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# Gas Hydrate Inhibited Water-Based Muds for Ultra-Deepwater Drilling

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## Abstract

In water depths greater than 4,000 ft, gas hydrate inhibition in water-based mud systems becomes very difficult and expensive to achieve. In ultra-deepwater, the mud weights required to drill without lost returns are typically low, especially for top-hole sections and in regions such as Brazil and West Africa. In order to provide thermodynamic gas hydrate inhibition, sodium chloride is, in most cases, the preferred hydrate inhibitor. Unfortunately the density of the brine phase often results in the mud weight being too high for the particular application. Hydrate inhibition is often boosted through the use of low-molecular-weight glycols. To achieve full thermodynamic inhibition with salt and glycol can often result in a very expensive fluid.

This paper presents the results from recent testing of kinetic hydrate inhibitors. The kinetic hydrate inhibitor discussed can be run at low concentrations and achieve effective inhibition of hydrates for the ultra-deepwater environment. Kinetic inhibitors function by delaying the initial formation and subsequently retarding the growth rate of hydrate crystals. Test results also demonstrate the ability of the kinetic inhibitor to provide some degree of temperature suppression. Results are presented highlighting the improvement in hydrate inhibition possible in a number of different fluid systems used in deep and ultra-deepwater drilling. The fluid systems tested include conventional salt/PHPA fluids, reservoir drill-in fluids, and new high performance water-based mud systems.

## Introduction

Synthetic-based mud systems have developed into the fluid of choice for deepwater drilling. However, recent advances in fluid technology have shown that water-based muds (WBM) can provide the same level of performance in challenging environments such as deepwater, where shale inhibition and high rates of penetration are important drilling parameters.[1] One big handicap faced by water-based muds has been the inability to provide thermodynamic gas hydrate inhibition for deepwater and ultra-deepwater applications, particularly when drilling with low-density fluids.

Sodium chloride is the cheapest and most effective additive for thermodynamic hydrate inhibition in water-based muds.[2] Often top-hole sections must be drilled with mud weights in the 9 to 10 lb/gal range, thus limiting the amount of salt (NaCl) that can be added to the fluid to provide hydrate inhibition. The increase in mud weight due to the addition of salt is a major hurdle when formulating hydrate-inhibited deepwater WBM systems. Traditionally, high levels of glycol, at times in excess of 20 wt%, are used to provide acceptable levels of hydrate inhibition.[3] These high glycol concentrations can significantly increase the cost of the drilling fluid, making the water-based fluid system uneconomical. This paper discusses alternative solutions for preventing gas hydrate-related problems when drilling in deepwater.

### *Thermodynamic Inhibition*

Gas hydrates form when a number of factors co-exist: free water, hydrocarbon gas, cold temperatures, high pressure, and time. Cold temperatures and high pressures are typical of the near mud-line conditions in a deepwater drilling operation. Subsequently, when drilling with water-based muds, particularly on exploration wells, the risk of hydrate formation associated with a gas influx is high. The consequences of gas hydrate formation while drilling are severe, and as such, every effort should be made to ensure the risk of hydrate formation is either eliminated or significantly reduced. Thermodynamic inhibitors are used to reduce the free water content of a drilling mud, and thus suppress the hydrate formation temperature.

As previously stated, sodium chloride, as measured by molality, is one of the most effective thermodynamic inhibitors. At high concentrations, calcium chloride is also a very effective hydrate inhibitor, but environmental and numerous technical constraints limit the use of calcium chloride in water-based muds. Potassium chloride is not an effective thermodynamic gas hydrate inhibitor relative to sodium chloride. Low-molecular-weight glycols can be used to supplement the thermodynamic inhibition, but very high concentrations of glycol are required if this is to be the primary inhibitor.

### *Kinetic Inhibition*

An alternative to thermodynamic inhibition is the use of kinetic inhibitors. Kinetic hydrate inhibitors do not necessarily prevent hydrate crystals from forming, but can delay the onset of hydrate formation and retard the rate of gas hydrate formation. Kinetic inhibitors have been used extensively in production systems, where the level of water in the production stream may be low, but have not been used extensively in drilling fluids.[4] Since time is one of the key variables in the gas hydrate formation equation, increasing the time required to begin hydrate formation can be an effective strategy for reducing the hydrate risk in deepwater drilling operations.

Effective kinetic inhibitors contain certain functional groups that are able to interfere with the hydrate crystal nucleation process.[5] The key functional groups adsorb onto the nucleating hydrate crystals and provide steric hindrance to further crystal growth. The hydrophilic groups in the chemical structure also preferentially form hydrogen bonds with water, reducing the association rate of water-hydrocarbon molecules. The result is a delay in the onset of hydrate formation, reduced rates of hydrate formation, and limits on the size of the crystals that develop. Some kinetic inhibitors have also demonstrated anti-agglomerate behavior, whereby the crystals that do form are prevented from associating. This is an important characteristic, as it helps to prevent the formation of large, solid hydrate blocks that can be disastrous from a drilling perspective.

