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History Matching of Hydrate Formation and Dissociation Experiments in Porous Media

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Abstract

Gas hydrates are crystalline, ice-like compounds of gas (e.g., methane) and water molecules that are formed under high pressure and low temperature. Many of the transport properties of porous media containing hydrates are unknown and difficult to measure experimentally. The goal of this work is to match laboratory experiments of hydrate formation and dissociation in cores to estimate some of these transport properties. An implicit, thermal, compositional simulator is used which accounts for four components (hydrate, water, methane and salt) and five phases (hydrate, aqueous, gas, ice, and salt precipitate). The transformation of methane and water to hydrate is modeled by a reaction with the kinetics controlled by the hydrate surface area. The key unknown is the variation of permeability within the core. Permeability and its spatial variation are used as parameters to match the experimental results.

Introduction

Gas hydrates are ice-like clathrates of gas and water molecules formed under high pressure and low temperature (Sloan, 1998). Methane and water react to form gas hydrates according to the equation:



where n is the hydration number. Hydrates are formed by gases like methane, ethane and carbon dioxide at hydrate stable pressure and temperature conditions. Three types of crystalline structure, namely structure I (SI), structure II (SII), structure H (SH), in order of increasing size, have been found (Sloan 1998). SI methane hydrate is common in natural deposits. The large amount of gas hydrates present in the earth's crust can be a potential source of energy or a potential hazard if the gas hydrate dissociate due to global warming and methane gas leaks in the atmosphere.

Finding an efficient and safe method of producing natural gas from hydrate deposits is important commercially. Four methods and their combinations have been proposed to produce gas from hydrate reservoirs: depressurization, thermal stimulation, inhibitor injection, and CO₂ injection (Makogon, 1997; Ji et al., 2001; Graue et al., 2006). Simulation models are needed to find efficient ways of producing natural gas from hydrate deposits.

Different numerical models have been proposed to estimate the gas production from hydrate reservoirs (Tsyppkin, 1991; Ji et al., 2001; Moridis, 2002; Sun & Mohanty 2006). In analytical model by Ji et al. (2001), the mobility of the water phase is ignored. The analytical model by Tsyppkin (1991) takes into account the flow of water, but it assumes a fixed relative permeability for each phase. These analytical models assume equilibrium decomposition, i.e., hydrate is assumed to dissociate instantaneously once the equilibrium condition is reached. Numerical models take into account multiphase flow, heat transfer and hydrate kinetics. The knowledge of transport properties and kinetics in porous media is necessary to build an accurate simulator for gas production from hydrate reservoir. Geological formation model of methane hydrate in marine sediments have been proposed by Xu and Ruppel (1999) and Rempel and Buffett (1997). Bhatnagar et al. (2006) have developed generalized 1-D model for hydrate saturation applicable to different geological settings.

A few hydrate experiments have been conducted in porous media to understand hydrate formation and dissociation. Yousif and Sloan (1991) have studied hydrate kinetics in a 1D Berea core, but they interpreted the results by an isothermal model. Recently, several hydrate formation and dissociation experiments in a ceramic core were reported (DOE Report, 2006). The present work is focused at the history matching of these hydrate formation and dissociation experiments using a kinetic simulator developed by Sun and Mohanty (2006). This simulator has been validated against several other simulators for the

problems in the code comparison study conducted by US DOE (Wilder et.al, 2008). The kinetic and transport parameters are varied to match the experimental results.

Experimental Method

The experimental data is taken from the DOE report (2006). Figure 1 shows the schematic of the core flood. The core was approximately 30.38 cm long and 3.81 cm in diameter. The porosity was 0.36. First, the core was saturated with methane at a pressure of 500 psi at the ambient temperature. Then it was injected with brine (with the outlet valve closed) until the pressure reached 2500 psi. The brine contained 6 wt% NaI. The gas saturation in the core was approximately 0.3 at 2500 psi and ambient temperature. This is considered as the initial condition for the hydrate formation experiment. At this state, the core was cooled by immersing the core holder in a liquid bath at 55 °F. As the fluids cool, their volume decreases. The core is kept connected to a brine pump which keeps the pressure constant at 2500 psi during this cooling step by pumping brine. Hydrate forms under these pressure and temperature conditions. This is continued for 124 hours; pressure and temperature are monitored. The system gets to a steady state with some amount of hydrate in the core. At t=124 hour, a piston pump connected to one end of the core is withdrawn at a constant rate of about 2.5ml/hr until t=172 hour. Withdrawal of the piston lowers the pressure and fluids are drawn into the piston. As the pressure falls, the hydrates start to dissociate. Methane gas and water are released. Dissociation of hydrate requires an enthalpy of dissociation. This heat is recruited from local porous medium in the short term and the temperature falls locally. Eventually, heat comes from the bath surrounding the core and temperature rises in the core. Temperature and pressure are monitored to show these temporal variations.

Modeling Methods

Numerical model.

The numerical model used is a 3-D finite-volume simulator that takes into account heat transfer, multiphase fluid flow, and kinetics of hydrates formation and dissociation (Sun and Mohanty, 2006). Energy and mass balance equations are solved in space and time domain. Four components (hydrate, methane, water and salt) and five phases (hydrate, gas, aqueous-phase, salt precipitate and ice) are considered in the simulator. The core of diameter 3.81 cm and length 30.38 cm was discretized typically in 5 radial grid blocks and 20 axial grid blocks. Single-point upstream weighting is used in the space discretization. The simulator uses a fully implicit scheme to solve the discretized equations in time. Newton-Raphson method is used to solve the non-linear equations. Water and ice are considered in equilibrium in a grid block at a particular temperature and pressure. The formation of gas hydrates uses kinetics from Kim et al. (1987). Primary variable switch method (PVSM) is used to track the phase saturations (Forsyth and Simpson, 1991). The simulator uses continuum-scale modeling, i.e., the coupling effects between thermodynamics, kinetics, and transport processes at the microscopic-scale are neglected.

Thermal properties.

