

GHGT-9

Effects of salinity on hydrate stability and implications for storage of CO₂ in natural gas hydrate reservoirs

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Abstract

The win-win situation of CO₂ storage in natural gas hydrate reservoirs is attractive for several reasons in addition to the associated natural gas production. Since both pure CO₂ and pure methane form structure I hydrate there is no expected volume change by replacing the in situ methane with CO₂, and there is not net production of associated water which requires extra handling. The geo-mechanical implication of the first of these may be a very important issue since hydrates in unconsolidated sediments are the most promising targets for exploitation of natural gas. The stability of CO₂ stored in the form of hydrate is probably one of the safest options today, even though also this option relates to safety of sealing cap-rock or clay layer. The stability of hydrates in a reservoir depends on many factors, including the interactions between minerals, surrounding fluids and hydrate. The natural level of salinity increases with depth in a reservoir. In addition formation of hydrate will lead to increased salinity of the fluids surrounding the formed hydrate. This may lead to liquid pockets of residual aqueous solution with increased salinity as well as very non-uniform hydrate. The latter due to the fact that hydrate composition and stability relates to properties of surrounding fluids. In the work presented here methane hydrates were formed in several sandstone cores. The cores were all partially saturated with brine of different salinities in order to identify the effect salinity has on the fill fraction, the amount of methane per available structural site in hydrates. The results indicate that salinities lower than regular sea water composition has no significant impact on the fill fraction of methane hydrate in porous media. When the salinity surpasses regular sea water composition there is a significant drop in fill fraction. The methane hydrate fill fraction is dominated by total brine salinity rather than brine distribution in the core.

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1. Introduction

Gas hydrates are clathrate structures consisting of a water molecule lattice interconnected through hydrogen bonds which creates different types of cavities which can enclathrate small non-polar or slightly polar molecules. Natural gas hydrates (NGH) are a sub-class of these hydrates in which the enclathrated molecules are predominantly hydrocarbons. The encapsulated natural gas molecule is referred to as the hydrate former, and the most abundant natural gas hydrate former in nature is methane (CH_4). There are several known hydrate structures, the most common being structure I and structure II [13]. The hydrate structure formed is dictated by the size of the hydrate former molecule and pure methane will form structure I. NGH are found in high pressure, low temperature environments such as permafrost regions in Alaska and Russia as well as deep sea areas such as off-shore Japan [4; 5].

NGH has long been a major focus in the petroleum industry as a flow assurance problem. Substantial research have been conducted during more than seven decades for the development of methods for minimizing the chances of hydrate formation and/or minimizing flow problems related to hydrate formation in all stages of the hydrocarbon exploitation stages, from reservoir and well, through pipelines and processing equipment. These most common preventive measures involves removing water, keeping Pressure-Temperature (PT) conditions outside hydrate stable region, or by injection of hydrate inhibitors such as salts and alcohols.

The amounts of natural gas trapped in hydrate structures around the world are huge. There are significant discrepancies between the estimated NGH reserves in the worlds, but even the conservative estimates points to the size of this reserve as being in the vicinity of twice the amount of conventional fossile fuel (oil, gas and coal) [5]. New hydrate occurrences are being discovered continuously. These estimates, along with the increasing prices of oil and gas and increasing energy need, has put NGH on the map for potential energy recovery during recent years. Different approaches are investigated for natural gas production from hydrate reserves. Changing the thermodynamic conditions so as to bring the hydrate outside its thermodynamically stable region has been the classical approaches. This can be accomplished by either depressurization and/or thermal stimulation or by adding chemicals which makes the fluid phases more stable than the solid hydrate. These chemicals could be traditional hydrate inhibitors like for instance methanol and other alcohols. The more novel approach of exposing the hydrate to a more thermodynamically stable hydrate former so as to induce an in-situ exchange between the two hydrate formers [6; 7] have obvious advantages in terms of geomechanical considerations since the volume of the resulting hydrate is similar to the original hydrate, even if the resulting hydrate structure type is different from the original structure.