## Modeling Hydrate Formation

When designing deepwater drilling fluids, thermodynamic software models are used to evaluate the risk of hydrate formation under the conditions expected at the mud-line while drilling the well. Design parameters typically include the mud-line temperature, the hydrostatic pressure at the mud-line for a particular fluid density, and the concentrations of inhibitors in the fluid. All simulations of hydrate formation potential are based on steady state thermodynamic properties, and do not take into consideration any transients. In addition, the understanding of the mechanisms associated with kinetic inhibitors is not complete. As such there is no method currently available to predict the behavior of proposed kinetic hydrate inhibitors. Thermodynamic modeling data is simply used to determine if it is possible to form gas hydrates under the temperature and pressure conditions of interest, without any assessment of the time required for hydrates to form. Depending on how close the actual wellbore conditions are to the thermodynamic equilibrium point, the time required to form hydrates could range anywhere from hours to seconds. The modeled thermodynamic hydrate equilibrium curves for the fluids evaluated in this paper are shown in Fig. 1.

## Deepwater Fluids

In order to assess the effectiveness of the kinetic inhibitor, three different water-based muds were proposed for testing: a conventional PHPA fluid, a new high-performance water-based mud, and a low-salt, light-weight reservoir drill-in fluid. The formulations for each of these fluids are given in Table 1.

## PHPA/NaCl Fluid

The PHPA-NaCl fluid has been one of the more common water-based mud systems used in deepwater, particularly for the Gulf of Mexico. The fluid allows a high concentration of sodium chloride to be incorporated into the formulation, aiding in gas hydrate inhibition, while at the same time, providing effective shale inhibition through the encapsulating nature of the PHPA polymer. The PHPA-NaCl system can function effectively with a limited amount of KCl (3 wt%) or without any KCl at all. The PHPA-NaCl also is compatible with a number of generic mud additives, including various glycols, allowing both hydrate and shale inhibition to be improved. The particular formulation evaluated in this instance has 20 wt% NaCl for hydrate inhibition. With this level of inhibition, the 10 lb/gal fluid could provide hydrate inhibition in water depths up to 1,650 ft. Clearly, higher levels of hydrate inhibition would be required for the fluid to provide true hydrate inhibition for wells drilled in significant water depths.

## HPWBM

Many recent efforts in drilling fluid research have focused on the development of water-based mud systems that provide synthetic-based fluid performance. Newly developed high-performance water-based mud (HPWBM) systems have been shown to deliver synthetic-based rates of penetration and shale inhibition, but have not been able to provide the same level of protection against gas hydrate formation. The achievable levels of thermodynamic inhibition are the same as for conventional water-based muds, leaving these high-performance fluids still one step behind synthetic-based systems. Inclusion of an effective kinetic inhibitor in the HPWBM formulation provides a pathway to achieving levels of protection against hydrate formation similar to those that SBM deliver. While the formulation for the 10.0 lb/gal HPWBM presented in this paper (20 wt% NaCl and 5 vol% di-ethylene glycol) only offers gas hydrate protection up to water depths of 2,000 ft, the kinetic inhibitor can allow the fluid to be used safely in greater water depths.

## Reservoir Drill-in Fluid

In many deepwater basins around the world, reservoirs are drilled with low-density fluids. The low density of the reservoir drilling fluids results in these fluids typically having low levels of gas hydrate suppression. The low density places limitations on the amount of salt that can be added to the fluid. In this particular case, a 9.5 lb/gal fluid has been chosen for analysis. This particular fluid had 10.9 wt% NaCl, together with 4 wt% KCl and 5 vol% di-ethylene glycol. Thermodynamic modeling of gas hydrate formation indicated that beyond 1400 ft of water, this particular formulation would not prevent gas hydrate formation at mud-line temperature and pressure conditions. For use in deepwater or ultra-deepwater, either the fluid should be reformulated to include significantly higher concentrations of glycol, subsequently increasing the cost of the fluid significantly, a kinetic inhibitor could be considered, or the well could be drilled without effective hydrate inhibition.

### Thermodynamic Gas Hydrate Tests

A modified pressure vessel is used for determining the thermodynamic equilibrium properties of each fluid tested. A temperature bath is used for cooling the entire cell, with thermocouples placed inside the cell to measure the actual temperature of the mud sample. For each test, 700 mL of mud is placed inside the vessel, which is then pressurized using a standard mixture of hydrocarbon gases, representative of natural gas found in the Green Canyon region of the Gulf of Mexico.

Once the cell has been pressurized, typically to 4,400 psi, the cell is cooled at a rate of 2°F per hour. During the cooling process, the pressure inside the cell naturally decreases. When conditions inside the cell become critical, gas hydrate crystals begin to form. This is not the thermodynamic equilibrium point. When hydrate crystals have been observed to form, the cell is then heated at a rate of 1½°F per hour. The heating rate is chosen so that a balance between approaching true equilibrium conditions can be reached, which would require an infinite heating period, and completing the test within a practical time frame.

The point at which the heating curve, plotted as temperature versus pressure, rejoins the cooling curve is defined as the last-crystal-to-melt point. At this particular temperature and pressure combination, gas hydrate crystals become unstable and are no longer able to remain in the crystal state. These conditions are defined as the thermodynamic equilibrium conditions. A series of tests are required, starting at different initial pressures, to construct the pressure-temperature hydrate-equilibrium curve for each particular fluid. For the work presented in this paper, complete equilibrium curves were not required. Figures 2, 5 and 8 show the cooling and heating cycles used to determine specific equilibrium points for each fluid tested.