Figure 2 shows the hydrate equilibrium (P_e - T) curve, and water-ice equilibrium curve with no salt in the system along with the empirical correlation obtained by Moridis (2003). P_e is the equilibrium pressure of three phase equilibria H+G+A and H+G+I at temperature T . The solid line at temperature 273.2K shows the equilibrium between water and ice. The whole curve shifts to the left as the salt concentration increases in brine due to colligative properties of salt. The region above the equilibrium curve is the hydrate stable zone and the region below is the gas stable zone. The region left of the solid line is the ice stable region and the region to the right is the water stable region. Solubility of methane in aqueous phase and water in gas phase, specific internal energy and specific enthalpy are taken from the literature and are listed by Sun et al. (2005). The heat transfer parameters for the base case are listed in Table 1.

Transport properties.

An empirical power law model (Civan, 2001)

$$\frac{K^e}{K_0} = \frac{\phi}{\phi_0} \left(\frac{\phi^e (1 - \phi_0)}{\phi_0 (1 - \phi^e)} \right)^{2\beta} \quad (2)$$

is used for calculating permeability. K^e is the effective permeability, K_0 is the reference permeability at reference porosity ϕ_0 . K_0 is 100md and ϕ_0 is 0.36 for the base case. The absolute permeability, K changes with ϕ according to Eq. 2 where ϕ_e equals to ϕ . ϕ^e is the effective porosity for the fluid phases which can be related to absolute porosity, ϕ as:

$$\phi^e = \phi(S_G + S_A) \quad (3)$$

β is a parameter assumed to be 2. S_j is the saturation of the j th phase based on absolute porosity whereas S_j^e is the effective saturation based on the effective porosity. The two saturations are related by

$$S_j^e = S_j \phi / \phi^e. \quad (4)$$

Brooks-Corey model is used for relative permeability, i.e.,

$$k_{rG} = k_{rG}^0 \left(S_G^{e*} \right)^{nG} \quad (5)$$

$$k_{rA} = k_{rA}^0 \left(S_A^{e*} \right)^{nA} \quad (6)$$

where k_{rj}^0 is the end point relative permeability and n_j is the exponential parameter for phase j . S_j^{e*} is normalized saturation of gas or aqueous phase based on the effective pore volume occupied.

$$S_j^{e*} = \frac{S_j^e - S_{jr}^e}{1 - S_{Gr}^e - S_{Ar}^e} \quad (7)$$

The capillary pressure is described by Eq. 8,

$$P_c = P_{ce} (S_A^{e*})^{-nc} \quad (8)$$

where n_c is a parameter for pore structure and P_{ce} is the entry capillary pressure which is related to effective porosity as:

$$P_{ce} = p_{ce0} \sqrt{\frac{\phi^e K_0}{\phi_0 K^e}} \quad (9)$$

where, p_{ce0} is the entry capillary pressure at the absolute porosity ϕ_0 . The residual saturation in Eq. 7 is also based on the effective porosity. For the present case, the residual saturation is assumed to be 0.1 for the aqueous phase and 0.2 for gas phase. Some of the hydrate properties are listed in Table 1.

Kinetic model.

The rate of methane to hydrate conversion is assumed to be governed by the Kim-Bishnoi model (Kim et al., 1987; Clarke and Bishnoi, 2000, 2001),

$$r^m = k A_s (f - f_{eq}) \quad (10)$$

where, r^m (mol/m³s) is the consumption rate of methane; k (mol/(m².Pa.s)) is the kinetic constant of hydrate formation or dissociation; A_s (m²/m³) is the reaction surface area per unit volume of core, which is the interface area between hydrate particles and the surrounding phases and is a function of effective porosity; f (Pa) is the fugacity of methane under the local temperature and pressure; f_{eq} is methane fugacity at the equilibrium pressure corresponding to the local temperature.

Results and discussion

Hydrate was formed at 2500 psi by cooling the core from 70 °F to 55 °F. Brine was injected to maintain the core pressure at 2500 psi. In the base case of simulation, the core was considered homogeneous with a porosity of 0.36 and a reference permeability of 100 md. At $t=0$ the saturation of gas was 0.3 and brine 0.7. Figure 3(a, b, c) shows the pressure, temperature and brine injection in the experiment and their comparison with the base case simulation results (reference permeability 100md). Time $t=0$ corresponds to the condition when the bath temperature is changed to 55 °F.

The fluid volume falls initially because gas contracts with the lowering of the temperature for about 6 hours. About 3 ml of brine is injected to keep the pressure at 2500 psi. Injection in the first 6 hours of simulation is slightly higher than that in the experiment. In experimental results between 6 hours and 12 hours the rate of brine injection increases. At this time hydrate starts forming. Volume shrinks because of hydrate formation. One molecule of methane reacts with ~6 molecules of water to form one molecule of hydrate. At 2500 psi, about 1 ml of methane gas reacts with about 0.8 ml of water to form 1 ml of hydrate. Thus the volume of shrinkage is 0.8 ml per ml of hydrate formed. This shrinkage is filled by the brine pumped which increases sharply at 6 hr. By about 12 hr, the hydrate formation and hence brine injection slow down, but continue at a slower rate up to 123 hours. In the case of simulation with reference permeability 100md, the hydrate formation completes at 12 hours and there is no further brine injection into the core. The total brine injection is approximately 27 ml for the experiment and 31 ml for the simulation.

In Figure 3 (b) surface temperature of the core in the simulation is compared with the temperature of the core in the experiment. The core temperature falls to about 55 °F in about 6 hours. The temperature has a local peak between 6 and 12 hr. This is the time at which the hydrates form rapidly. Hydrate formation is an exothermic process; the heat of hydrate formation is released into the core. The conductivity of the core and core holder is not large enough to conduct this heat to the bath rapidly. Thus the local temperature goes up. Beyond 12 hr, hydrates form, heat is released, but the rate is slow enough for it to be conducted away; therefore the temperature does not change much beyond 12 hr. The temperature change in the simulation is qualitatively similar; the temperature peak is a little higher than that in the experiment.

Figure 3(c) compares the pressure. The pressure is maintained at 2500psi at the injection end of the core during the experiment. It dips to about 2450 psi at the pressure tap in the middle of the core between 6 hr and 12 hr for the experiment

while the dip in the simulation results is insignificant. This again can be attributed to the homogeneity and high permeability in the simulation which maintains close to uniform pressure everywhere in the core.