Salt is a hydrate inhibitor and changes the thermodynamic stability of natural gas hydrate (see Figure 1) due to the fact that the resulting ions in the aqueous solution of the salt will reduce the chemical potential of liquid water and for sufficiently high concentration of ions the water will be more stable as liquid water rather than hydrate water. Figure 1 illustrates the importance of knowing the salinity of the hydrate forming water as it will indicate the stability of hydrate as well as indicate the amount of natural gas trapped in the hydrate structure. Salt is not included in hydrate structure and will form a salinity gradient at the hydrate forming front, with decreasing salinity in the direction of the hydrate formation [8]. The salinity of the residual free water in the surroundings of the hydrate formed will increase during hydrate formation. This will lead to a constant reduction in water activity coefficient only affected by dilution due to diffusion and other transport mechanisms. This reduction in activity coefficient may eventually limit further hydrate formation.

In this work methane hydrates were formed in a number of sandstone cores. A range of different salinity brines were used for the experiments. Two separate experimental setups were used in parallel. One of the experimental setups utilized magnetic resonance imaging (MRI) in conjunction with conventional PVT measurements to monitor in-situ processes such as phase distribution during experiments and hydrate formation pattern.

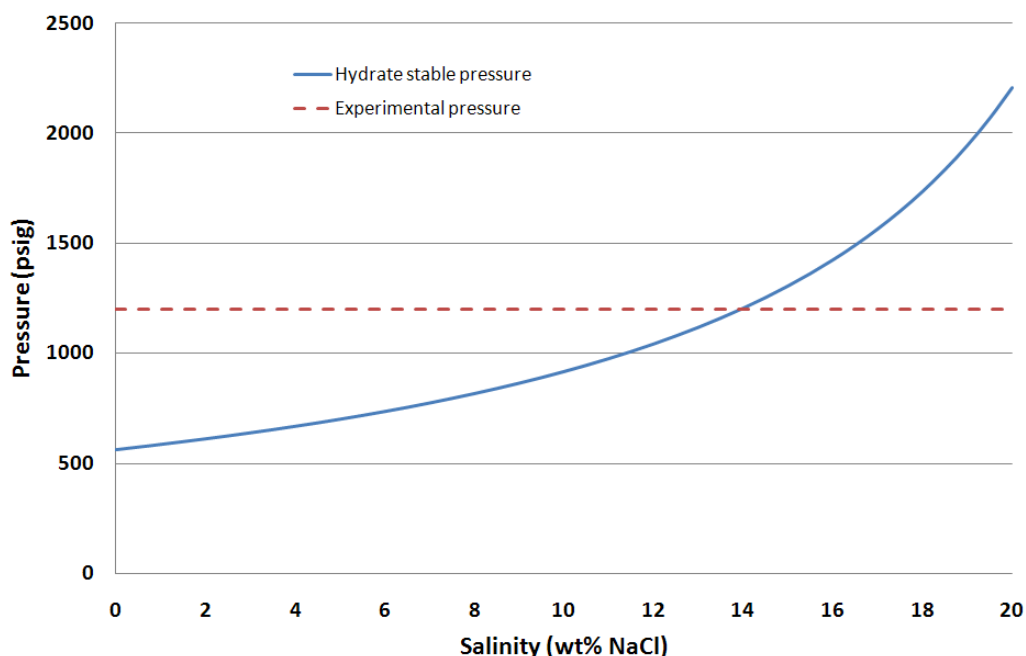


Figure 1: Methane hydrate formation pressure as function of brine salinity at 4.0°C. Hydrates are stable above the blue line and the red dotted line indicates the experimental pressure. This graph indicate that methane hydrates will not form at given experimental conditions with salinities above 14wt% NaCl. The hydrate stability graph is generated using CSMGem Hydrate Production Program [9].

2. Experimental Procedure

All experiments are performed using Bentheim sandstone, outcrop sandstone from the Bentheim quarry in Lower Saxony, Germany. This sandstone exhibits homogeneity regarding mineralogy (99% quartz), pore size distribution (125 μm) and permeability (1100 mD).