The region between the initial hydrate formation conditions and the last-crystal-to-melt point is sometimes referred to as the metastable region. In this region, hydrates can form but it becomes a matter of time. Depending on how close the temperature and pressure conditions encountered in the field are to the last-crystal-to-melt conditions, the time required for hydrates to form can vary from seconds to minutes to hours. The current state-of-the-art in hydrate technology does not provide methods for predicting this time factor. For field operations, fluid design typically is based upon full thermodynamic inhibition, whereby gas hydrates are not able to form at all under the most severe temperature and pressure conditions. In the ultra-deepwater environment, it is often impossible to formulate an economic, water-based drilling fluid that provides absolute thermodynamic hydrate inhibition. The specific thermodynamic equilibrium point for each fluid tested is provided in Table 2.

### Kinetic Inhibitor Testing

Modifications to the pressure vessel used for the thermodynamic testing also included a magnetically driven agitator inside the cell. A recorder is used to monitor the torque required to maintain a constant rate of revolution of the agitator (300 rpm). The measured torque gives a clear indication of the presence of continuous hydrate crystal formation. Should hydrate crystals that grow in an infinite fashion begin to form, the interface between the mud sample and the hydrocarbon gas space will form a layer of solid hydrate crystals, which will be indicated by a definitive increase in required torque to maintain a constant rate of rotation.

Figures 4, 7, and 10 give examples of torque measurements recorded for each series of fluid testing. Only the torque data for the fluid with the kinetic inhibitor included in the formulation is shown in Fig. 4. Problems with the recorder during the experiment did not allow the torque data for the fluid without the kinetic inhibitor to be recorded. Figure 4 does show clearly that the fluid with the kinetic inhibitor does not form a solid mass of hydrate crystals.

For the reservoir drilling fluid, the kinetic test was modified to simulate a shutdown period with the mud in contact with the gas. During the cooling stage, the fluid is continually agitated. Once the temperature in the cell had reached 35°F, the temperature was held constant until hydrates began to form. For the fluid without the kinetic inhibitor, hydrates began to form approximately four hours after the fluid reached 35°F. The cell continued to be agitated for another five hours, during which time hydrates continued to form. Hydrate formation was indicated by the sharp drop in pressure (Fig. 5 and Fig. 6) as well as the increase in measured torque (Fig. 7). At this point the agitator was switched off for 24 hours, with the cell temperature maintained at 35°F. After 24 hours had elapsed, the agitator was switched back on in order to determine the extent of solid hydrate crystal formation. The sharp peak in torque after the static period (Fig. 7) indicates clearly that a layer of hydrate crystals did form a crust at the interface between the fluid sample without the kinetic inhibitor and the hydrocarbon gases.

The same procedure was repeated for the reservoir drill-in fluid containing the kinetic hydrate inhibitor. The onset of hydrate formation was not as clear in this instance as the kinetic inhibitor was functioning effectively and did not allow solid masses of crystals to form, as indicated by the lack of torque increase prior to shutting down the agitator. Hydrate formation most likely began around 24 hours after initiating the cool down of the cell, compared to 19 hours for the fluid without the kinetic inhibitor. After shutting down the agitator for the fluid containing the kinetic inhibitor for 24 hours, a small spike in the torque reading is detected once the agitator is switched on again. The torque spike is evident for only a very short period of time, suggesting that the hydrate crystals that did form at the interface between the fluid and the hydrocarbon gases were easily dispersed. This observation fits well with the theory that the hydrates form a slurry in the presence of the kinetic inhibitor (or anti-agglomerate), as opposed to a continuous solid sheet.

## Experimental Results Summary

Several key observations can be made regarding the performance of the kinetic inhibitor based on the thermodynamic and kinetic testing performed. An effective kinetic inhibitor should retard the rate of hydrate formation. Using the data presented in Figures 3, 6 and 9, it is clear that the fluids containing the kinetic inhibitor do not form hydrates at the same rate as the fluids without the kinetic inhibitor. The slope of the pressure versus time curve after hydrates begin to form is much steeper for the fluids without the kinetic hydrate inhibitor. In Table 3, the slope of the curve for the first hour of hydrate formation is compared for each fluid. The rate of hydrate formation is indicated by the rate at which the pressure in the cell decreases (psi/hr). In all cases, the fluids with the kinetic inhibitor experience significantly retarded rates of pressure decline than the fluids without the kinetic inhibitor.

Kinetic inhibitors can also decrease the actual volume of gas hydrate crystals that form. In order to gauge the reduction in hydrate volume associated with the presence of the kinetic inhibitor, a comparison of the total pressure drop during the course of the experiment can be made. The data for this comparison is extracted from Figures 2, 5 and 8. Table 3 also compares the magnitude of the pressure drop from the initial hydrate formation point to the beginning of the heating phase. Again in each instance, the fluid containing the kinetic hydrate inhibitor experiences a significantly lower pressure drop than the fluid containing no kinetic inhibitor.

Another important factor that is central to the performance of a kinetic hydrate inhibitor is the ability of the product to delay the onset of hydrate formation. In Table 3 a comparison is made of the delay in hydrate formation of the fluid containing the kinetic inhibitor relative to the fluid that did not contain the inhibitor, using data from Figures 3, 6 and 9. In the context of deepwater drilling, the observed delay in hydrate formation presents a significant advantage when managing a well control situation.

