classified into three basic different types based on the water molecule arrangement in the formation of hydrate crystal. It includes cubic structure I (sI), cubic structure II (sII), and the last seldom group which is hexagonal structure H (sH).

a. Structure I (sI): comprises small cavity sizes housing of natural gas molecules such as methane, carbon dioxide, nitrogen, oxygen, and hydrogen sulfide. The cage structure of this group has different variations which are determined by the guest molecule sizes. In some cases, some of these guest molecules may be considered too large or quite negligible for their existence in the gas hydrate structure. This type I unit cell is made up of 2- dimensional cages which give a total of 46 water molecules, whereas the type II unit cell is made up of 16D and 8H cages which give a total of 136 water molecules. The shape of the small cage is a pentagonal dodecahedron (5^{12}) while the irregular dodecahedron shape of the large cage is a hexagonal truncated trapezohedron [tetra decahedron, $5^{12}6^{2}$].

b. Structure II (sII): Gas molecular sizes that fall within this structure must be bigger than ethane but not more than pentane. Examples of gas molecules in this structural category include propane, isobutene, isobutane, etc. A single cell of a type II structure has about 16 units of small cages with 8 big cages. Small cages just like type I have an irregular dodecahedron [pentagonal dodecahedron, 5^{12}] shape while the big cage has a hexadecahedron [$5^{12}6^{4}$] shape.

c. Structure H: holds large gas molecules and has a hexagonal shape. The cavities can accommodate large molecules. Examples include: 2-3 dimethylbutane, isopentane, 2-methyl butane, neohexane, methylcyclopentane, 2, 2, 3-trimethylbutene [20-21]. The unit cell contains 2 small cages and 1 big cage. The type H unit cell is made up of 34 water molecules. The shape of the small cage is $4^{3}5^{6}6^{3}$ while the shape of the big one is $5^{12}6^{8}$. Large and small (guest) gases fuse together to form a stable type H structure. Structure H hydrate is peculiarly found around the Gulf of Mexico. The different hydrate structures are defined by the water molecules per structure and the guest molecules [22].

It must be noted that in reality, for a given hydrate structure, there exist more than one particular cavity, hence, a mixture of cavities is present in every accommodated gas mixture. Gas molecules are held closer together to form a crystal lattice at low pressure; this process enables the hydrate of gases to be used as gas concentrators or hydrocarbon reservoirs.

3. Conditions that favour gas hydrate formation

High pressure, presence of water, low temperature, hydrocarbon (e.g. methane), and transient conditions like well shut down and well startup [23].

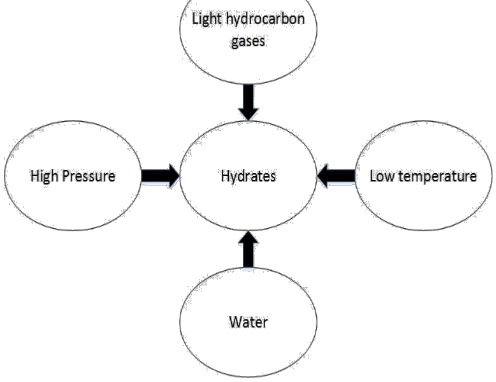

Figure 1. Hydrate forming conditions

3.1. Key indicators of hydrate presence

i. Increased differential pressure in the transmission system within a short period after restart.
ii. Reduction in the rate at which water is produced.
iii. Difficulty or inability to open the valve.

iv. Reduction or complete stop in the hydrocarbon flow rate.
v. Variation in the heat capacity and sound (acoustic) of the transmission line.
vi. Variation in the system pressure.

3.2. Factors to look out for while trying to mitigate hydrate formation

i. The temperature and pressure of the control system.
ii. The favourable and unfavourable implications of diverse gas components toward the potential of hydrate formation.
iii. Monitoring the operation condition of the safety valve actuator.
iv. The implication of formation water contamination on the entire system.
v. Examining and optimizing the control fluid for efficient inhibition properties.

3.3. Nature and process involved in the formation of gas hydrate

Hydrate of gas is a composition of gas and water which crystallizes into an ice-like solid. The formation of gas hydrate in a transmission line constitutes a serious flow assurance problem which may be plugging the transmission lines or even damaging the equipment involved [24-27].

The subsea environment (temperature and pressure) supports hydrate formation; hence, there is a high tendency of having the challenge of hydrate formation in the equipment located in the subsea environment, since the conditions cause plugging of equipment [28]. Formation and accumulation of hydrates of gas inside the transmission systems may occur as a natural phenomenon whereas, it can also be human-induced when the characteristics of the transmission system are altered to make hydrate formation favourable. An example of human-induced hydrate formation is seen at transient flow conditions in the form of flow shut down or start-up. Regarding the subsea environment when the fluid flow is stopped, the system temperature gradually drops and gets stabilized with the existing temperature of the subsea environment which is favourable for hydrate formation. As long as the transmission line or system temperature is lower than the equilibrium temperature of gas hydrate, there is a high chance for the formation of hydrate with the availability of other necessary conditions. In a steady state system which is the opposite of a transient state, there is little or no chance of hydrate formation since the fluid temperature exceeds the hydrate equilibrium temperature.

In the transmission system where the throttling process that involves temperature change and heat transfer are experienced such as valves, the Joule-Thompson effect is inevitable. At this point especially for subsea valves, there are high chances of hydrate formation. This throttling process creates a transient state (isenthalpic process). The gas expansion effect of Joule-Thomson at the valve region brings about immediate cooling of the fluid which supports hydrate formation.

In the process of detecting hydrate formation for partially dispersed systems in multiphase flow conditions and detection of hydrate deposits, hydrate formation in partially dispersed multiphase flow conditions was analyzed with a high-pressure industrial scale flow loop. It was discovered that when the temperature is systematically controlled the amount of hydrate formed in the system can be greatly limited. Grasso [29] mentioned that deposited hydrate crystals on pipe surfaces contribute significantly to the total pressure drop recorded. The experimental results showed that velocities of liquid and gas contribute greatly to the number of formed hydrates in a flow system.

4. Hydrate formation in the drilling and production process

The prevailing quest in the petroleum industry to explore and exploit the deep water for oil and gas resources has drawn attention to offshore drilling which is vulnerable to hydrate formation. With the increasing depth of wells, the possibility of hydrate formation while drilling increases. There has been a recorded case of hydrate formation at a water depth of 1,150ft (350m) off the west coast of the United States of America. The hydrate occurred at a temperature of 45°F (7°C) and made it practically difficult to retrieve the wear bushing. This process implies that there was no way to access the casing hanger pack-off when there was leakage, hence, a blowout occurred since there was no way to pump mud into the casing [30].

The fluid used in drilling otherwise called mud is a mixture of several salts and compounds that has several functions such as: providing hydrostatic pressure, removal of cuttings from wells to the surface, cooling and lubricating the moving parts of the drilling assembly and medium for pulse transmission in measurement. During drilling operations, there may be reasons to stop circulation and when such occur, there is always a drop in the temperature of the drilling mud which exposes the well to a high risk of hydrate formation. The formation of hydrate causes the drilling fluid to lose its rheological properties which affect the flow properties of that fluid. In the worst-case scenario, the solid plug of hydrate formed could completely block the fluid movement.

The drilling fluid can be water-based or oil-based. Using oil-based mud instead of water-based mud could help to control the formation of gas hydrates [20]. Until recently, it is believed that oil-based mud could be used without fear for the formation of gas hydrates. An experimental analysis using a blind cell and a windowed cell, at a pressure range of 3 MPa (450 psi) to 31 MPa (4500 psi) gave a different view. The two apparatuses used had a mixing system since gas hydrate formation is a surface phenomenon. In the analysis, four samples were analyzed. The samples include pure water, 20 wt. % $CaCl_2$ brine, oil-based mud with 20 vol. % water, and oil-based mud with 20 vol. % brine. The cooling and heating temperature range was about 1.7 K/h (3°F/h). The testing time of the system was increased from one day to weeks for proper analysis. The result proved that the addition of dissolved solids into the aqueous phase affected surface activity and gas solubility, and then reduced the gas hydrate formation temperature. The noticeable effects caused by the dissolved salts in the brine and the oil phase were additive, and adequate inhibitor concentration can prevent the formation of hydrates [20, 31].