Three different core geometries were used: 2 inch (5.15 cm) diameter with 10 cm length; 2 inch (5.15 cm) diameter with 14 cm length; and 1.5 inch (3.8 cm) diameter with 10 cm length and an open fracture in the longitudinal direction.

The first setup (Setup 1) is illustrated in (Figure 1). This setup is core sample setup, with a high pressure core holder submerged in actively cooled fluid. The core holder is a Hassler-type consisting of an outer stainless steel cylinder with a flexible Viton sleeve inside. The confining fluid is a viscous mineral oil, controlled by a high pressure pump capable of delivering constant pressure. The system pressure (CH_4) is controlled by a high pressure gas pump.

In order to achieve as homogeneous distribution of brine as possible in the core, the core is submerged in the saline solution letting it imbibe into the highly water-wet sandstone. When the saturation has reached app. 50%, determined by weight, the core is placed in the core holder where confining pressure is applied and the holder is submerged into the cooled liquid kept at 20°C. At this point methane is introduced to the core and both confining and pore pressure is slowly pressurized to 1500 psig (10.1 MPa) and 1200 psig (8.2 Mpa) respectively. After the pressure has stabilized, the cooling fluid is cooled to $4.0 \pm 0.1^\circ\text{C}$ so that the system is within methane hydrate stable conditions. Temperature, pressure and the amount of methane injected are monitored throughout the entire experiment.

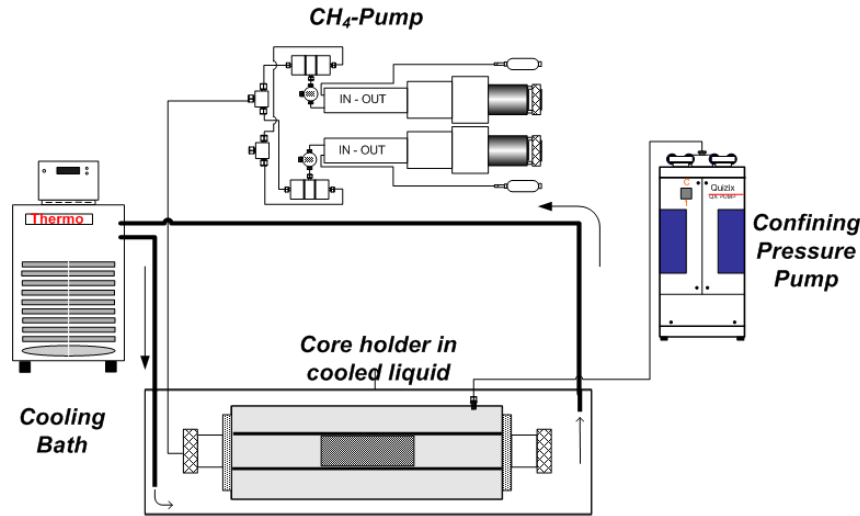


Figure 2: Experimental setup 1

The second setup (Setup 2) is more complex in that it includes an MRI for in-situ imaging capabilities. The presence of an MRI makes this experimental setup much more complex and a lot of the equipment used is proprietary and designed to minimize the interaction between the strong magnetic field and the core sample system.

This setup contains a high pressure fiberglass core holder with an outer confining sleeve and an inner core sleeve. The confining fluid is pressurized by a high pressure pump and is actively cooled and circulated through the core holder by a circulation pump. The confining fluid used is a Fluorinert which has no hydrogen and is therefore invisible to magnetic resonance imaging. The system pressure is directly controlled by a high pressure gas pump (see figure ***). Because of the complexity of this setup, the cores are saturated by injecting the brine through the system line after assembly. The confining pressure and pore pressure is then increased stepwise to 1500 psig (10.1 MPa) and 1200 psig (8.1 MPa), respectively. Fluorinert is used as the fluid for confining pressure and Methane is used for pore pressure. The system is then cooled to 4.0°C. Hydrate formation is monitored through both MRI acquisitions and PVT measurements. As hydrates form, methane will enter the lattice structure and result in reduction of free methane in the system. This consumption of methane can be monitored as a reduction in total system volume in our isobaric system.