Figure 4(a, b) compares the experimental results for dissociation of hydrates with the base case simulation. The hydrate formation is stopped at 123 hr and the dissociation is initiated. A piston pump connected to the inlet of the core is withdrawn at a rate of 2.5ml/hr to decrease the pressure. The pressure and temperature of the core are monitored. In the experiment, the pressure falls at a fast rate for the first 3 hours, then falls slowly from 3 to 15 hours and then falls at a medium rate. The decline in the simulated pressure has the same 3 stages, but it is different from the experimental data quantitatively. Because of fluid withdrawal, the pressure declines fast in the beginning. In the experiment, there is some amount of gas at the beginning of depressurization; in the base case simulation, there is no initial gas. Thus in the simulation, pressure falls at a faster rate. As the pressure hits the equilibrium brine-gas-hydrate pressure, hydrate starts dissociating and some of the methane gas starts flowing out. This is also seen on the effluent density in the experiments. The pressure does not fall in the second stage as fast as before, because of the gas release between 5 and 15 hr due to hydrate dissociation. During this time, the temperature of the core surface falls below the previous temperature by about 2 °F and returns back (Figure 4b). Hydrate dissociation is an endothermic process. Heat of hydrate formation is taken locally to dissociate the hydrate. After the most of the hydrates dissociate, the heat is supplied by the bath to maintain the temperature at 55 °F. Beyond 15 hr, there is only small amount of dissociation, if any. After 15 hours when the piston cell volume is expanded, the methane gas in the core expands. The pressure follows Boyle's Law with increasing volume of gas in the core. The depletion experiment is stopped at 47 hours. The final pressure is 625 psi. In the case of simulation with 100md permeability (Figure 4a), the pressure is maintained at about 1333 psi between 1 and 21 hr after which it starts to follow the Boyle's law. With a homogeneous core of 100md considered in the base case simulation the formation and dissociation experiments can be matched qualitatively, but not quantitatively.

Sensitivity analysis.

The sensitivity of the simulation results was studied with respect to several simulation parameters: core permeability, kinetics of hydrate formation reaction, and heat transfer coefficient between core and temperature bath.

Permeability.

Figure 5 compares the simulation results for brine injection, temperature and pressure for a homogeneous core with different reference permeability. At the permeability of 100 md, it takes about 12 hr to form all the hydrates in the core (in simulation). If the reference permeability is 0.1 md, the hydrate formation slows down as shown in Figure 5(a) by the amount of brine injected to maintain the pressure. The hydrate formation completes in 76 hr after which no brine is injected into the system. The hydrate formation is slower than in experiment from 6 to 12 hours, but faster after 12 hours. When the reference permeability is 0.01 md, hydrate formation is extremely slow; less than half the hydrate is formed in 123 hours. Simulation shows that the pressure in the core decreases due to hydrate formation and low permeability; the pump is not able to maintain 2500psi pressure leading to less hydrate formation. Figure 5(b) shows the temperature comparison. As the permeability decreases, the temperature peak decreases and the reversal of temperature starts earlier. This is due to lower rate of hydrate formation with decreasing permeability. For 0.01md permeability the hydrate formation is so slow that there is no peak in the temperature curve. Figure 5(c) shows the pressure curve for different permeabilities. For 0.1md permeability the pressure falls more as compared to 100 md case. This is because hydrate formation shrinks the volume and due to low permeability brine injection takes time to fill that volume during which pressure falls. For 0.01 md permeability pressure fall is even more.

Reaction rate and heat transfer coefficient.

Figure 6(a, b) shows the sensitivity of the hydrate formation process to hydrate formation kinetics and heat transfer coefficient between bath and the core. For the base case, the Arrhenius constant for formation reaction is 36 kg/MPa/m²/s. For slow kinetics, it was decreased to 3.6 kg/MPa/m²/s and as the reaction rate slows down the peak of temperature rise shifts right (Figure 6a). The temperature rise in the core also decreases. Due to slow formation rate of hydrates the injection rate of brine also slows down as shown in Figure 6(b). For the base case, the heat transfer coefficient between the bath and the core is considered to be 10 W/m²/s. When the heat transfer coefficient is decreased to 5 W/m²/s the peak in temperature rise become flat because the heat transfer to the bath is slow due to the decreased coefficient. As the temperature in the core increases the hydrate formation rate slows down slowing the brine injection rate as shown in Figure 6(b). The combination of slow kinetics and low heat transfer coefficient shifts the peak of temperature rise and decreases the temperature rise and the peak flattens.

In simulation a homogenous porosity and permeability core is considered, while the core can be heterogeneous. Some of the volume in the core which might be blocked by low permeability region will not be easily accessible and hydrate formation will be slow in that region. Hydrate formation shrinks the volume and brine is injected to keep the pressure constant. Hence the brine injection rate will be slow for that region. So sensitivity to heterogeneity is studied.,.

Heterogeneity.

From the brine injection curves in Figure 5, the experimental result matches with the homogeneous 100md permeability simulation for the first 12 hours after which simulated hydrate formation rate exceeds that of the experiment. This could be due to the presence of some low permeability regions in the real core. We have considered permeability variations in a core, as shown in Figure 7. A low permeability region is considered in the middle of the high permeability core. Table 2 lists the permeability variations studied. To vary the permeability (without hydrate) of a core at a particular location the reference permeability in equation 2 is varied for those locations. In the simulation, the middle 10 grid blocks are given a low reference permeability as opposed to 100md in all other grid blocks. Everything else was kept the same as in the base case. If the low permeability region is at the middle and the low permeability is 0.1 md, then this kind of permeability variation is represented as '0.1md at 50'. If the 0.1md permeability region is after 75% of axial core distance from side 'A' in Figure 7, it is represented as '0.1md at 75'.

Figure 8(a) compares simulated brine injection during hydrate formation in the heterogeneous cases. If the low permeability region is at the middle and permeability of the low permeability region is greater than 5 md, then the brine injection profile is not very different from the homogeneous case. As the permeability of the low permeability region decreases, the hydrate formation slows down. For 1 md low permeability region, it takes more than 123 hr to complete hydrate formation. For 0.1 md low permeability region, the right half of the core essentially gets disconnected from the left side after hydrate forms and hydrate formation is very slow in the right half. When a low permeability (0.1md) region is at 75% distance from the injection side the 25% of the core is difficult to access. The hydrate formation completes in first 3/4th of the core and brine injection is complete for that part. For the rest 25% of the core brine keeps injecting at a very slow rate.