## Conclusions

A material has been identified and tested that provides genuine kinetic hydrate inhibition characteristics for water-based fluids in the deepwater drilling environment. The material tested is effective in a diverse range of water-based mud systems and is compatible with all components of these fluids. The product is able to delay the onset of hydrate formation, retard the rate of gas hydrate formation, and reduce the volume of gas hydrates formed. Another major factor in the performance of the material is its ability to function as an anti-agglomerate. The torque measurements performed on all three fluids indicate that solid hydrate plugs will not form when this material is present in the mud system. The kinetic hydrate inhibitor evaluated in this paper can provide a safe operating environment for water-based muds in deep and ultra-deepwater environments where thermodynamic inhibition cannot be achieved.

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**Table 1 - Fluid formulations prepared for hydrate formation testing**

| | 10 lb/gal PHPA | | 10 lb/gal HPWBM | | 9.5 lb/gal RDF | |
|---|---|---|---|---|---|---|
| | a | b | a | b | a | b |
| Water (bbl) | 0.85 | 0.85 | 0.8 | 0.8 | 0.84 | 0.84 |
| Xanthan (lb/bbl) | 0.5 | 0.5 | 1.5 | 1.5 | 1.25 | 1.25 |
| PHPA (lb/bbl) | 1.0 | 1.0 | | | | |
| Bentonite (lb/bbl) | 5 | 5 | | | | |
| Cellulose/Starch (lb/bbl) | 2.5 | 2.5 | 2 | 2 | 6 | 6 |
| Shale encapsulator (lb/bbl) | | | 2.5 | 2.5 | 8 | 8 |
| Shale inhibitor (lb/bbl) | | | 10.5 | 10.5 | 1.5 | 1.5 |
| Drill solids (lb/bbl) | 20 | 20 | | | 20 | 20 |
| NaCl (lb/bbl) | 73.2 | 73.2 | 70.2 | 70.2 | 37.5 | 37.5 |
| KCl (lb/bbl) | | | | | 13.8 | 13.8 |
| Diethylene glycol (lb/bbl) | | | 18.4 | | 19.3 | |
| Kinetic inhibitor (lb/bbl) | | 18.4 | | 18.4 | | 19.3 |

**Table 2 - Specific thermodynamic equilibrium points for fluids tested**

| Measured data | PHPA | | HPWBM | | RDF | |
|---|---|---|---|---|---|---|
| | a | b | a | b | a | b |
| Temperature ($^oF$) | 59 | 57 | 50 | 49 | 65 | 60 |
| Pressure (psi) | 4075 | 3950 | 3650 | 3750 | 4150 | 3900 |

**Table 3 - Hydrate formation rates and reaction delay for fluids tested**

| | PHPA | HPWBM | RDF |
|---|---|---|---|
| Total pressure drop without KI (psi) | 708 | 404 | 493 |
| Total pressure drop with KI (psi) | 56 | 159 | 215 |
| Initial hydrate formation rate without KI (psi/hr) | 113 | 131 | 95 |
| Initial hydrate formation rate with KI (psi/hr) | 6 | 15 | 17 |
| Hydrate formation delay with KI (hr) | 2.6 | 2.5 | 6.8 |

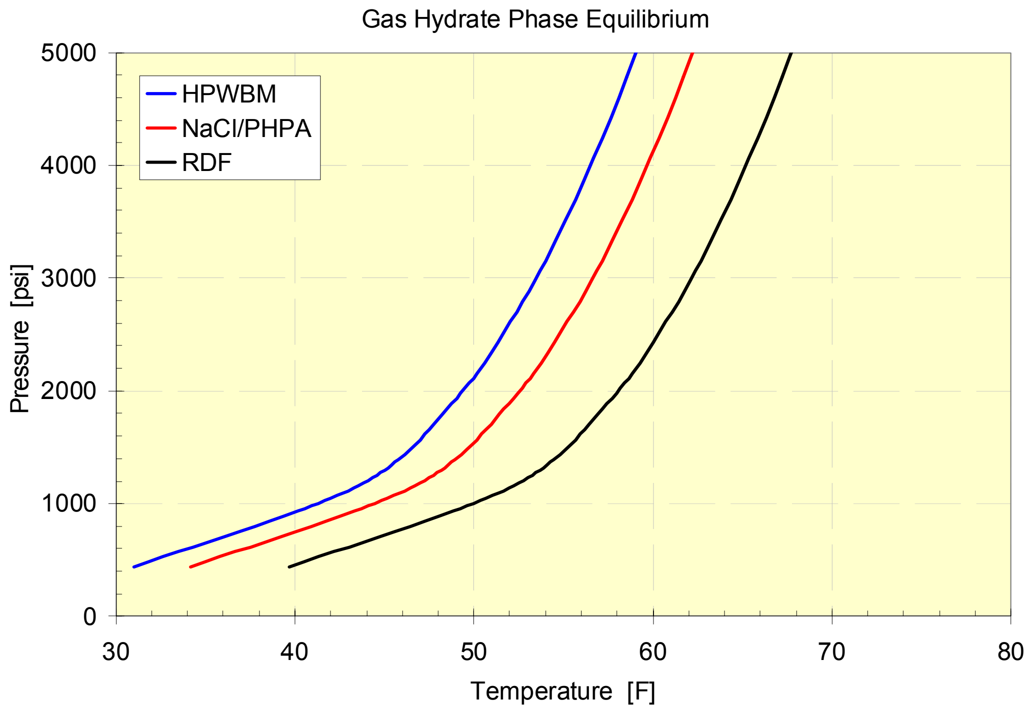

Fig. 1 - Modeled thermodynamic gas hydrate equilibrium curves for PHPA, HPWBM and RDF.