To verify the possibility of hydrate formation in an ESP well system, an experiment [32] was conducted in a methane-hydrate production well located in Nankai Trough. The well was completed with ESP string including a gas separation system and heater. To monitor and compare the process, a gas-liquid two-phase flow model that comprises temperature and pressure was developed to predict the time and region at which hydrates will begin to form in dedicated gas/water lines and mixing delivery lines. The model considered other physical factors that can affect the process such as the heater power and the frequency at which the ESP operates. The accuracy of the model is verified by comparing the result with the initial hydrate gas production test done on wells in Nanki Trough. Combining the proposed model with the phase equilibrium model, estimation of the gas hydrate formation temperature limit can be done to avoid the risk of hydrate formation in ESP wells. The study revealed that a greater risk of hydrate formation lies above the discharge location of the pump, in the middle, and beneath the seawater section of the drainage water line. So apart from chemical inhibitor injection, increasing the frequency at which the ESP and heater operate can drastically reduce the risk of hydrate formation.

Exploratory drilling in Nanki trough which is off the Japan coast through a coring operation observed the presence of methane hydrate in the recovered core samples. Dissociation of the methane hydrate in marine sediment tends to deform stratified sediments of methane hydrate which can lead to severe caving and can affect production if not properly handled. Methane has a self-preservation effect hence, methods involved in dissociating its hydrate include depressurization, heat injection, and the use of inhibitors. Masui 2005 used an ice-sand and water-sand mixture as a specimen to conduct an experimental study of determining the shear strength of methane-hydrate. After subjecting both specimens to a depth of 800m under the influence of tri-axial pressure to mimic deep sea conditions the observed result showed that at a methane hydrate saturation point of less than 25%, there is no significant shear strength increase in the ice-sand sample whereas the shear strength of the water-sand mixture increased progressively with increasing methane hydrate saturation. This study reveals the deformation behaviour and changes in the shear strength of sediments during methane-hydrate production.

In a gas dominant system, the flow pattern contribution to hydrate formation was investigated in a deep water gas field in a remote location where long-tie-backs were used in complex seabed topographies for gas production. The study [33] focused more on acquiring knowledge and data in multiphase lyre pilot loops in the gas dominant conditions without additives in multiphase flow (stratified and annular flow). The results showed that there is a direct correlation between the flow pattern inside the flow line and hydrate formation/ plugging mechanisms.

Shimizu [34] conducted an experiment on methane hydrate formation processes in methane/ water bubbling flows using a flow loop. Different variables which are transient with different phase flows were monitored such as Pressure drop, particle sizes, flow morphology, and paths of phase flow. The study realized that methane-hydrate shells that cover unconverted bubbles produce methane-hydrate slurry and with much turbulent shear force, the bubbles can flow in a colloidal form with fine particles of crystals. The conclusion is that in reality, for methane-hydrate formation, the pattern of flow depends much on the velocity of fluid flow and the phase path in the flow channel.

The increased demand for gas in the world has made methane hydrate an area of attention. The natural gas reservoir is always exploited by depressurization using electric submersible pumps (ESP). The wellbore temperature and pressure profile tend to form hydrates, the ESP system usually causes an increase in the pressure of the well at the prevailing low temperature on the seabed, and these favourable hydrate formation conditions increase the ESP accessories which include the motor and heater added to the ESP string give rise to increased temperature hence reduces the risk of hydrate formation [35].

A geophysical experiment aimed at detecting the possibility of hydrate formation in a porous medium during water flooding of an undersaturated oil reservoir [36] showed that gas hydrates may form from dissolved gas during cold water injection at the temperature of 2^{o}C to 5^{o}C in undersaturated oil reservoir that is shallow. In the experiment, cold seawater was used to displace live oil through consistent cooling and injection till hydrate crystals are detected.

A study to detect the presence of hydrate was done by Degado [37] where he deployed the knowledge of rheological properties of fluids like yield stress and viscosity to detect the hydrate presence in a system of crude oil. The crude oil system contains some percentage volume of water, the concentration of salt (sodium chloride), and gas content. The result of the rheological experiment showed a change in the external phase of oil to water in the gas hydrate slurry that formed from a CO_2^- rich gas and this phenomenon were a result of natural surfactants activated by CO_2^- in crude oil.

In the Gulf of Mexico where many deep-water oil and gas explorations are ongoing, the temperature at the sea bed is constant at approximately 40°F during transient operations (shut-in, start-up) the risk of hydrate formation at subsea equipment (SSV, Choke valve) is high where the ambient temperatures are typically around 40°F.

4.1. Solutions to hydrate formation in the drilling lines

Neto [38] predicted hydrate formation in offshore pipelines using a mechanist computational fluid dynamic (CFD) tool. The principle of mass, energy, and momentum conservation was used to get the pressure, temperature, velocity, and profile of concentration along pipelines to ensure that both transport phenomena and phase equilibrium are included in the study. The study produced a kinetic model using an equation of transport. The study concluded that with the prevailing offshore conditions of temperature and pressure on pipelines, an equilibrium position cannot be attained. This is because, as a result of the limited residence time of reactants in the system, some methane particles could not dissolve in the liquid phase and hence, convert to hydrate particles. A likely cause of this phenomenon can be linked to the metastable behaviour that is normally seen in some operations in fields.

To effectively manage hydrate formation in subsea production, May [39] did a quantitative prediction of hydrate formation risk implementation study to determine its practicability. The study deployed automated lag-time devices, (high pressure) and a high-pressure acoustic levitator to determine the numerical chances of hydrate formation. Repeated hydrate nucleation and growth rate probability distribution which depends on the time the hydrate crystals start to form (induction time) and temperature of sub-cooling is measured for gases, the proportion of inhibition material and shear rates were all measured. The conclusion drawn from the study is that with improved models, hydrate formation can be accurately predicted.

During production, to remove the solid plugs of formed hydrates that block the choke and kill lines, the following techniques can be applied: radial heat tracing, pipe warm-up, and hot water circulation through a coiled tube [40]. The feasibility study on the application of radial heat tracing in a deep-water offshore environment was analyzed using an energy balance mathematical formulation. The study revealed that the melting process is sensitive to parameters such as heat flux, hydrostatic pressure over the plug, insulation thickness, and quality (thermal conductivity). The operational method of this solution is to either melt the hydrate plug or to keep the choke and kill lines warm enough to prevent the formation of hydrates. The heat flux required to sufficiently heat the choke and kill lines to a predetermined target temperature which must be above the mudline temperature is always calculated using mathematical formulation. Results of analysis have always shown that the bulk of the heat energy consumed in this process is utilized in raising the temperature above the mudline temperature to prevent hydrate formation.

As a method of preventing and possibly removing formed hydrate solid plugs in the choke and kill lines, a computer model was developed which employs hot water circulation from the surface through coiled tubing to the choke and kill lines. Analysis of the sensitivity of the melting process to the water circulation rate, pipe insulation, and the inlet water temperature suggested that the choke and kill lines must be thoroughly insulated to ensure good energy conservation.

5. Correlation models for calculating and predicting hydrate formation and corrosion rates

The most basic issue in predicting the favourable conditions of pressure and temperature for hydrate formation is the design time of hydrate-related processes [41-45]. Computation of the hydrate formation condition can be done manually for quick estimation, but unfortunately, one of the disadvantages of this method is that there could be some level of inaccuracies associated with it [46]. Two methods are commonly used for quick estimation of the conditions at which hydrates are formed. It includes the gas gravity method and the constant equilibrium method [47-48]. Trekell Campbell method and Baillie-Wichert method are still applicable [32, 49]. The gas gravity method also known as the Katz model (1945) introduced the fundamental method of estimating the favourable conditions of pressure and temperature at which hydrates are formed from liquid-vapor compound (three-phase). Here, the constant specific gravity lines in a temperature and pressure diagram show the conditions under which hydrates form [50].

In the gas gravity method, the gas density is calculated by knowing one of the two concentrated factors of pressure or temperature. Then, using another diagram, another concentrated factor is determined for the point of the hydrate [51-57].

The constant equilibrium method otherwise called the K-value method was proposed by Carson, Katz, and Wilcox (1942) [58-66]. Their proposal defined a solid steam distribution coefficient which is graphically analyzed. One of the stated prevailing conditions is that as long as the pressure does not exceed 1000psi, this method (equilibrium constant, K) can be used [67-68]. However, it has been presented that the best practices for preventing blockage of hydrates are still evolving [69].

Moreso, Sayani [70] came up with a simple statistical model to predict hydrate formation conditions (temperature). The work used a simple statistical correlation with thermodynamic equilibrium conditions from existing contemporary literature and standards. To mimic accurate real-time pipeline conditions. The obtained model was compared with the recent literature standards as a means of validation, the result showed a high level of reliability when deployed in predicting the temperature at which gas hydrates are formed.