On this setup the core is partially saturated with brine by injecting the brine from the system line after core holder assembly. The brine distribution is then monitored by taking one dimensional MRI profiles along the core length. The confining pressure and system pressure is then incrementally increased to 1500 psig () and 1200 psig () respectively. Finally the system is cooled to 4.0°C and hydrate formation is monitored in-situ by three dimensional magnetic resonance acquisitions.

In the interpretation of experimental results we should first define some common terminology. Hydrate nucleation is by definition the onset of the first crystals which are stable enough for individual stable growth and as such they will grow provided they are supported by mass, get rid of excess heat and are not outcompeted by more stable particles. This critical size is normally on a nanometer scale and not visible within the resolution of the experimental set-ups used in this work. The growth of hydrate after the initial nucleation is usually slowed down by molecular transport through hydrate since hydrate is preferentially formed on the interface between hydrate former phase and aqueous phase. The initial hydrate film will slow down further access to mass for further growth. Formation of hydrate from methane and water in a traditional PVT cell in the absence of porous media will therefore typically result in what is called induction time. This is a macroscopically defined term which characterises the onset of massive hydrate growth. It is not a precise term since it depends on the monitoring approach and sensitivity to the onset of rapid growth. The distribution of flow in a porous medium will create a different situation of large exposed contact areas between hydrate formers and water which will result in a large number of parallel processes which consumes hydrate former and water and under the formation of hydrate. The natural physics of the system will induce stochastic elements to the behaviour of these systems and as such a number of parallel runs would be needed in order to provide a qualified estimate of the average induction time for a given system.

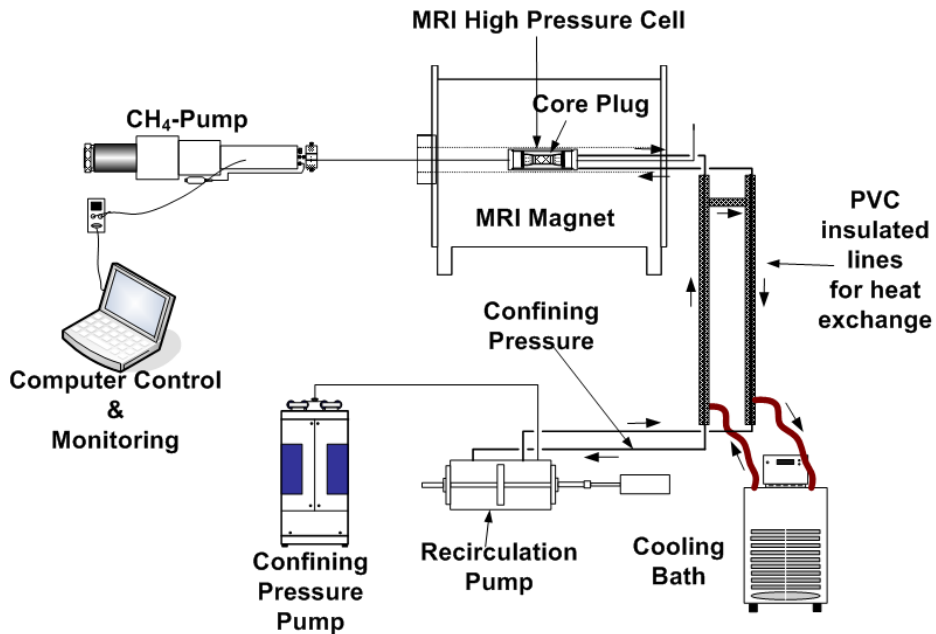


Figure 3: Experimental setup 2

3. Experimental results

Figure 4 shows the time between initiating cooling of the system to definitive identification of hydrate formation, this is obviously not the same as induction time seeing as it takes time before the system reaches hydrate stable conditions and this time is different for each salinity investigated. However, it does support deviations in induction time if comparing same salinity experiments as well as suggests that higher salinities are more likely to result in longer induction times.