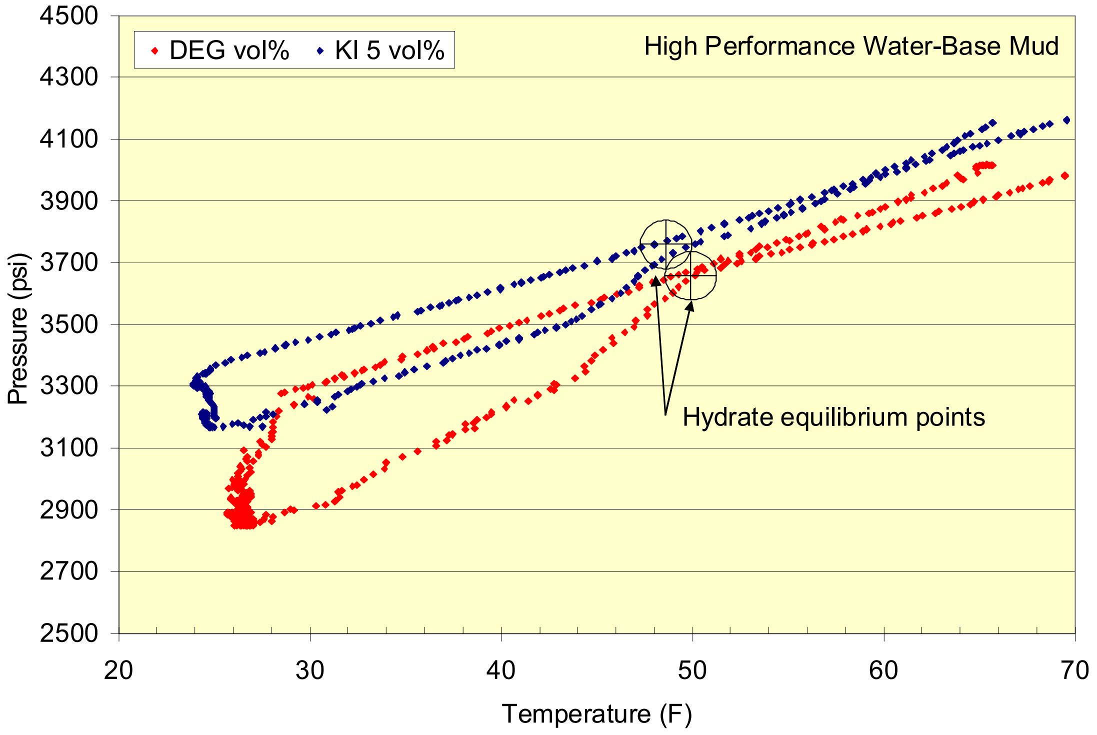

Fig. 2 - Thermodynamic gas hydrate equilibrium determination for HPWBM.

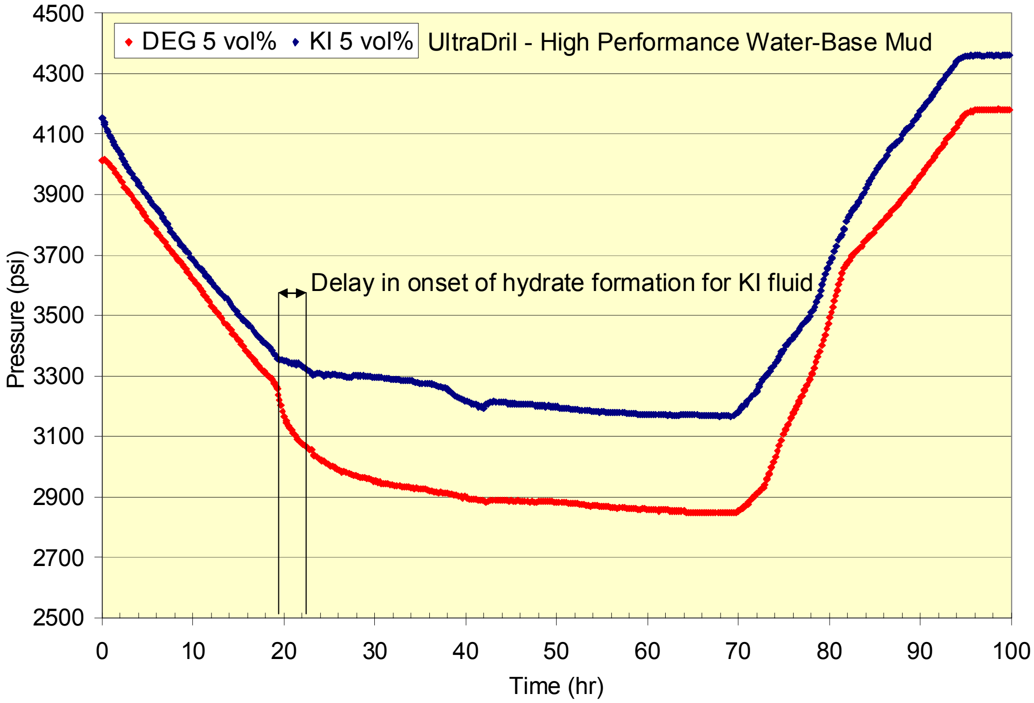

Fig. 3 - Pressure versus time curve during hydrate formation in HPWBM.