Adams [71] carried out a modelling study to investigate the hydrate formation hysteresis in porous media using a sand pack that was subject to cooling-heat cycles for a specified range of temperature. In the study, hysteresis was monitored in five cycles with each cycle having a different melting temperature with resultant different intensity of temperature relaxation effect on the observed hysteresis. The thermocouple which measures the temperature difference displays the evidence of hysteresis when the temperature differences of the thermocouple are observed in three separate readings. The melting temperature of the previous cycle and the thermal cooling rate of the sand pack are important determinant factors for the formation of hydrates.

Temperature changes bring about an increase in temperature of the sand pack system up to the peak temperature which indicates hydrate formation usually near the thermocouples. Analysis of the different temperature peaks of each of the cycles shows hysteresis. During hydrate formation in the sand pack, there is usually a decline in the system's pressure which can be explained to be a rapid loss of free gas from the system. The pressure and temperature profile follow the same trend which relates to gas saturation and hydrate formation. A model for predicting the time for hydrate formation was proposed which depends on the melting temperature of the porous sand pack medium.

Nucleation and growth are the two basic steps in the process of hydrate formation and these processes depend on time. To understand the conditions that lead to the formation of hydrates and their corrosive effects on the transmission system and other equipment better, the principles of hydrate formation dynamics and hydrate crystal accumulation are very fundamental. Equation 1 can be used in calculating the formation rate of hydrates;

$$R = 4\pi K \mu_2 \left(f - f_{\mathrm{eq}}\right) \tag{1}$$

In the equation, R represents the formation rate of hydrate; K represents an obtained empirical kinetic parameter; f_{eq} refers to the gas fugacity at the equilibrium condition; μ_2 means the second moment of hydrate crystal particle size distribution; f represents the gas fugacity at any point.

The California Natural Gas Association (CNGA), natural gas mixture equation of state can be used to determine the required fugacity. In doing this, Z, which is the compressibility factor, is calculated using Equation 2.

$$Z = \frac{1}{1 + \frac{344400 * P * 10^{1.785SG}}{T^{3.825}}} \tag{2}$$

where SG connotes the gas-specific gravity to air; P represents the gauge pressure (psig), and T means the temperature measured in Rankine (^{o}R).

The μ_2 which is the second moment of hydrate crystal particle size distribution can easily be determined using Equation 3:

$$4\mathrm{r}^2 \mu_0 = \mu_2 \tag{3}$$

where r = mean particle radius for hydrate crystal and μ_o= moment of hydrate crystal particle size.

Meanwhile, to get the value of μ_o in Equation 3, we first use Equation 4

$$\mu_0 = \frac{3\mathrm{M}\left(N - N_{\mathrm{eq}}\right)}{4\pi V \rho r^3} \tag{4}$$

For Equation 4, *N* represents the gas mole number that is contained in the solution at the existing condition, M means the hydrate molecular mass, P represents the formed hydrate density, *and* N_{eq} just like *N* stands for the mole number of gas which is contained in solution but at equilibrium condition, V means water volume for the corresponding number of gas moles.

With the advancement in technology, the hydrate formation estimation method by hand calculation is gradually being replaced with computer-aided methods. The hand calculation method may be a quick approximation method but it may likely be less accurate when compared to computer software used in hydrate formation prediction. Meanwhile, the rate of hydrate formation is predicted and calculated using different correlations and phase diagrams depending on the corresponding gravity of the gas.

Examples of hydrate formation calculation software are PIPESIM, PVTsim, and HYSYS. The development of these software programs was robust and rooted in different models of thermodynamic and fluid flow systems. Centre for Hydrate Research, Colorado School of Mines in the past years' developed programs that are used in calculating the rate at which hydrate forms. Examples of the such program include CSMHYD and CSMHyK. These programs can handle steady state and transient fluid flow in systems where they calculate the rate at which hydrates are formed in transmission lines [72-73].

A study [74] on how to deploy machine learning in gas hydrate formation and trendline prediction showed that machine learning algorithms such as gradient boost regressor, extreme gradient boost, linear regressor, and Artificial Neural Network (ANN) can be successfully used in solving flow assurance problem with the accuracy of more than 90%. In the prediction and simulation, three (3) different green hydrate inhibitors which were extracted from plants were used in small quantities with the obtained optimal dosage ranging from 0.02 wt% to 0.1 wt%.

Hydrate formation prediction in the deep offshore gas well production process involves some degree of risk. Wenyuan [57] noted that no method of hydrate formation gives a perfect result at the moment and came up with a model that practically predicts the hydrate formation region. The analysis of the model showed that there is a slow and consistent decrease in gas temperature as the gas travels from the bottom of the well to the wellhead and this process is accelerated near the mud line. Again, at a high gas depletion rate, the effect of heat transfer on gas temperature reduction is very negligible while the reverse is the case at a low gas depletion rate, i.e. the effect becomes obvious. There exists a direct relationship between the hydrate equilibrium temperature and well depth as a result of pressure change in the wellbore, which means, and decrease in the hydrate equilibrium temperature occurs with a decrease in the depth of the well. The hydrate formation region is normally seen in the upper half of the wellbore. The study observed that the length of the hydrate formation region is normally reduced by increasing the production of gas from the reservoir which also increases the temperature of the formation and that of the distribution pipe. The relationship between inhibitor and hydrate formation region with hydrate equilibrium temperature is inversely proportional, which means, that as the inhibition content increases, the hydrate equilibrium temperature and formation region decrease and vice versa.

Green [75] introduced a difference factor in the existing thermodynamic models used in predicting hydrate formation during surface production well testing. The difference introduced was in the Langmuir constant of guest molecules which is one of the variables in the process of hydrate formation. The variation effect of choke size on the existing Langmuir constant during hydrate formation was evaluated using field data (temperature, pressure, size of choke) from the hydrate well. The general correlation was used to validate the Langmuir constant at a field with choke size difference incorporated in the model. The observed result is that the choke size varies inversely to the Langmuir constant and therefore causes a reduction in the rate of hydrate formation.

An experiment [76] to determine the effects of inhibitors in the hydrate formation process demonstrated the combination of various mechanisms with agglomeration as the most dominant in certain systems and deposition in others. Phase separation of the dispersed phases was detected at the onset of hydrate formation in all the tested hydrocarbon systems. The cause of this instantaneous and brief phase separation was not fully understood. Hydrate deposits with high porosity and sloughing were observed in the experiments when the subcooling was high and when there was a high-temperature gradient in the cell, while deposits with lower porosity formed when the subcooling and temperature gradient was low. Hydrates were deposited mainly at the upper cell surface, which was not directly exposed to liquid flow in the experiments with mineral oil, whereas hydrates were deposited at all surfaces in the experiments with condensate. Under-inhibited systems can under certain conditions have an increased risk of hydrate agglomeration compared to non-inhibited systems. Anti-agglomerants promote the formation of transportable hydrate slurry, but a transient agglomeration of hydrates could be observed at low concentrations.

Wang [57] modelled a method of managing hydrate formation using an anti-agglomerants injection in a subsea tie-back. The result was a hydrate simulation tool that can predict the formation of hydrate in systems dominated by oil involving multiphase flow in the pipeline. The model gave special attention to the percent volume of water cut which is much prevalent in transient flow operations such as restarting and shut-in operations. To verify and validate the accuracy of the model, the obtained results are compared with field data as a standard.

Several parameters such as the fluid data, reservoir geometry, and production information of an actual offshore well are inputted into the system model to replicate the good condition and from the modelled system, predict the possibility of hydrate formation, rate of hydrate formation, degree of plugging risk at different scenarios such as water cuts, gas-oil ratio, and different liquid hold up. The result of the model evaluation showed that the model perfectly predicted hydrate plug formation when compared to actual field data. So this prediction model is very important for optimizing. Designing and managing hydrate formation in flow systems.

Again, to predict the rate and conditions for the formation of hydrates effectively, alterations of the Vander Waaland Platteeuw model involving its statistical thermodynamics will offer a good solution.

An experimental study was conducted using pure methane to calculate the favourable conditions at which hydrates form. The obtained result showed that a temperature range of 32°F – 60°F and a corresponding pressure range of 290 – 870 psi is ideal. From observations made in the result of the experiment, a sensitivity analysis was conducted and it showed that natural gas composition has significant effects on the pressure and temperature required for hydrate formation. It went further to point out various impurities that also affect the hydrate formation rate. Such impurities include carbon dioxide, hydrogen sulfide, and nitrogen. There is also another method of predicting hydrate formation known as the Chen-Guo method which was based on thermodynamic alteration. An attempt to compare this method with the Van der Waal-Platteeuw method (1959) on a natural gas sample which has a high percentage of carbon dioxide revealed a great variation among both methods. The result showed that when the system temperature is kept constant, the hydrate formation rate and pressure increase randomly.