The temperature rise in Figure 8(b) decreases with the decrease in amount of hydrate formation until 12 hr. Figure 4(c) shows the pressure which remains approximately constant. This implies that the initial dip in pressure (experimental results) is from a low permeability region near side A of the core. In case of simulation, the low permeability region extends through the whole cross-section blocking the 2nd half of the core by a low permeability region. This may not be true in the experiment core. The core used in experiment may have several low permeability regions without totally blocking any cross-section.

Figure 9 shows in-situ profiles for the '1md at 50' case. Figure 9(a) shows hydrate saturation profiles after 4, 12 and 120 hr. Hydrate starts forming in low permeability region and near side B. The hydrate starts forming near side B because injection of brine from side A pushes the gas away towards side B. The gas that is pushed often builds up near/in the low permeability region and hydrate saturation is high in that region. Due to high hydrate saturation effective porosity decreases and permeability decreases further. Figure 9(b) shows gas pressure profiles after 4, 12 and 120 hr. The gas pressure is low in the 2nd half. This is because of the low permeability region, which does not allow much brine to flow through it. The hydrate formation continues as pressure increases with injection of brine. Figure 9(c) shows the temperature profile after 4, 6, 9 and 120 hr in Kelvins. The temperature increases the most in the low permeability region due to high hydrate formation. After 9 hours the temperature in first half is higher because hydrate formation is fast there due to high pressure being maintained in that region. After about 12 hours the hydrate formation rate decreases and temperature is constant everywhere. Figure 9(d) shows the aqueous saturation profiles after 4, 12 and 120 hours; the aqueous saturation is low in 2nd half because of the low permeability region. Aqueous saturation is lowest in the low permeability region because more gas and water are consumed there during hydrate formation.

Dissociation simulation is performed for the heterogeneous case with a low-perm region of 1md in the middle of the core. The dissociation temperature decrease shows the two dips in Figure 10(a). The 2nd half of the core is blocked and after formation of hydrates the pressure in the region was lower than 2500psi (about 1450psi), maintained at the end A of the core. When the pressure lowers at the end A, hydrate dissociation takes place in the first half of the core and the temperature decreases. The low-perm region hinders the pressure distribution. When the pressure lowers in the 2nd half of the core the temperature decreases again but to a lesser extent as a small amount of hydrate dissociates.

Figure 10(b) shows the pressure for dissociation. The pressure for simulation is shown for a grid block in the 2nd half of the core, as shown in Figure 7. The pressure is low (about 1450psi) and maintains at about the same pressure until all hydrates in the first half of the core dissociate. Then the pressure falls for some time and then hydrate in 2nd half starts dissociating to form gas which increases pressure. After hydrate dissociation is complete, the Boyle's law is followed. This effect of decreasing and then increasing pressure is prominent due to the full blockage of a part of core axially. If the inaccessible volume comprises of several isolated volumes, then the pressure curve will be smooth and may match the experimental results.

Figure 11 shows in-situ profiles of hydrate saturation, gas pressure and temperature. The hydrate saturation profile in Figure 11(a) shows that hydrate dissociates in the 1st half of the core as the pressure decreases only in the 1st half (Figure 11b). After some time the dissociation in the 2nd half starts and pressure in first half increases due to gas coming from the 2nd half of the

core. Temperature does not vary much, but it decreases in first half first and then dissociation in 2nd half lowers the temperature there (Figure 11c).

Conclusion

- The hydrate formation and dissociation in a core are sensitive to permeability, permeability variation and heat transfer.
- The position and permeability of low perm region are very important parameters.
- During hydrate formation heat is released which increases the local temperature temporarily. The reverse occurs during hydrate dissociation.

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Table 1: Parameters for hydrate and sand

Hydrate Density	910kg/m ³
Hydrate heat Conductivity	0.49W/m/K
Hydrate Heat Capacity	1.62kJ/kg/K
Ice density	917.1kg/m ³
Sand density	2670kg/m ³
Sand Heat Conductivity	5.57W/m/K
Sand Heat Capacity	0.83kJ/kg/K
Porosity	0.36
Reference permeability	100md

Table 2: Heterogeneity cases used in simulation

Distance of low-perm region from injection side as a fraction of core length	Reference permeability of the low-perm region	Name
0.75	0.1md	0.1md at 75
0.5	0.1md	0.1md at 50
0.5	10md	10md at 50
0.5	5md	5md at 50
0.5	1md	1md at 50