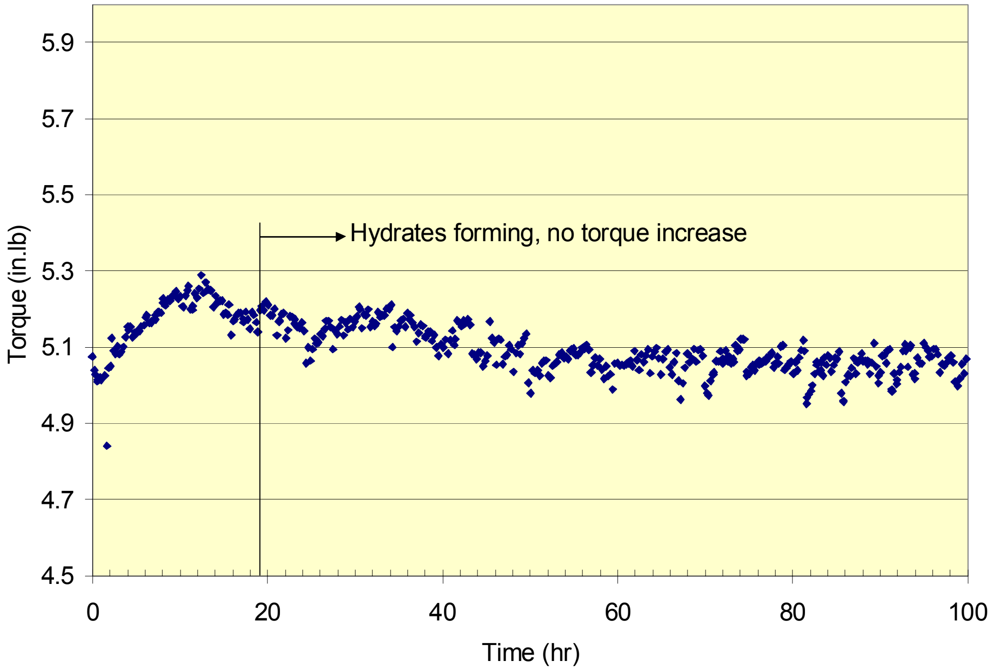

Fig. 4 - Torque versus time curve during hydrate formation in HPWBM.

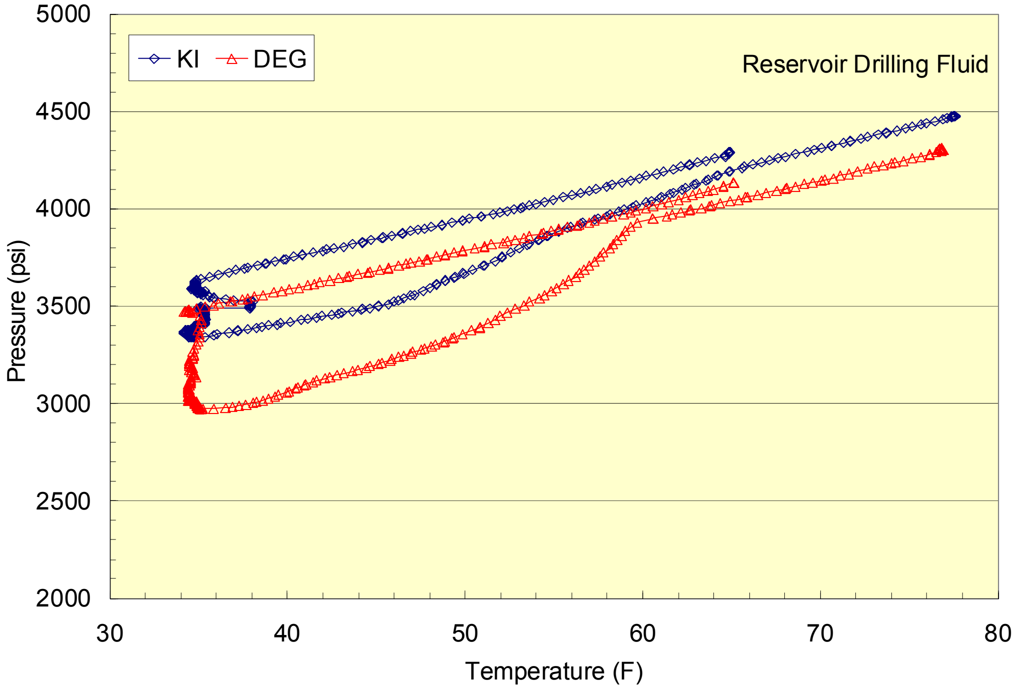

Fig. 5 - Thermodynamic gas hydrate equilibrium determination for RDF.