Another model for predicting the formation of hydrate was developed by Kashchlev and Firozabad [74]. In the process of developing the model, a few assumptions were made which include constant temperature, rapid drop in the system pressure indicating that hydrate is formed, disturbed gas current, the conglomeration of crystals which causes obscurity of the pipe walls as they cling on it, dissolution of components of gas in the water to form hydrate solids. The model is given as Equation 5:

$$J = [\mathrm{A}/(1 + k_n C_a)] e^{\Delta\mathrm{\mu}/\mathrm{kT}} * \exp\left(-\frac{4\mathrm{C}^3 \upsilon_h^2 \sigma_{\mathrm{ef}}^3}{27\mathrm{kT}\Delta\mathrm{\mu}^2}\right) \qquad (5)$$

The model became necessary when evaluating the contribution of inhibitors to hydrate formation. It is used in transmission systems for diagrammatic representation and evaluation of the formation of gas hydrate synthetic inhibitors is present. Graph of velocity versus time was developed and used for hydrate formation calculation of synthetic inhibitors especially in determining the hydrate formation rate of the North-South roomier line. The rate at which hydrates grow is determined by the kind and properties of inhibitor(s) involved. The growth rate of hydrates increases with the density of the synthetic inhibitor affects the rate of hydrate formation.

Esbergon (1963) developed a mathematical model that predicts hydrate formation. A peculiar parameter modification in his model is the velocity. In calculating the hydrate growth rate at a steady and stable pressure, the velocity of used methane is involved. The different nomenclatures involved are: ρ_w which is the density of the solvent (water); V_1 is the volume of the dissolvent; MW_W is the molecular weight of the solvent (water); X_{H-L}^i means partial molar mass of hydrate formed between hydrate and liquid (shared surface); X_{G-L}^i means the partial molar mass of hydrate formed between gas and liquid (shared surface); K^* which is contained in the model is determined with the formula (Equation 6):

$$\left(\frac{1}{k}\right) = \left(\frac{1}{k_1 A_1}\right) + \left(\frac{1}{k_r A_p}\right) \qquad (6)$$

For Cheng and Guo's model (1996) of hydrate prediction, a mixture containing 5 binary gas mixtures of ethylene/ methane, pure ethylene, and 4 binary gas mixtures of propylene/ methane whose pressure and temperature ranges are given as 0.52 - 6.6MPa and 273 to 287K respectively were used. The mixture has propylene and ethylene as part of its content in the ranges of 0.65 – 72 mol% and 7.1 – 100 mol% respectively. The test result revealed that at the increasing rate of methane concentration in the mixture with higher pressure, more hydrates are formed. It also deduced that at constant temperature conditions with pressure and specific gravity at inverse proportion (i.e. higher pressure and lower specific gravity), more hydrates are formed [77-78].

A considerate investigative study of various parameters and scenarios involved in the hydrate formation simulation revealed that as the subcooling of hydrate nucleation increases, the hydrate fraction reduces to as low as zero. Weighting parameters for hydrate oil slip (COIL) were quoted to have the greatest effects on hydrate fraction. The study [79] considered different parameters with their effects on hydrate formation under cold start-up and regular with their effects on hydrate formation under cold start-up and regular mode of operations in the pipeline and offshore pipe network. Such parameters considered in the study include the weighting parameter for hydrate-oil slip (COIL), temperature/ subcooling of hydrate nucleation, and adhesive force of hydrate. The study was done by simulation using OLGA-CSMHyK-MVTIFLASH tool under cold start-up and regular mode of operations while considering the three (3) hydrate formation indicators which are a fraction of hydrate formed, the relative viscosity of slurry and propensity of hydrate which is measured in the form of temperature difference (DTHYD). This study was done with oil whose GOR is 184m^3/m^3 and 35% water cut in a 6km pipeline with a tieback subsea network which is made up of the main flowline and two branches. Heat transfer values of 22.7w(m^{2}k) were used while comparing all the parameters to 0.2 fraction of hydrate threshold as a standard from existing literature. Hydrate force of adhesion used ranged from 0.005N/m to 0.5N/m with a subcooling temperature range of 3.61^{o}C to 10^{o}C, the weighting parameter for hydrate oil slip value ranged from 0.2 to 1.0 while investigating the effects of methanol injection. When the hydrate nucleation temperature was increased from 3.61^{o}C to 10^{o}C, the fraction of hydrate dropped from 1.7% down to zero. It is with noting that the viscosity of the oil is affected by the adhesive force when placed side by side with other indicators. The injection of methanol which is a good inhibitor is to prevent hydrate formation. The study concluded that hydrate formation investigation should be wholesomely done considering the three hydrate formation indicators than considering only one indicator which gives an unreliable and less accurate result.

6. Contribution of inhibitors to hydrate formation

For processed water that flows through a transmission line, the ions (electrolytes) function as inhibitors. Research to ascertain the inhibition effect of different mixtures on the locus of the 3-phase equilibrium curve was conducted using about 8 different quaternary mixture systems of water/ sodium chloride/ methane/ methanol [40, 52]. An average of 16 data values which have an average concentration value range of 2 to 4 mol% NaCl were inter-mixed with methanol whose weight percentage ranged from 10-40 and the experiment was carefully observed. To substantiate the result accuracy, the Cailletet apparatus and Roman spectroscopy were both used for measurement. With the Cailletet apparatus, the pressure value for hydrate formation ranges between 2 and 14 MPa while that of Roman spectroscopy ranges from 2 to 70MPa. At an average pressure value of 10MPa, the temperature value ranges between 0.3 and 1 Kelvin. To draw a valid conclusion of the study, a comparison of the study was made with existing data of the ternary system of $CH_4/H_2O/NaCl$ and $CH_4/H_2O/CH_3OH$. The conclusion has it that NaCl + CH_3OH mixture has a higher inhibition effect compared to the total inhibitive effect of all the inhibitors put together. Therefore, the combined effects of methanol and electrolytes must be put into consideration when developing hydrate prediction models to capture the inhibitive effects of mixtures [80].

An experiment to determine and rank the inhibition effects of ethylene glycol and methanol was carried out. In the process, a pressure test of CO_2 in water for hydrate formation was done. The result analysis showed that methanol has higher inhibitive effects compared to ethylene glycol. A revalidation test of this experiment was done for a CO_2-rich quaternary mixture of gas which contains 88.53 mol% of carbon dioxide, 6.83 mol% of methane, 4.26 mol% of nitrogen, and 0.38 mol% of ethane amidst 10 wt. % ethylene glycol and 10wt%

NaCl. The above result also validates the less inhibitive effect of ethylene glycol when compared to methanol.

To evaluate the accuracy of different hydrate formation prediction software and at the same time verify the effects of different mono-ethyl-glycol (MEG) products on hydrate formation and inhibition, a comparative study [81] was done where three different software were used in the software prediction likewise; three different MEG products were used to ascertain the impact of MEG on hydrate formation. In the software comparison experiment, distilled water and methane gas were benched and marked as standard to compare the obtained results at a pressure range of 50 – 300 bars. An aqueous solution of 10wt% of MEG was tested at a pressure range of 50 – 200 bar deploying the isobaric method using a stirred cryogenic sapphire cell. The starting point of hydrate formation (induction time), dissociation initiation point of the hydrate, and dissociation endpoint of the hydrate were carefully noted and analyzed. The obtained hydrate formation results were compared with the three prediction software tools which use the Peng-Robinson equation of state for simulation. To determine the MEG product with the best hydrate inhibition performance, the hydrate inhibition performance of each of the three MEG products was analyzed.

The final result showed that only one of the software too gave an accurate prediction with the experimental result as it concerns the dissociation start points which have an average deviation value to be 0.54°C. The other two software prediction tools predicted results that have an average value of the hydrate formation start and dissociation start curve points with deviation values of 0.06°C and 0.03°C respectively. Amongst the three MEG product samples tested, one has the most inhibition effect after shifting the hydrate curve to the left by a temperature value of 2.07°C compared to 100% distilled water which was used as the benchmark curve. The other two MEG products shifted the curve by temperature values of 1.81°C and 1.71°C respectively. Therefore, it can be concluded that not all hydrate prediction software can accurately predict the rate of hydrate formation, and also, not all MEG products are efficient hydrate inhibitors.

Straume [82] examined hydrate formation in condensate and mineral oil systems with a good understanding and safe implementation of hydrate strategic management in multiphase systems of gas, oil, and water. The study incorporated a mixture of (mineral oil, gas, and water) and (condensate, gas, and water) using a visual rocking cell to measure the stage and rate of hydrate formation. The tests were done with and without inhibitors (MEG) and model anti-agglomerants. The test observation showed that there is a smaller risk of hydrate deposition on oil-wetted surfaces than on condensate/ gas phase exposed surfaces through hydrate deposits found in the oil system. The three (3) basic experimental processes include the Growth of hydrate particles, bedding and agglomeration. Under high subcooling conditions, it was observed that hydrate deposits with high porosity formed and this resulted in the sloughing of the formed hydrate deposits as a result of wetting and weighting of the deposits, the introduction of anti-agglomerants gave rise to the transportable slurry in the mineral oil system with 30% water cut. The condensate and mineral oil is non- emulsifier but the backflow induced in the rocking motion of the cell brought about shear stabilized emulsion of the liquid phases before the formation of hydrate.