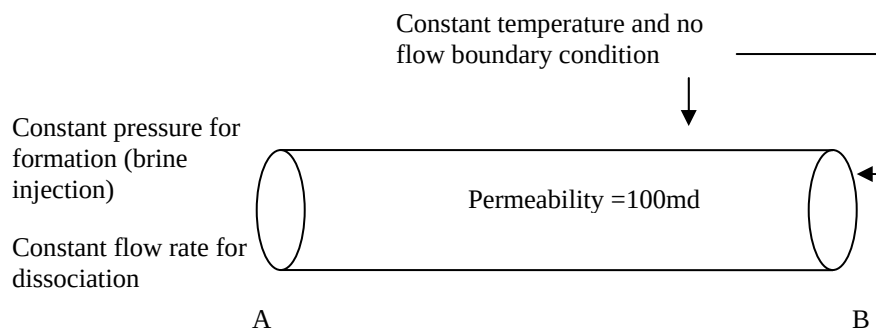


Figure 1: Schematic of experimental apparatus for hydrate formation

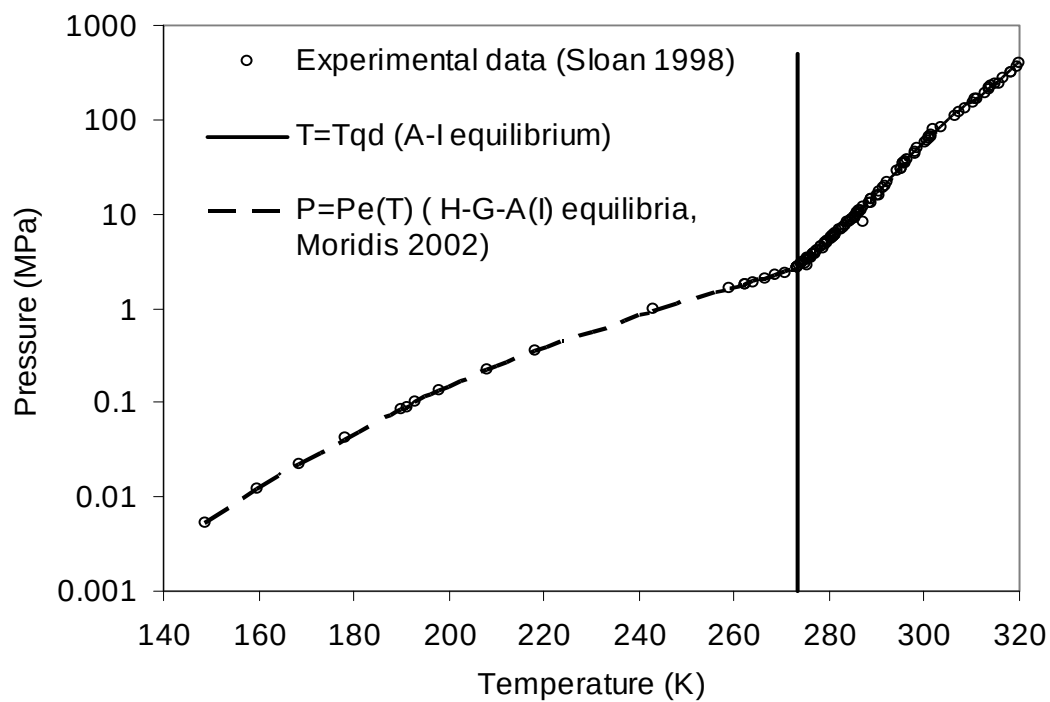


Figure 2: Equilibrium curve for methane hydrate

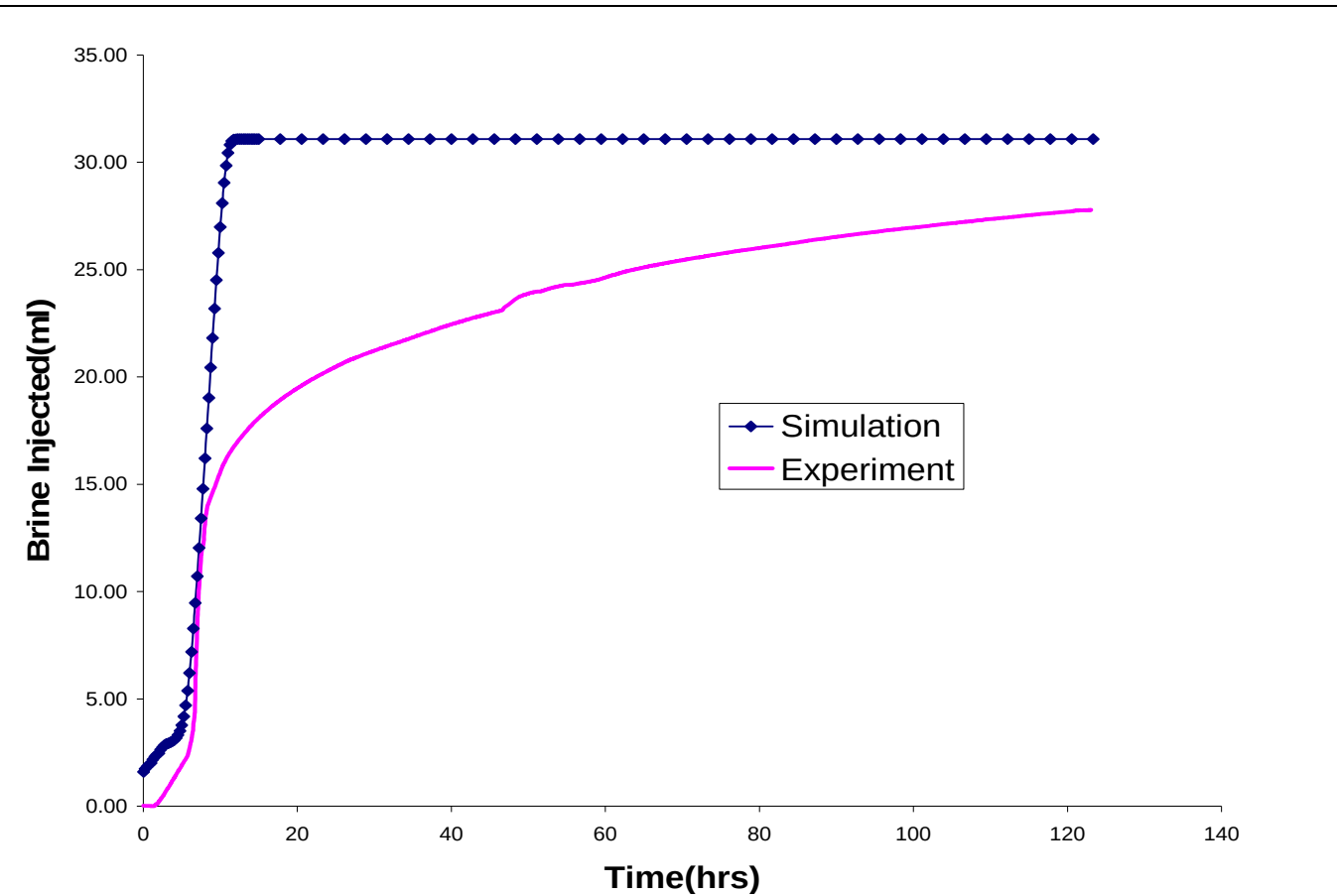