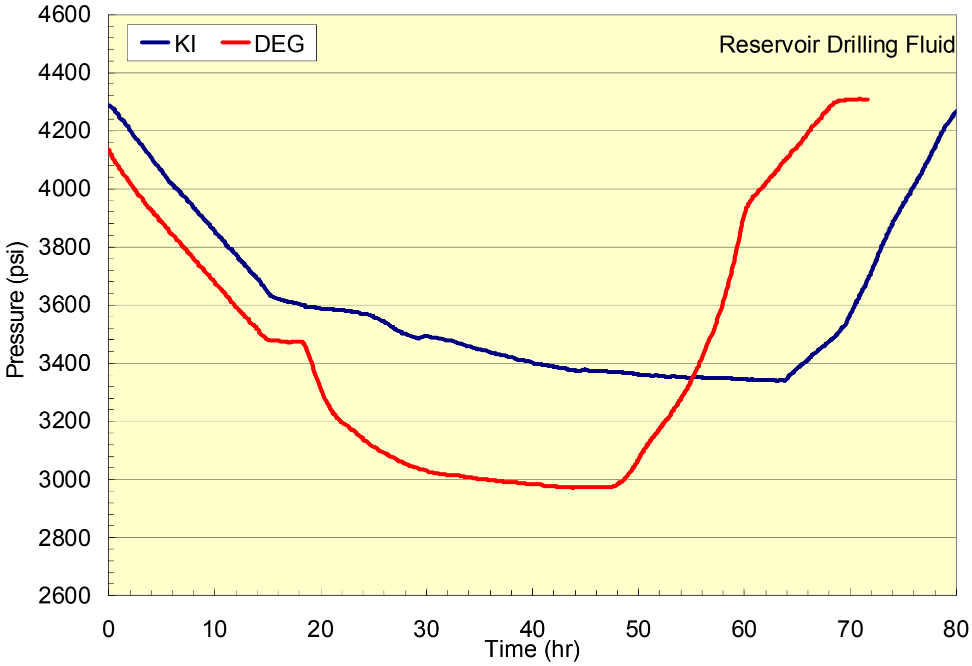

Fig. 6 - Pressure versus time curve during hydrate formation in RDF.

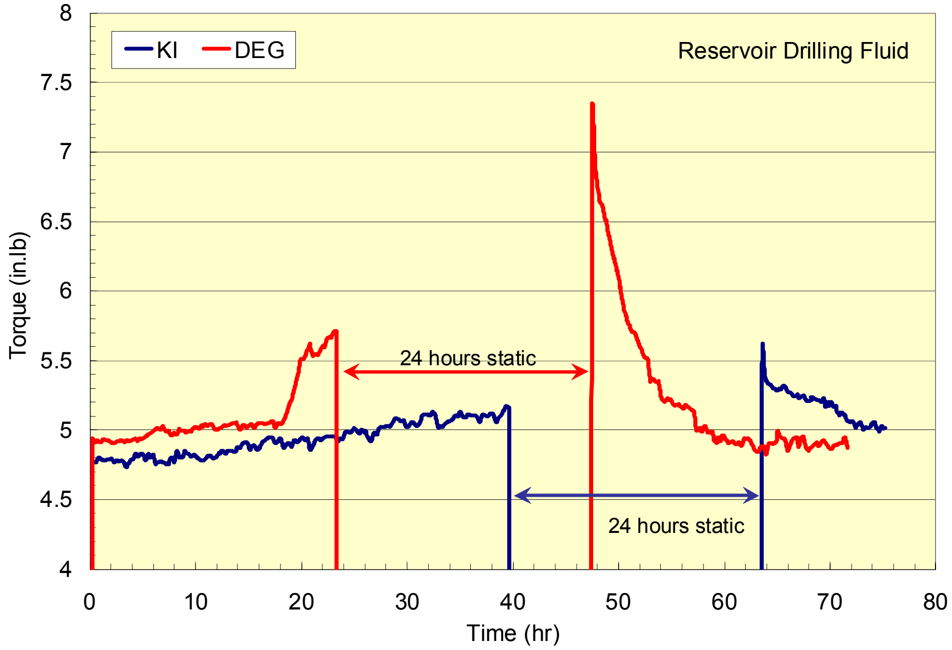

Fig. 7 - Torque versus time curve during hydrate formation in RDF.