With the increased interest in LPG as a source of heating fuel, it has become very important to give due diligence to its transportation. The presence of moisture in LPG during production, transportation, and storage makes it susceptible to hydrate formation. In light of this, Olabisi [83] evaluated the mechanism of hydrate formation and methods of hydrate inhibition in LPG using methanol and ethanol. The effectiveness of the inhibitors was measured based on the temperature degree of depression effect by equal amounts of the inhibitors. A comparison of their effectiveness was done using 20% of both ethanol and methanol. The obtained result showed that the inhibition effect of methanol was greater than ethanol in hydrate formation inhibition of LPG. The dehydration effect of LPG hydrate formation was done using different water content percentages ranging from 2.5wt% to 7.0wt%.

In a quest to determine the natural gas hydrate equilibria in brine with the attendant effects of inhibitors on hydrate formation, an isothermal approach method of the experiment was done using a PVT cell. The experiment [84] was done at temperature and pressure conditions that were constant to determine the point of hydrate formation in the presence and absence of hydrate inhibitors. The inhibition properties of Kinetic Hydrate Inhibitors (KHI) and Low Dosage Hydrate Inhibitors (LDHI) were evaluated to obtain the dissociation points which are noted by sudden drop or peak in the respective pressure profile and by visual observation. The offshore environment was mimicked by experimenting with temperatures between -0.5°C to 3°C. The result comparison of two samples of KHI showed that the one with 1wt% under 12°C subcooling and temperature of 2.66°C has an induction time of 184 minutes and outperformed the other samples whose composition is 1wt% under 10°C subcooling and temperature of 0.75°C has an induction time of 311minutes. The sample performed well with lower induction time and was subject to 0.5wt%, subcooling of 10°C, and temperature of 1.21°C, there was no hydrate formed. LDHI was also subjected to subcooling of 10.36°C and 7.5°C and temperature of -0.43°C and -0.12°C respectively, with induction time of 47 minutes after 22 hours, no hydrate formed.

A study [84] on the prevention of hydrate formation in wells containing saline aquifer during CO_2 injection was carried out to ascertain the ideal operating conditions of the gas in the formation. Existing CO_2 hydrate studies were used in the concept selection stage by applying sensitivity studies that represent conditions of operations with hydrate curves from laboratory experiment data and other thermodynamic-based simulators. From the thermodynamic calculation done, the minimum water content requirement and hydrate tendency were determined. It recommended the injection of thermodynamic inhibitors (MEG and methanol) and specifically pointed out that MEG which is less susceptible to the risk of salting-out effects than methanol is preferable during water flushing operations.

To understand the formation and interaction effects of gas hydrates in water continuous and partially dispersed systems, Vijayamohan [3] carried out an experimental study. The study explained the dynamic manner in which gas hydrates interact and interfere with a different fluid flow such as water continuous, oil continuous, and partially dispersed flow (which contain oil, water, and gas). The result showed that with improved inhibitor injection strategies, controlled amounts of hydrates formed which have effects on the pressure drop of the pump.

Majid [85] did a study on gas hydrate formation and how to transport hydrate particles using an industrial-scale high-pressure flow loop without plugging the flow channels, especially in the multiphase flow system. The experimental study was done considering fully dispersed and partially dispersed systems since hydrate formation and plugging mechanisms for both systems are different. The experimental setup mimicked an actual flow system found in the oil and gas pipeline field. Two important hydrate formation properties which are water-cut and pump speed i.e. the velocity of fluid mixing were systematically evaluated using different data points. Water cut data points of 30, 50, and 90 percent volume were picked with pump speed data points of 0.91, 1.89, and 2.99 meters per second. The obtained result after a careful analysis showed that the pump speed is inversely related to the pressure drop in the system with every water cut which means that, for every water-cut percentage used, as the pump speed increases, the pressure drop continually decreases. It was observed that there was flow loop plugging using a water cut of 50 percent volume and pump speed below 0.91m/s. There was an observed phenomenon of emulsion breaking for every test done with 90 percent volume water cut where oil and aqueous water break upon hydrate formation.

7. Hydrates and corrosion

Corrosion which occurs dominantly on metals is the reduction of the metallic properties which is caused by the variable and continuous processes that release ions from the pipe into the environment [74].

Some of the major factors that contribute to corrosion of pipes include environmental factors (temperature, humidity, and oxygen saturation), properties of pipe, soil properties if the pipe is buried, and presence and properties of fluids. Other physical factors that contribute to the corrosion rate are as follows: presence and concentration rate of formation water, mass flow rate, presence of acidic gases which comprises carbon dioxide and hydrogen sulfide, with pH.

7.1. Corrosion in pipelines

Water is one of the required factors for corrosion to occur. A pipeline that transmits well fluids without water has fewer chances of corrosion because hydrocarbon is non-corrosive. Oxygen, carbon dioxide, hydrogen sulfide, and hydrogen (the product of the cathodic reaction) influence the rate of corrosion of metallic pipelines used in gas transmission. Carbon dioxide goes into reaction with any available water to form carbonic acid with low pH and therefore accelerates the corrosion rate.

The pipeline is always insulated with a coating against corrosion. This insulation protects the pipe from several forms of degradation like micro-deformation, macro-deformation, accumulation of structural damages, strain, and nucleation of micro-cracks.

7.2. Hydrate corrosion processes on pipeline

The movement of hydrates along the pipelines erodes the surfaces of the pipelines. This superficial erosion wears off the passive layer of the metallic pipes. The worn-out passive layer is a thin film that functions to stabilize and retard the reaction effects of corrosion. Multiphase flow such as turbulent flow which possesses high shear stress value has high erosive effects on the walls of the pipelines. It is deduced that the higher the turbulence of the fluid flow, the higher the erosive-corrosion effects. Again, the pressure of sediments/ solids catalyzes the erosive-corrosive actions on metallic pipelines by their traction effects on the walls of the pipelines. Hydrate which is a solid crystal erodes the pipeline surfaces. It also accumulates and restricts flow. This process creates differential pressure and aid corrosion of the internal pipeline surfaces.

7.3. Corrosion mechanism in pipelines

A mixture of different components flows through the pipeline. Examples of such components include: the formation of water, hydrogen sulphide, carbon dioxide, sediments, etc. these components have a different reactions with the pipe walls and these reactions are usually corrosive. For instance, sour corrosion is the dissolution of hydrogen sulphide gas components to form a sour acid component whose corrosive effect erodes the internal walls of the pipeline. Again, sweet corrosion which involves the dissolution of the carbonic acid compound in water to form weak carbonic acid has corrosive effects on pipelines. The formed acidic oxide also reacts with iron metal hence the reduction reaction of the formed component corrodes the metallic pipelines. The cathodic reduction reaction is illustrated below using the equation:

$$\mathrm{Fe} + H_2\mathrm{CO}_3 \rightarrow \mathrm{FeCO}_3 + H_2(g) \qquad (7)$$

In the above reaction, the iron metal is reduced to iron carbonate with the evolution of hydrogen. Carbon dioxide catalyzes the rate of hydrogen evolution and this process invariably increases the rate of corrosion of the metallic steel pipe through which the fluids flow. Equation 8 shows that the carbonic acid provides additional hydrogen ions or is reduced as shown;

$$2\mathrm{H}^+ + 2\mathrm{e}^- \rightarrow H_2(g) \qquad (8)$$

$$+2\mathrm{e}^- \rightarrow H_2(g) + 2\mathrm{HCO}_3 \qquad (9)$$

7.4. Corrosion rate

An experiment to determine the corrosion rate among different metallic steel pipes was done. Metallic steel pipe (St 20) whose material is made of low carbon ferrite pearlite was used for transmission lines. The material composition is shown in Table 1.