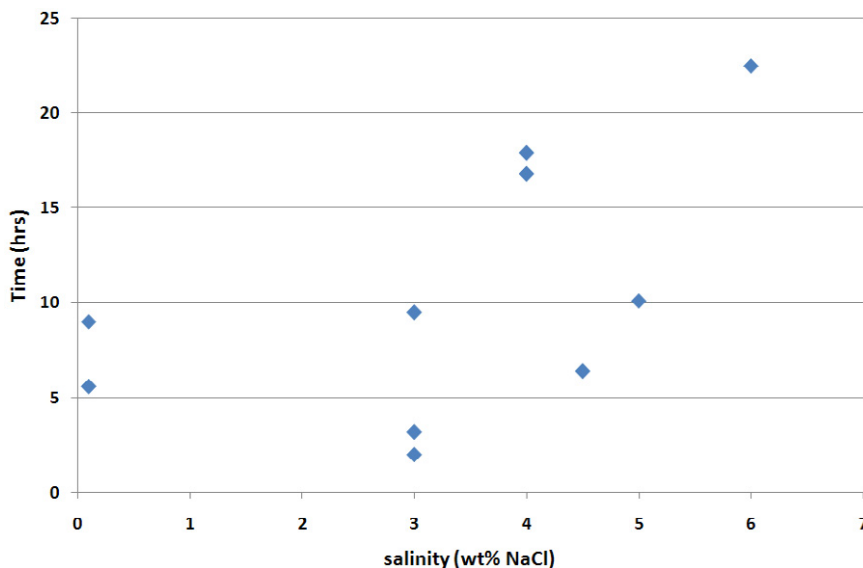


Figure 4: Time from initiated cooling to initial sign of hydrate formation for different salinities.

Hydrate formation can be monitored through both changes in system volume in the isobaric system (consumption of methane) and through decreasing MRI-intensity. The MRI intensity is directly proportional to the amount of hydrogen atoms in its field of view, meaning it directly measures the aqueous and gaseous phase in the system. The

MRI intensity is expected to decrease as hydrate forms and converts to a solid phase, undetectable by standard spin sequences. The amount of methane consumed during hydrate formation correlates to the amount of structural cages formed in the hydrate phase. The injection of methane as well as changes in MRI intensity during hydrate formation should therefore be inversely proportional when normalized and compared (see Figure 5).

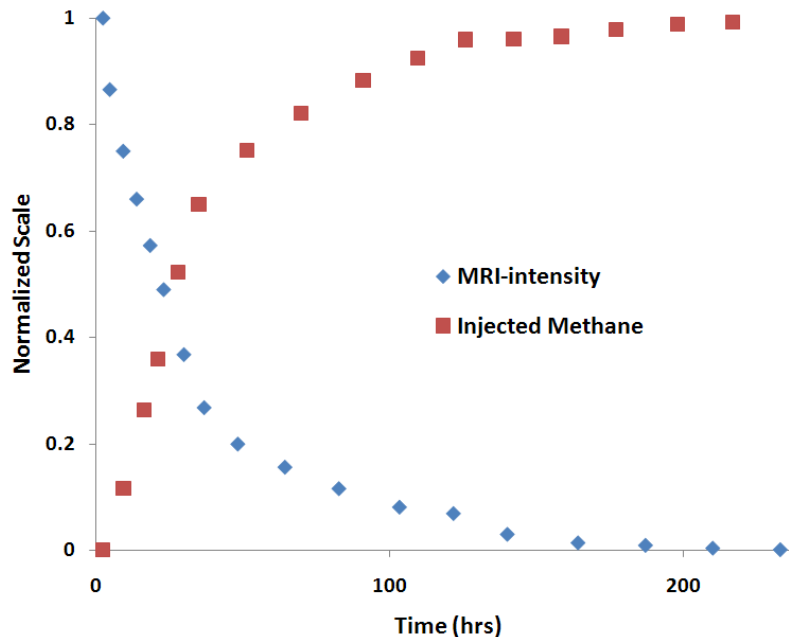


Figure 5: Comparing injection of methane and decrease in MRI-intensity during hydrate formation.