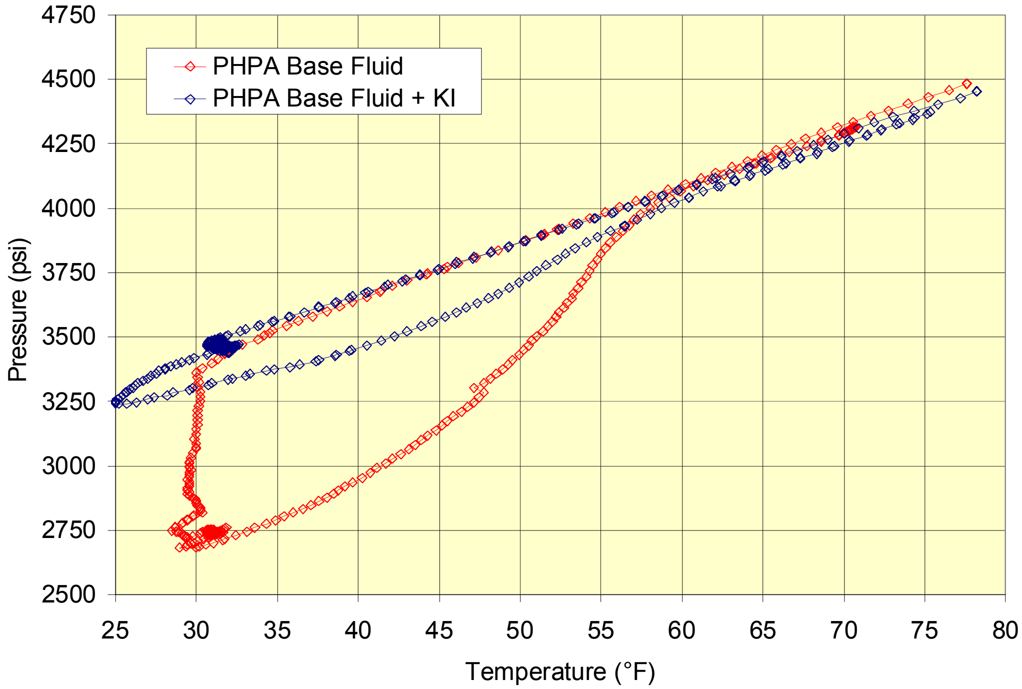

Fig. 8 - Thermodynamic gas hydrate equilibrium determination for PHPA.

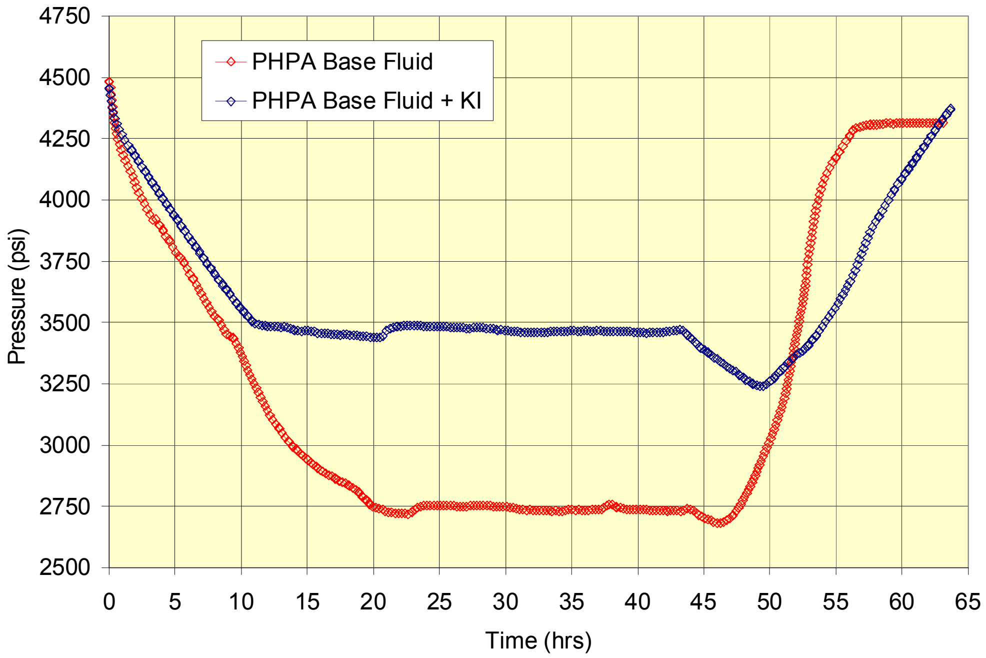

Fig. 9 - Pressure versus time curve during hydrate formation in PHPA.

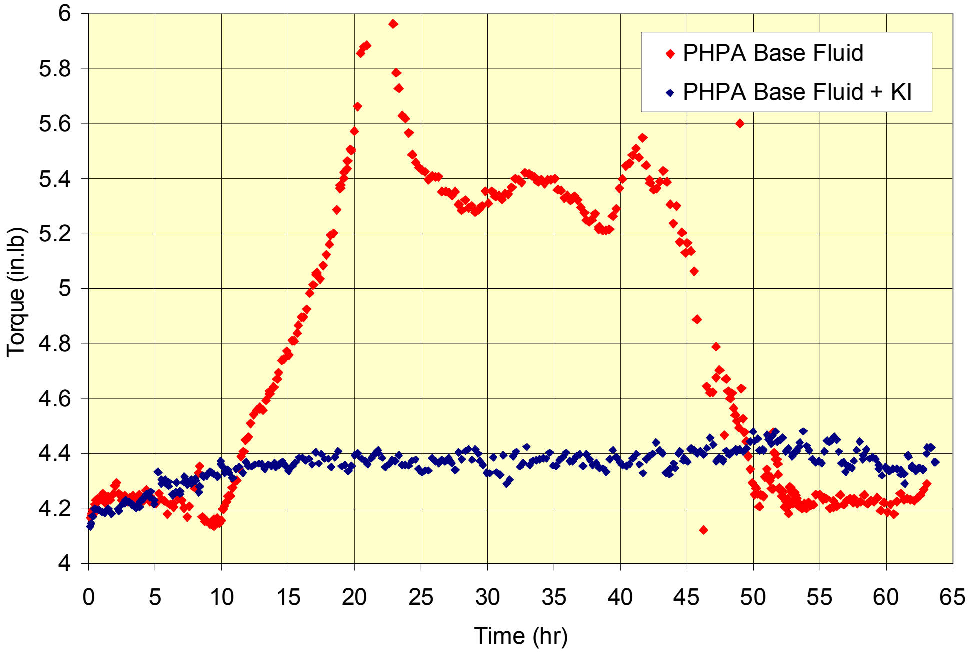

Fig. 10 - Torque versus time curve during hydrate formation in PHPA.