Table 1. Composition of the metallic steel pipe (St 20) [86]

S/N	Chemical composition of the St 20 steel metal	Percentage	S/N	Chemical composition of the St 20 steel metal	Percentage
1	Manganese	0.35 – 0.65	6	Chromium	<0.25
2	Silicon	0.17 – 0.38	7	Copper	<0.25
3	Carbon	0.17 – 0.25	8	Nickel	<0.25
4	Phosphorous	<0.04	9	Arsenic	<0.08
5	Sulphur	<0.04			

Different factors were monitored in the experiment such as the mechanical stresses undergone by the pipes, the corrosive effects of the environment on the metallic pipes, and the amount of hydrate that formed. The degradation rate of the metallic material and hydrate formation rate were evaluated. A careful examination revealed that the concentration rate of chloride affects the corrosion rate. Again, it was observed that the mechanical stress effect has much more destructive effects on localized corroded metals than on uniformly corroded metals. The weakened inter-atomic interaction in the metallic structure which is caused by the gap created between the grains leads to metal dissolution in the tensile region. A careful analysis showed a 25% reduction in the durability of the steel pipe which is exposed to hydrate and also a 15% reduction in ME5 solution [87-88]. The impacts of temperature, pressure and pH on corrosion rate have been highlighted [10].

7.5. Pipeline repair

The conventional method of the corroded, eroded, or damaged pipeline has always been either discarding the corroded section and putting in place a new pipe or reinforcement of the damaged parts with a surface steel sleeve. The contemporary method involves the use of a composition known as a fiber-reinforced polymer. This overwrap method of pipe repair is not only easy and fast but highly efficient and effective [89]. It is more efficient compared to the former method because, during repair, the fluid flow need not be stopped hence; repair is done while the fluid keeps flowing. Again, it eliminates the disastrous risk of explosion during remedial welding. A comparative study of both methods revealed that the latter method saves 24% cost of welded steel sleeve repair using the former method and 73% cost of replacement. Studies have it that an acceptable corrosion rate for metallic steel is pegged at less than 0.1mm/year [90].

8. Control and prevention of hydrate formation

Different approaches can be applied in mitigating hydrate formation such as thermal (heating), injection of chemicals, depressurization, and removal of water [81]. All these methods are deployed simultaneously depending on the complexity of the systems involved. Injection of chemicals is achieved using inhibitors such as methanol, monoethylene glycol (MEG), and any low dosage hydrate inhibitor (LDHI). Both methanol and MEG are synthesized from non-renewable materials, and have detrimental effects in the environment [91]. Monoethylene glycol (MEG) is the preferred hydrate inhibitor in industries because it has high efficiency and is reusable through MEG regeneration [14]. MEG is injected into the flowline after the wellhead thereby blending evenly with the fluid flowing in the line. The process through which MEG inhibits the formation of hydrate is by reducing the thermodynamic hydrate phase equilibrium to reduced temperature [92]. The processing pathway involves the removal of water contained in well fluid and chemical injection which inhibits hydrate formation. MEG is preferred over methanol because it has low solubility in liquid hydrocarbon hence the recovery/regeneration is very economical with negligible losses.

9. Conclusion

Hydrate formation in transmission lines possess great danger with huge corrosive economic impact if not mitigated. Katz gravity method is the most preferred manual method of determining the rate of hydrate formation. The formation of hydrate is preventable when adequately monitored using the appropriate models and correlations. Also, wells with a high concentration of formation water have greater chances of hydrate formation and likewise internal corrosion; hence, an adequate mitigation plan against a such occurrence such as a good hydrate inhibition plan should be put in place. More studies should be done to determine the best hydrate inhibitor and their operational requirements which will prevent hydrate formation and will not contribute to the corrosion problems in pipelines. This has become very necessary because studies have shown that many hydrate inhibitors solve the problem of hydrate formation but still go ahead and introduce another problem of internal corrosion. The development of a mathematical model that can predict the rate at which hydrate is formed with a high level of accuracy in real-time to prevent corrosion and plugging of the pipeline is very important.

References

[1] Lawal KA, Crawshaw JP, Boek ES, Vesovic V. Experimental investigation of asphaltenes deposition in capillary flow. Energy Fuels, 2012; 26 (4): 2145-2153. https://doi.org/10.1021/ef201874m.
[2] Mohammad T, Rooney D, Othman E, Aparicio S, Atilhan M, Khraisheh M. Gas hydrate inhibition: a review of the role of ionic liquids. Ind. Eng. Chem. Res., 2014; 53 (46): 17855-17868. https://doi.org/10.1021/ie503559k.
[3] Sloan ED. Clathrates hydrates of natural gases, 2nd Edition, Revised and Expanded, CRC Press, 1998.
[4] Fang-Yu L, Marta R, Sara S, Nick Z. The role of natural gas as a primary fuel in the near future, including comparisons of acquisition, transmission, and waste handling costs of as with competitive alternatives. Chemistry Central Journal, 2012; 6 (Suppl. 1): S4.
[5] Rajnauth J, Barrufet M, Falcone G. Hydrate formation: considering the effects of pressure, temperature, composition, and water. Energy Science and Technology, 2012; 4(1): 60-67. http://dx.doi.org/10.2118/131663-MS.
[6] Eric Broni B, Richard A, Cornelius BB. Gas hydrate formation phase boundary behaviour of a synthetic natural gas system of the Keta Basin of Ghana. The Open Petroleum Engineering Journal, 2017; 10(65): 64-72. http://dx.doi.org/10.2174/1874834101701010064.
[7] Muhammad AT. Fluid flow assurance issues: a literature review. SF J Petroleum, 2018; 2:1.
[8] Constantin C, Boyko N. Natural gas production from gas hydrates – an economic perspective. Cf. Oil &Gas Journal, 2003.
[9] Guo XZ, Li J, Song L, Rui L. Monitoring and alarming system for hydrate in gas wells. Advances in Petroleum Exploration and Development, 2017; 13 (1): 25-28. http://dx.doi.org/10.3968/9477.
[10] Emmanuel OO. Corrosion and hydrate formation in natural gas pipelines. Ph.D. Thesis, Curtin University, 2012.
[11] Dinesh BH. A probabilistic approach to assess hydrate formation and design preventive measures, MSc Thesis, Memorial University of Newfoundland, 2016.
[12] Sharareh A. Prediction of gas-hydrate formation conditions in production and surface facilities. MSc Thesis, Texas A&M University, 2005.
[13] Bjorn K, Jinzhou Z, Na W, Saeidi N. Hydrate-a mysterious phase or just misunderstood? Energies, 2020; 13: 880. https://doi.org/10.3390/en13040880.
[14] Straume EO, Kakitani C, Morales RE, Sum AK. Study of gas hydrate formation and deposition mechanisms in hydrocarbon systems. 16th Brazilian Conference of Thermal Sciences and Engineering, 2016 http://dx.doi.org/10.26678/ABCM.ENCIT2016.CIT2016-0255.
[15] Amir S. Offer a new model to prevent the formation of hydrate in a gas pipeline in a gas refinery. International Journal of Innovation and Applied Studies, 2012; 1(2): 226-231. http://www.issr-journals.org/ijias.
[16] Nura M, Donglin Z, Tariq A, Ismaila IP. Pipeline gas hydrate formation and treatment: a review. 3rd National Engineering Conference on Bridging the Gap between Academia and Industry, ACICon, 2018.
[17] Constantin C, Boyko N. Natural gas production from gas hydrates – an economic perspective. Cf. Oil and Gas Journal, 2003.
[18] 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.
[19] Gudmundsson JS, Parlaktuna M, Khokhar AA. Storage of natural gas as frozen hydrate. SPE Prod. & Fac., 1994; 9(01): 69–73. http://doi.org/10.2118/24924-PA.
[20] Carroll J. Natural gas hydrates, 2nd Edition. Elsevier Journal, 2005; 288.
[21] Makogon YF. Hydrates of hydrocarbons. PennWell, Tulsa, Oklahoma, 1997.
[22] Drumond B, De Castro J, Fialho B, Vitorazi L, Ferraz I. Pectin as natural gas hydrate inhibitor: application of the Avrami model. Brazilian Journal of Petroleum and Gas, 2019; 13(2). http://dx.doi.org/10.5419/bjpg2019-0008.

[23] Sun R, Li C, Yu S, Wang S, Sun O, Liu E. Hydrate formation conditions of natural gas with high content of carbon dioxide and the calculation model. Society of Petroleum Engineers, 2010. http://doi.org/10.2118/131812-MS.

[24] Vijayamohan P, Majid AA, Chaudhari P, Sloan ED, Sum AK, Dellecase E, Volk M, Koh CA. Gas hydrate formation and interactions for water continuous and partially dispersed systems. Paper presented at the Offshore Technology Conference, Houston, Texas, USA, 2016. https://doi.org/10.4043/27277-MS.

[25] Dinesh BHA. Probabilistic approach to assess hydrate formation and design preventive measures. M.Sc Thesis, Memorial University of Newfoundland, 2016.

[26] Abdel-Aal HK. Natural gas processing. National Research Center (NRC), Cairo, Egypt, 2012.