Figure 3(a): Brine injection during hydrate formation

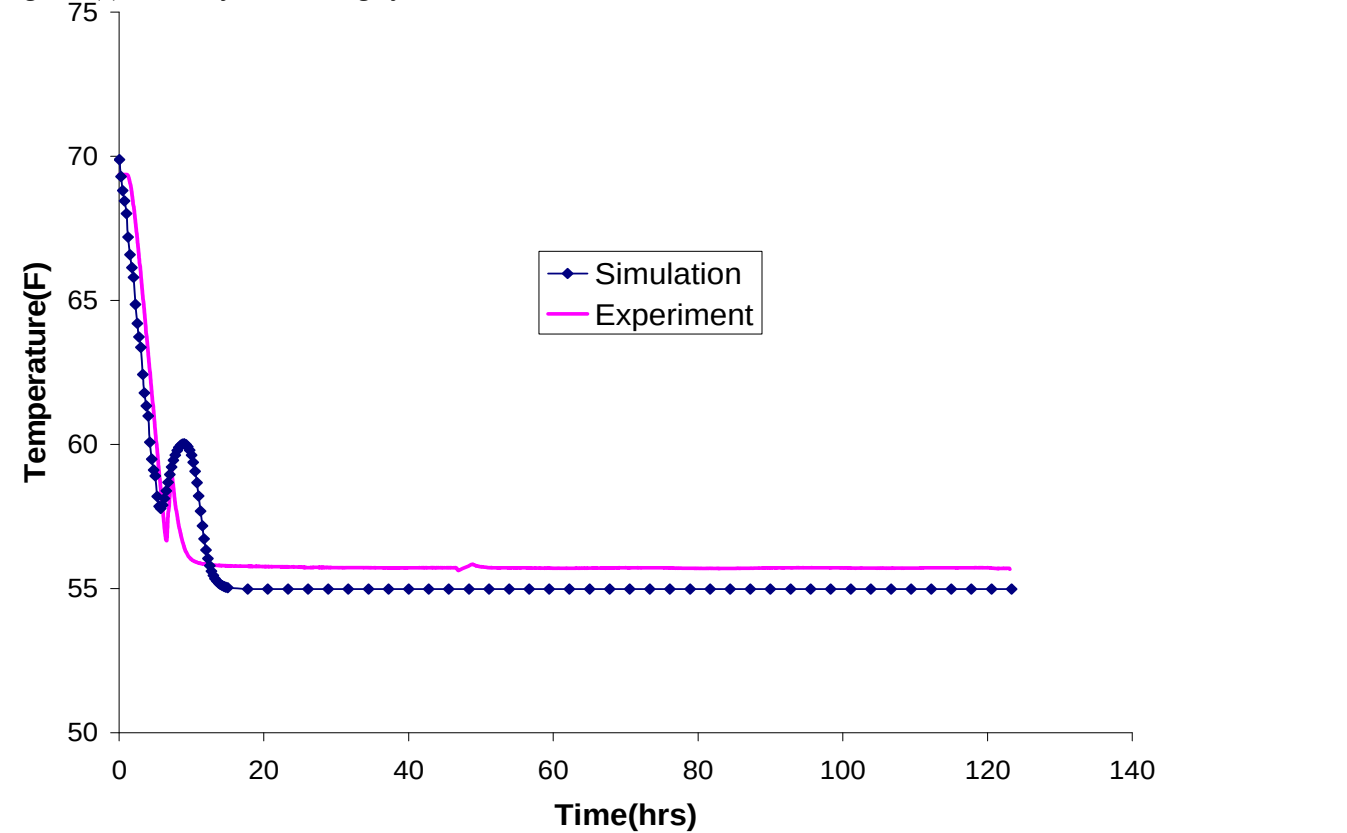


Figure 3(b): Core temperature evolution during hydrate formation

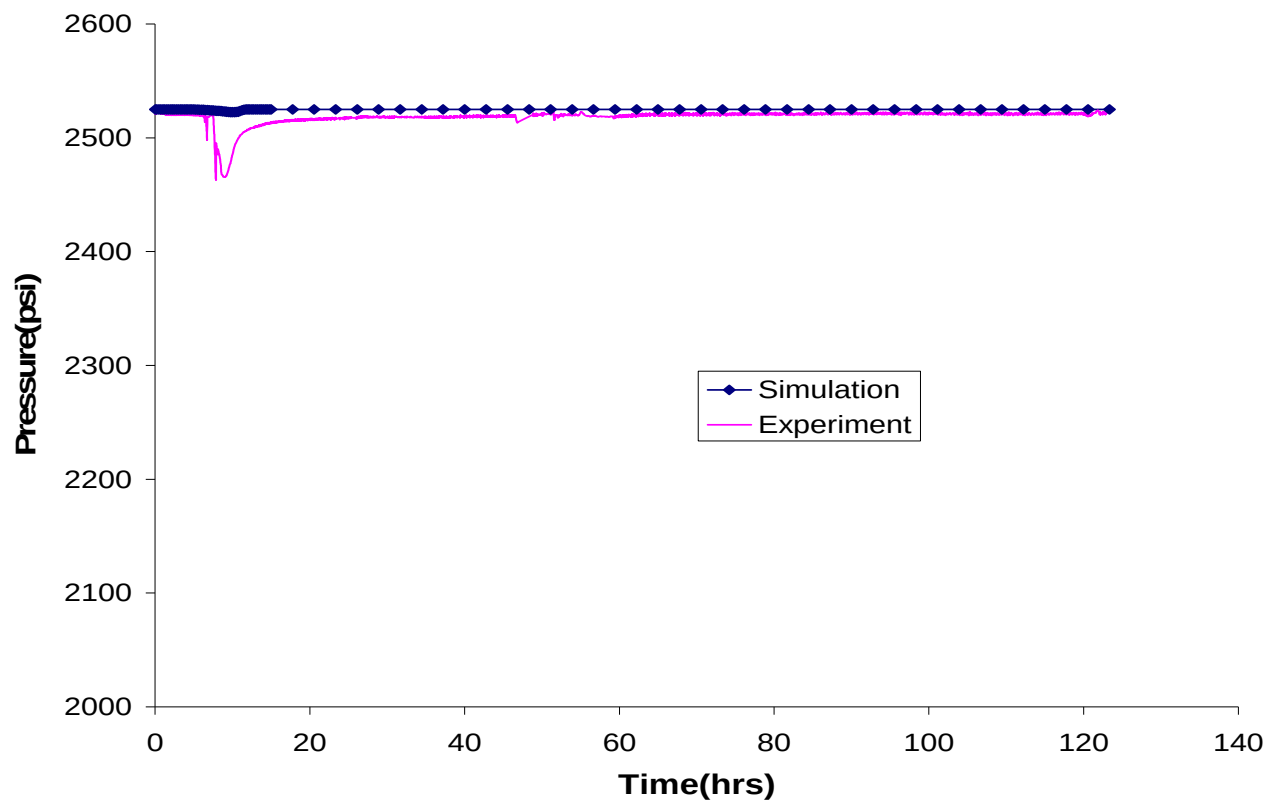