A number of different salinities were used for the methane hydrate formation experiments and the formation rate, formation pattern as well as the total consume of methane during hydrate formation was monitored. The total amount of hydrates formed does indicate an decrease with increasing salinity (see Figure 6), as expected due to the decrease in water activity coefficient. The total amount of methane consumed by the hydrate structure indicates little difference for initial salinities ranging from 0.1 to 4.0 wt% NaCl. These similarities in results for such a large range of salinities indicate that, at least for the low salinity experiments, the end of hydrate formation is reached before the residual salinity reaches 14wt% NaCl. In that case the physical structure of the pore system is probably the reason for the inhibition of further hydrate growth. This potential transition of hydrate inhibition from a physical restriction to a thermodynamic instability can be investigated by comparing the amount consumed methane with the expected salinity of the residual free water, assuming the simplified case that no salt is trapped in hydrate structure and 100 percent filling of structure I cages is possible (see Figure 7). This comparison show good correlation between the estimated salinity of the residual brine and the thermodynamic limit for methane hydrate stability for initial salinities above 4.0wt% NaCl. For salinities at 4.0 wt % NaCl and lower the correlation is not obvious. At 0.1wt% NaCl this might indicate that there are pore structure effects limiting further hydrate formation. At initial salinities from 3–4 wt% NaCl the figure indicates residual salinity higher than what is thermodynamically stable. This is unlikely and the discrepancy may be an indication of salt being trapped in the hydrate structure, although further experiments are needed to support this.

4. Discussion

The formation of hydrates from saline water in porous media is affected kinetically by the impact of salinity on a reduction in the thermodynamic driving force. But the formation rates and formation progress is very much affected by the changes of the surrounding fluid phases since consumption of water over to solid hydrate will lead to upconcentration of the surrounding aqueous phase and corresponding increased salinity. At the initial stages there may be some dilution of this but eventually when the pores gradually gets more filled with hydrate the flow patterns reduces and dilution gets higher degree of diffusional character. Higher initial salinity is expected to result in smaller hydrate cores since surrounding water gets more rapidly outside hydrate stability region and it will also be more time consuming to dilute these surrounding fluids since the surrounding fluids proportional to the higher initial

salinity. In summary all of these effect are expected to increase the induction time for the onset of massive hydrate growth and this is what is also observed in the experimental study