[27] Ma QL, Chen GJ, Zhang LW. Experimental and modelling study on gas hydrate formation kinetics of (methane + ethylene + tetrahydrofuran + H_2O). *J.*Chem. Eng. Data, 2009; 54 (9): 2474-2478. https://doi.org/10.1021/je900017k.

[28] Barker JW and Gomez RK. Formation of hydrates during deep-water drilling operations. *J. Pet. Technol.* 1989; 41 (03): 297–301. https://doi.org/10.2118/16130-PA.

[29] Ahmad Majid AA, Grasso GC, Jefferson LC, Qin H, Tomas C, Estanga D, Mayela R, Bhosa B, Waturuocha A, Volk M, Koh CA. A review of hydrate formation for partially dispersed systems in multiphase flow conditions and the detection of hydrate deposits. Paper presented at the Offshore Technology Conference, Houston, Texas, USA, 2017. https://doi.org/10.4043/27877-MS.

[30] Aregba AG. Gas hydrate-properties, formation, and benefits. Open Journal of Yangtze Gas and Oil, 2017; 2: 27-44. https://doi.org/10.4236/ojogas.2017.21003.

[31] Uwaezuoke N. Performance of equation-of-state for hydrocarbon dew point control in gas flow-line in a Nigerian field. Journal of Petroleum Engineering & Technology, 2019; 9(1): 7-13.

[32] Masui AH, Hironori YO, and Kazuo A. Effects of methane hydrate formation on shear strength of synthetic methane hydrate sediments. Paper presented at the Fifteenth International Offshore and Polar Engineering Conference, Seoul, Korea, 2005.

[33] Cassar C, Sinquin A, Teixeira A, Glenat P, Leininger JP. Hydrate formation in gas dominant systems: influence of the flow pattern. Paper presented at the Offshore Mediterranean Conference and Exhibition, Ravenna, Italy, 2015.

[34] Shimizu T, Yamamoto Y, Tenma N. Methane-hydrate-formation processes in methane/water bubbly flows. SPE J., 2017; 22 (03): 746–755. https://doi.org/10.2118/176156-PA.

[35] Ping XH, Guoqing XC, Bai ZZ, Weitao LP, Ma B. Prediction of pressure and temperature profiles and hydrate formation region in ESP-lifted natural gas hydrate wells. Paper presented at the SPE Western Regional Meeting, Bakersfield, California, USA, 2022. https://doi.org/10.2118/209288-MS.

[36] Geranutti BP, Mathias KS, Prasad M, Zerpa LE. Geophysical measurements for detection of hydrate formation in core flooding experiments with undersaturated oil and seawater injection. Paper presented at the SEG International Exposition and Annual Meeting, Virtual, 2020. https://doi.org/10.1190/segam2020-3426878.1.

[37] Delgado-Linares JG, Pohl MM, Ahmad AA, Yoda TC, Norio Z, Luis E, Manika P, Carolyn AK. Early detection and assessment of asphaltene precipitation and gas hydrate formation at field conditions. Paper presented at the Offshore Technology Conference, Houston, Texas, USA, 2022. https://doi.org/10.4043/31712-MS.

[38] Neto ET. A mechanistic computational fluid dynamic CFD model to predict hydrate formation in offshore pipelines. Paper presented at the SPE Annual Technical Conference and Exhibition, Dubai, UAE, 2016. https://doi.org/10.2118/184491-STU.

[39] May EF, Peter JL, Vincent WS, Jeong KN, Bruce W, Kuteyi TO, Stanwix LP, Johns ML, Zachary MA. Managing hydrate formation in subsea production. Paper presented at the Offshore Technology Conference, Houston, Texas, USA, 2020. https://doi.org/10.4043/30710-MS.

[40] Kotkoskie TS, Al-Ubaidi B, Wildeman TR, Sloan ED. Inhibition of gas hydrates in water-based drilling muds. SPE Drilling Engineering, SPE Drill Eng., 1992; 7(02): 130-136. https://doi.org/10.2118/20437-PA.

[41] Obanijesu EO, Akindeju MK, Vishnu P, Tade MO. Modelling the natural gas pipeline internal corrosion rate resulting from hydrate formation. Computer Aided Chemical Engineering, 2011; 29: 1160-1164.https://doi.org/10.1016/B978-0-444-54298-4.50011-8.

[42] Kobayashi T, Mori YM. Thermodynamic simulations of hydrate formation from gas mixtures in batch operations. Energy Conversion and Management, 2007; 48 (1): 242-250. http://dx.doi.org/10.1016/j.enconman.2006.04.008.

[43] Creek JL, Xu ZG. Predicting hydrate plug formation in oil-dominated flowlines. Journal of Petroleum Science and Engineering, 2010; 72 (3-4): 302-309. http://dx.doi.org/10.1016/j.petrol.2010.03.031.
[44] Englezos P. Clathrate hydrates. Industrial Engineering Chemistry Res. 32, 1993.
[45] Bozorgian A, Arab AZ, Mohammadi A, Honarvar B, Azimi A. Optimization of determination of CO_2 gas hydrates surface tension in the presence of non-ionic surfactants and TBAC. Eurasia. Chem. Commun.2, 2020; 420-426.https://doi.org/10.33945/SAMI/ECC.2020.3.12.
[46] Ahmed E, Ali E. Optimal hydrate inhibition policies with the aid of neural networks. Energy Fuels, 1999; 13 (1): 105-113. https://doi.org/10.1021/ef980129i.
[47] Carroll JJ. Chapter Three; Hand Calculation Methods. 51-93. In natural gas hydrates, A guide for engineers, 2nd Ed. Elsevier B.V, 2009. https://doi.org/10.1016/B978-0-7506-8490-3.X0001-8.
[48] Aregbe AG. Gas hydrate properties, formation, and benefits. Open Journal of Yangtze Gas and Oil, 2017; 2(1): 27-44. https://doi.org/10.4236/ojogas.2017.21003.
[49] Mousavi SV, Bozorgian A, Mokhtari N, Gabris MA, Nodeh HR, Ibrahim WA. Novel cyanopropylsilane-functionalized titanium oxide magnetic nanoparticle for the adsorption of nickel and lead ions from industrial wastewater: equilibrium, kinetic and thermodynamic studies. Microchemical Journal, 2019; 145: 914-920. http://dx.doi.org/10.1016/j.microc.2018.11.048.
[50] Ribeiro M, Boudoukhani M, Belmonte-Reche E, Nuria G. Xanthan-Fe_3O_4nanoparticle composite hydrogels for non-invasive magnetic resonance imaging and magnetically assisted drug delivery, ACS Appl. Nano Mater, 2021; 4 (8): 7712-7729. https://doi.org/10.1021/acsanm.1c00932.
[51] Bozorgian A, Arab Z, Mohammadi A, Honarvar B, Azimi A. Prediction of gas hydrate formation in industries. Prog.Chem. Biochem. Res. 3, 2019; 31-38. http://dx.doi.org/10.33945/SAMI/PCBR.2020.1.4.
[52] Bozorgian A, Zarinabad S, Samimi A. Optimization of well production by designing a core pipe in one of the southwest oil wells of Iran. Journal of Chemistry Rev. 2020; 2(2): 122-129. http://dx.doi.org/10.33945/SAMI/JCR.2020.2.5.
[53] Bradley HB. Petroleum Engineering Handbook. United States: N.p., 1987. https://www.osti.gov/biblio/5770327
[54] Ng HJ, Petrunia JP, Robinson DB. Experimental measurement and prediction of hydrate forming conditions in nitrogen-propane-water system. Fluid Phase Equilibria, 1977/1978; 1 (4): 283-291. https://doi.org/10.1016/0378-3812(77)80011-3.
[55] Ng HJ, Robinson DB. The measurement and prediction of hydrate formation in liquid hydrocarbon-water system. Ind. Eng. Chem. Fundamen. 1976; 15 (4): 293-298. https://doi.org/10.1021/i160060a012.
[56] Jager M, Peters C, Sloan ED. Experimental determination of methane hydrate stability in methanol and electrolyte solutions. Fluid Phase Equilibria, 2002; 193 (1/2): 17-28. http://dx.doi.org/10.1016/S0378-3812(01)00623-9.
[57] Pourabadeh A, Nasrollahzadeh B, Razavi R, Bozorgian A, Najafi M. Oxidation of FO and N_2 molecules on the surfaces of metal-adopted boron nitride nanostructures as efficient catalysts. Journal of Structural Chemistry, 2018; 59: 1484-1491. https://doi.org/10.1134/S0022476618060355.
[58] Baillie C, Wichert E. Chart gives hydrate formation temperature for natural gas. Oil and Gas Journal, 1987; 85:14.
[59] Sloan E. Clathrate hydrates of natural gases. 2nd Ed., Marcel Dekker, New York, 1998.
[60] Ameripour S, Barrufet M. Improved correlations predict hydrate formation pressures or temperatures for systems with or without inhibitors. J. Can. Pet. Technol. 2009; 48 (05): 45-50. http://dx.doi.org/10.2118/09-05-45.
[61] Obanijesu E, Pareek V, Tade M, Modelling the contribution of gas hydrate to corrosion rate along the subsea pipelines. Petroleum Science and Technology, 2014; 32 (21): 2538-2548. https://doi.org/10.1080/10916466.2013.842586.
[62] Kobayashi T, Mori YH. Thermodynamic simulations of hydrate formation from gas mixtures in batch operations. Energy Conversion and Management, 2007; 48 (1): 242-250. http://dx.doi.org/10.1016/j.enconman.2006.04.008.
[63] Creek J, Xu Z. Predicting hydrate plug formation in oil-dominated flowlines. Journal of Petroleum Science and Engineering, 2010; 72 (3/4): 302-309. http://dx.doi.org/10.1016/j.petrol.2010.03.031.