Figure 3(c): Core pressure during hydrate formation

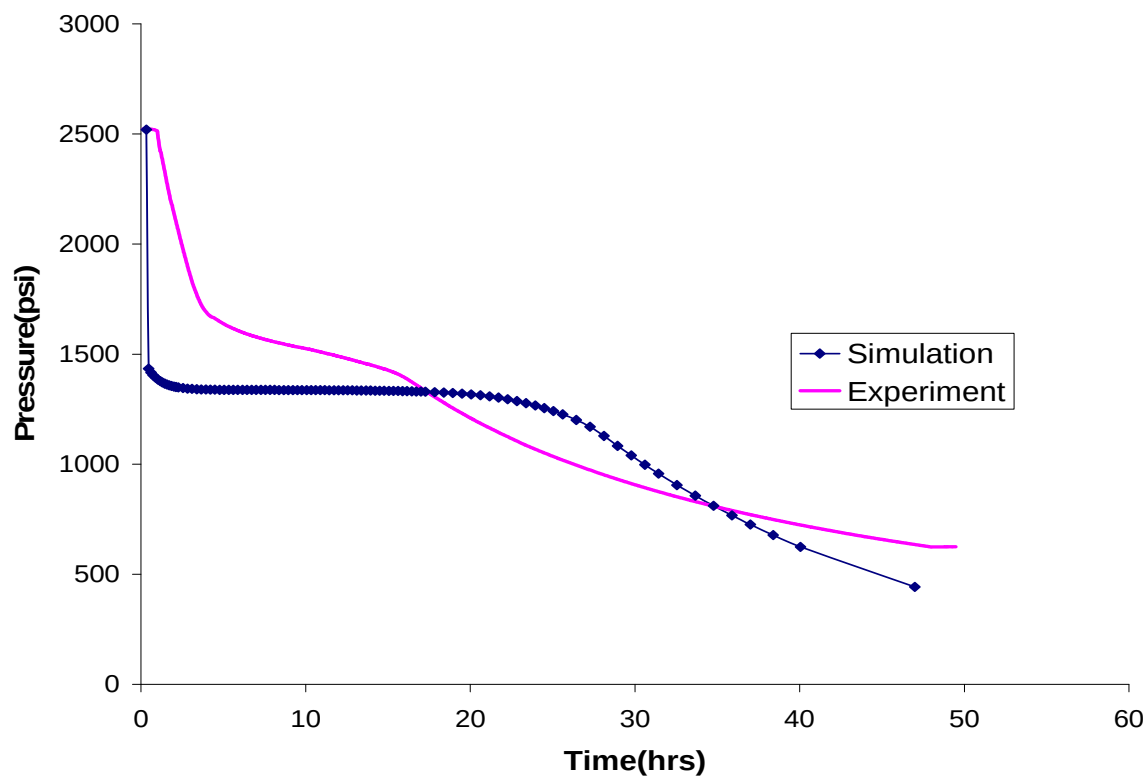


Figure 4(a): Core pressure during hydrate dissociation

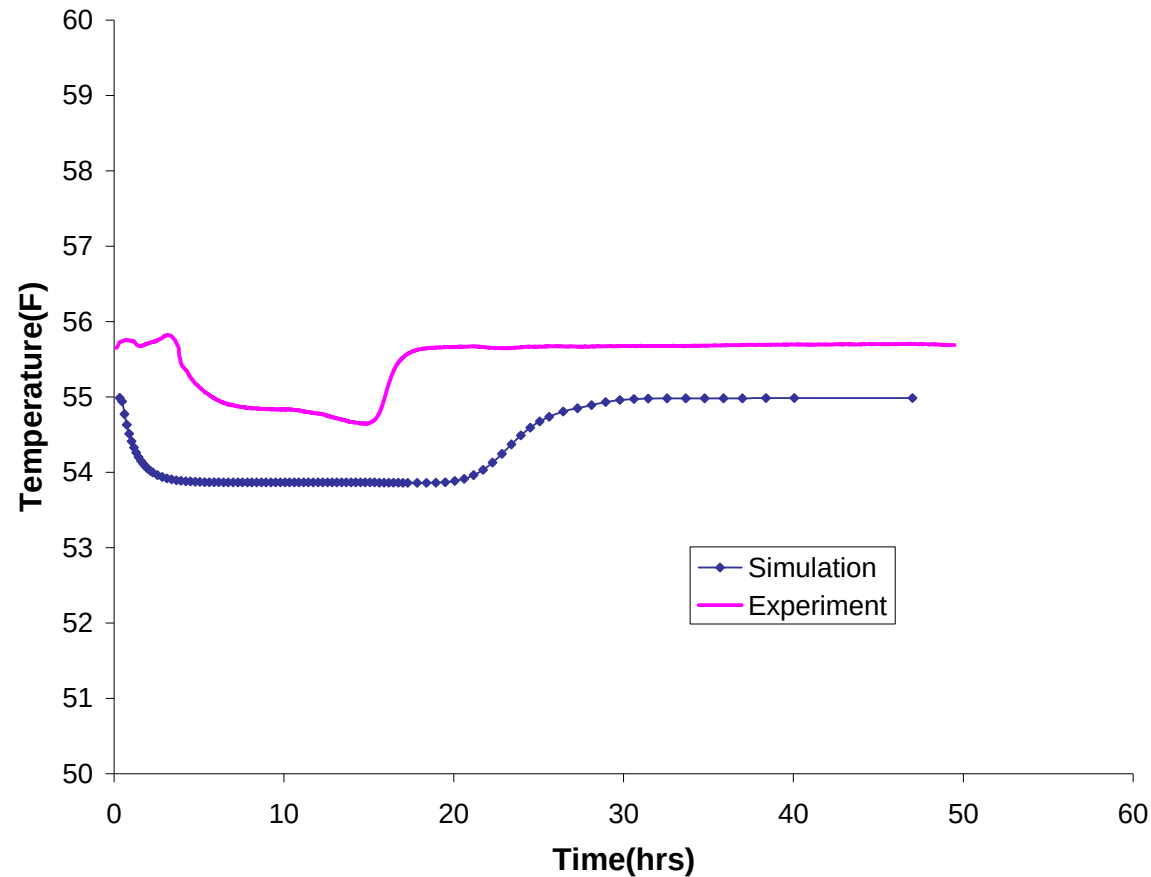


Figure 4(b): Core temperature during hydrate dissociation