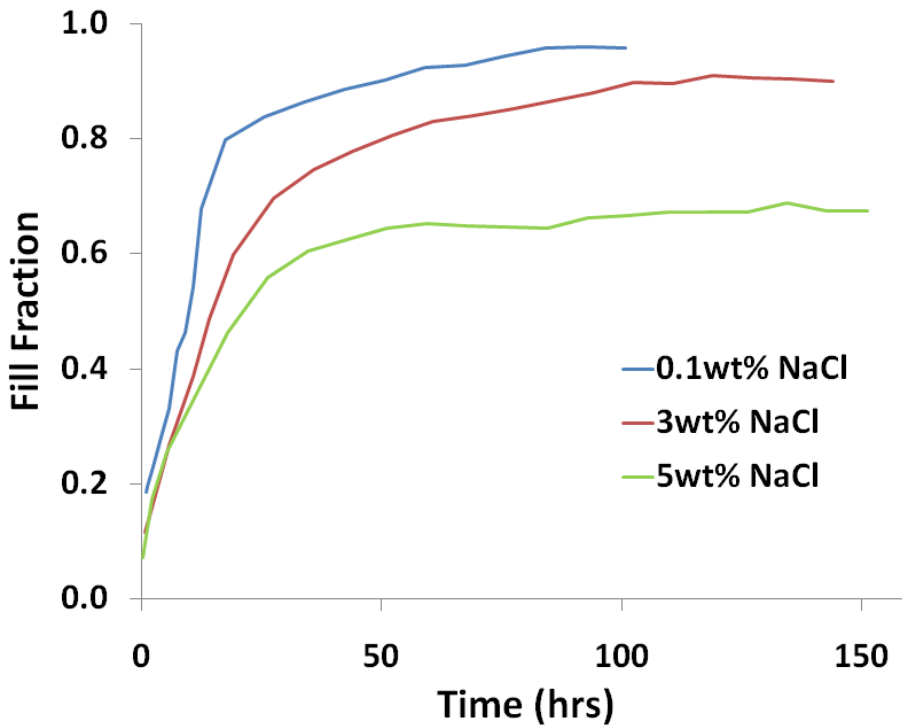


Figure 6: Hydrate formation rate for three different initial salinities.

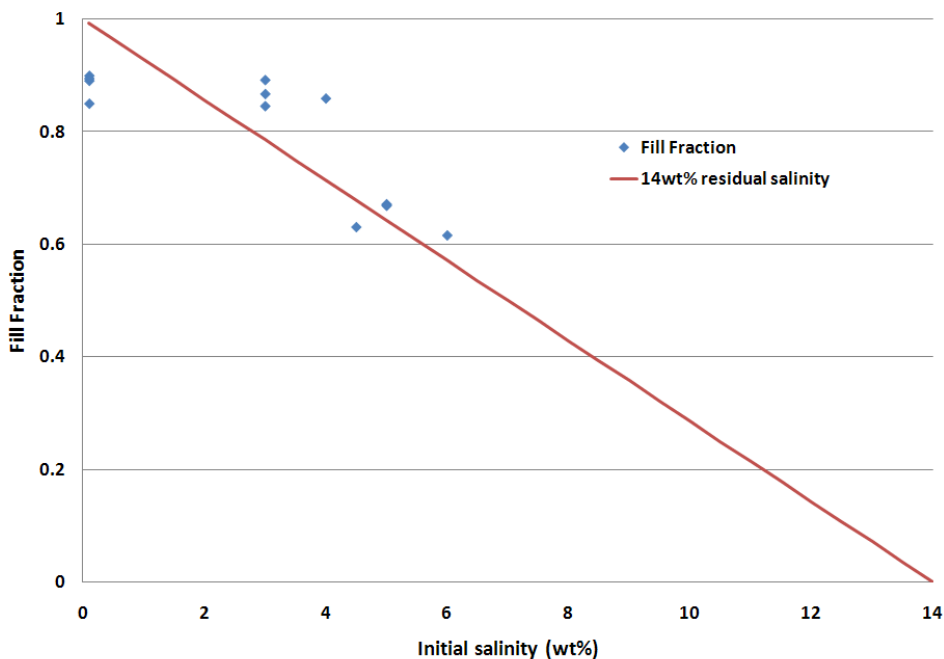


Figure 7: Experimental results of hydrate formation compared to thermodynamic stability limit of 14wt% salinity. There are three overlapping experiments at 5wt% NaCl. Fill fraction is defined as the relation between the amount of methane consumed during hydrate formation and the amount of methane needed to include all water molecules in hydrate structure.

5. Conclusion

Methane hydrates have been formed in Bentheim sandstone using a series of brine salinities. The experiments indicate that higher initial salinity will lead to longer induction time and less hydrate formation partly due to the lower energy state of the system. The experiments also indicate that for low initial salinity, the porous media may have an effect on the restriction of further hydrate formation before the salinity threshold for thermodynamically stable methane hydrate is reached. The salinity of the residual free water after hydrate formation seems to be the limiting factor for further hydrate formation when the initial salinity is higher than 4.0wt % NaCl. These experiments show the impact of salt on hydrate structures in porous media and support the importance of knowing the salt concentration of free water in a hydrate zone.

6. Acknowledgement

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