[64] Ma Q, Chen G, Zhang L. Experimental and modelling study on gas hydrate formation kinetics of (methane + ethylene + tetrahydrofuran + H_2O). *J. Chem. Eng. Data*, 2009; 54 (9): 2474-2478. https://doi.org/10.1021/je900017k.

[65] Kobayashi R, Song K, Sloan E, Bradley H. Petroleum Engineers Handbook. Society of Petroleum Engineers, 1987.

[66] Tavasoli H, Feyzi M, Dehghani N, Alavi F. Prediction of gas hydrate formation condition in the presence of thermodynamic inhibitors with the Elliott–Suresh–Donohue equation of state. Journal of Petroleum Science and Engineering, 2011; 77(1): 93-103. https://doi.org/10.1016/j.petrol.2011.02.002.

[67] Bozorgian A, Arab A, Mohammadi A, Honarvar B, Azimi A. Prediction of gas hydrate formation in industries. Prog.Chem. Biochem. Res. 2019; 3 (1): 31-38. http://dx.doi.org/10.33945/SAMI/PCBR.2020.1.4.

[68] Ribeiro CP, Paulo LCL. Modelling of hydrate formation kinetics: state-of-the-art and future directions. *Chemical Engineering Science*, 2008; 63 (8): 2007-2034. https://doi.org/10.1016/j.ces.2008.01.014.

[69] Sloan ED. Hydrocarbon hydrate flow assurance history as a guide to a conceptual model. Molecules, 2021; 26 (15): 4476.https://doi.org/10.3390/molecules26154476.

[70] Sayani, Jai Krishna Sahith, Kamireddi, Venkateswara Rao, Pedapati, Srinivasa Rao, Georgios Kolliopoulos. Development of a simple statistical model for the prediction of gas hydrate formation conditions. Paper presented at the PSIG Annual Meeting, San Diego, California, USA, 2022.

[71] Adams JJ, Akkutlu IY, George JM. Modeling of hydrate formation hysteresis in porous media. Paper presented at the SPE Europec featured at 81st EAGE Conference and Exhibition, London, England, UK, 2019. https://doi.org/10.2118/195540-MS.

[72] Zerpa L, Sloan E, Sum A, Koh C. Overview of CSMHyK: a transient hydrate formation model. Journal of Petroleum Science and Engineering, 2012; 98/99: 122–129. http://doi.org/10.1016/j.petrol.2012.08.017.

[73] Youhong S, Shuhui J, Shengli L, Guobiao Z, Wei G. Growth kinetics of hydrate formation from the water-hydrocarbon system. Chinese Journal of Chemical Engineering, 2019; 27 (9): 2164-2179. https://doi.org/10.1016/j.cjche.2019.03.022.

[74] Fan SS, Chen GJ, Ma QL, Guo TM. Experimental and modeling studies on the hydrate formation of CO_2 and CO_2-rich gas mixtures. Chemical Engineering J., 2000; 78(2-3): 173-178. https://doi.org/10.1016/S1385-8947(00)00157-1.

[75] Ng HJ, Robinson DB. The measurement and prediction of hydrate formation in liquid hydrocarbon-water system, Industrial & Engineering Chemistry Fundamentals, 1976; 15(4), 293-298. https://doi.org/10.1021/i160060a012.

[76] Moghaddam SF, Hamid A, Majid A, Lesley J. Consideration of various parameters and scenarios in the simulation of hydrate formation. Paper presented at the SPE Canadian Energy Technology Conference, Calgary, Alberta, Canada, 2022. https://doi.org/10.2118/208881-MS.

[77] Lawal KA, Ovuru MI, Eyitayo SI, Matemilola S, Adeniyi AT. Underground storage as a stranded associated gas in oil fields. Journal of Petroleum Science and Engineering, 2017; 150. 366-375. https://doi.org/10.1016/j.petrol.2016.12.020.

[78] Florian S, Carsten S, Heyko J, Timo S, and Sven W. Research on gas hydrate plug formation under pipeline-like conditions. International Journal of Chemical Engineering, 2015; https://doi.org/10.1155/2015/214638.

[79] Pourabadeh A, Nasrollahzadeh B, Razavi R, Bozorgian A, Najafi M. Oxidation of FO and N_2 molecules on the surfaces of metal-adopted boron nitride nanostructures as efficient catalysts. J. Struct. Chem., 2018; 59:1484-1491.

[80] Shaw BA, Kelly RG. What is corrosion? Electrochemical Society Interface, 2006; 15(1), 24–26.

[81] Ma CF, Chen GJ, Wang F, Sun CY, Guo TM. Hydrate formation of (CH_4+C_2H_4) and (CH_4+C_3H_6) gas mixtures. Fluid Phase Equilibria, 2001; 191 (1-2): 41-47. https://doi.org/10.1016/S0378-3812(01)00610-0.

[82] Straume EO, Merino-Garcia D, Sum AK, Morales REM. Hydrate formation in condensate and mineral oil systems. Paper presented at the OTC Brasil, Rio de Janeiro, Brazil, 2015. https://doi.org/10.4043/26189-MS.

[83] Olabisi OT, Ikiensikimama SS, Appah D. LPG hydrate formation and prevention using ethanol and methanol. Paper presented at the SPE Nigeria Annual International Conference and Exhibition, Lagos, Nigeria, 2015. https://doi.org/10.2118/178333-MS.

[84] AlHarooni KM, Barifcani A, Pack D, Iglauer S. Evaluation of different hydrate prediction software and impact of different MEG products on gas hydrate formation and inhibition. Paper

presented at the Offshore Technology Conference Asia, Kuala Lumpur, Malaysia, 2016. https://doi.org/10.4043/26768-MS.
[85] Steinsmo U, Rogno T, Drugli JM. Recommended practice for selection, quality control and use of high-alloy stainless steels in seawater systems, In marine corrosion of stainless steels, Publication No. 33 (ed. D. Feron), European Federation of Corrosion, London, 2001; 115–123.
[86] Ameripour S. Prediction of gas hydrate formation conditions in production and surface facilities. A thesis submitted to Texas A&M University, 2005.
[87] Mannel D, Puckett D. Natural gas hydrate transportation. University of Oklahoma, Norman, 2008; 1-54.
[88] Poberezhny L, Chudyk I, Hrytsanchuk A, Mandryk O, Kalyn T, Hrytsuliak H, Yakymechko Y. Influence of hydrate formation and concentration of salts on the corrosion of steel 20 pipelines. Management Systems in Production Engineering, 2020; 28 (3): 141-147. https://doi.org/10.2478/mspe-2020-0021
[89] Lawal K, Crawshaw J, Boek E, and Vesovic V. Experimental investigation of asphaltene deposition in capillary flow. Energy Fuels, 2012; 26 (4): 2145-2153. https://doi.org/10.1021/ef201874m..
[90] Ju DL, Myungho S, Susilo R, Englezos P. Dynamics of methane−propane clathrate hydrate crystal growth from liquid water with or without the presence of n-heptane. Crystal Growth & Design, 2006; 6 (6): 1428-1439.https://doi.org/10.1021/cg0600647.
[91] Oluwaseyi BO, Sunday OI, Yahya OS. Sequential stage treatments of crude glycerol towards synthesis of Monoethylene Glycol for gas hydrate inhibition. Petroleum and Coal, 2021; 63(3): 833-841.
[92] Amir SA. New model to prevent the formation of hydrate in a gas pipeline in a gas refinery. International Journal of Innovation and Applied Studies, 2012; 1 (2): 226-231. http://www.issr-journals.org/ijias.

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