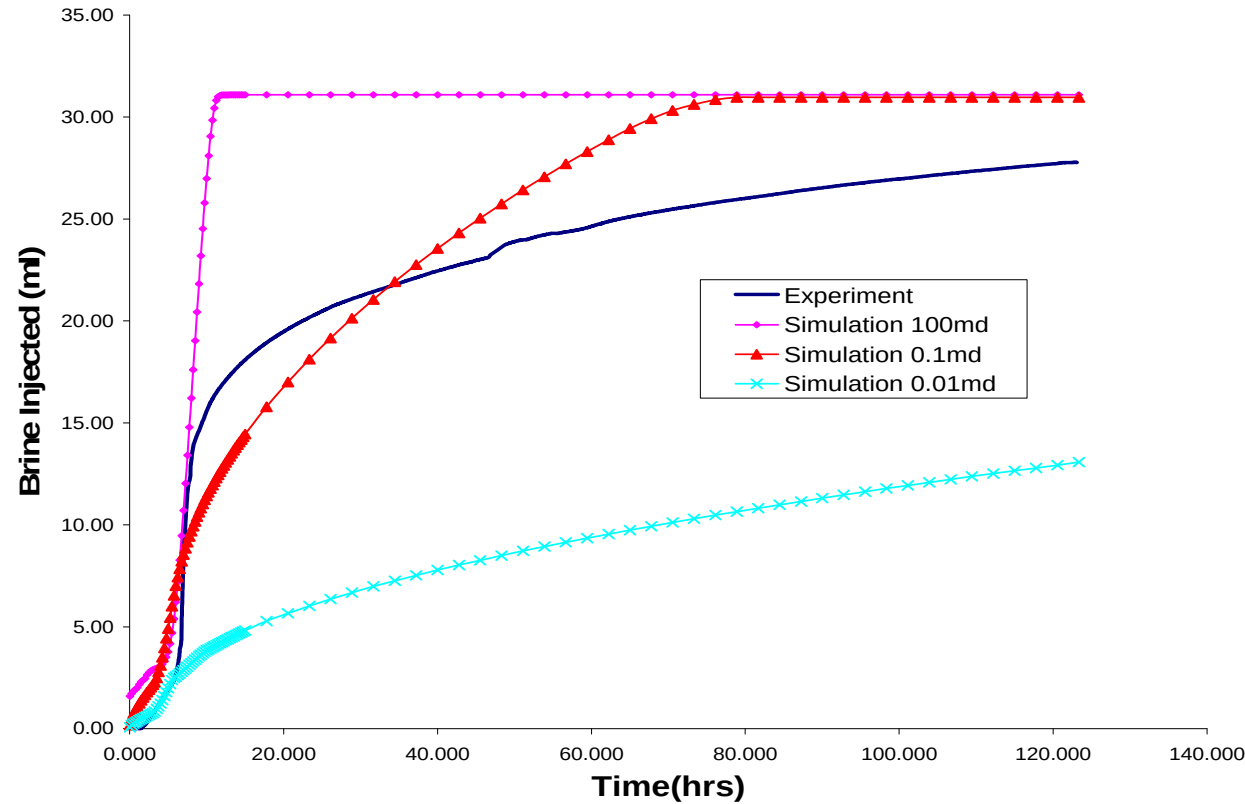


Figure 5(a): Brine injection sensitivity with permeability for formation experiment

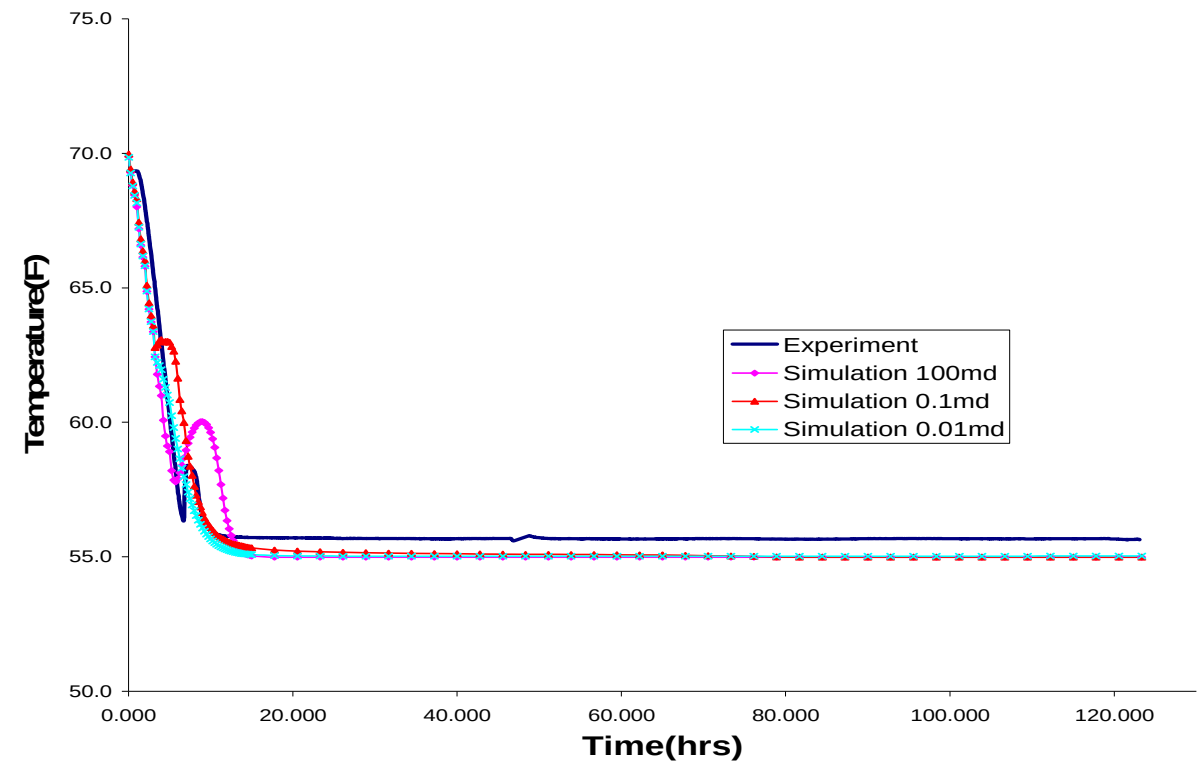


Figure 5(b): Temperature sensitivity with permeability for formation experiment

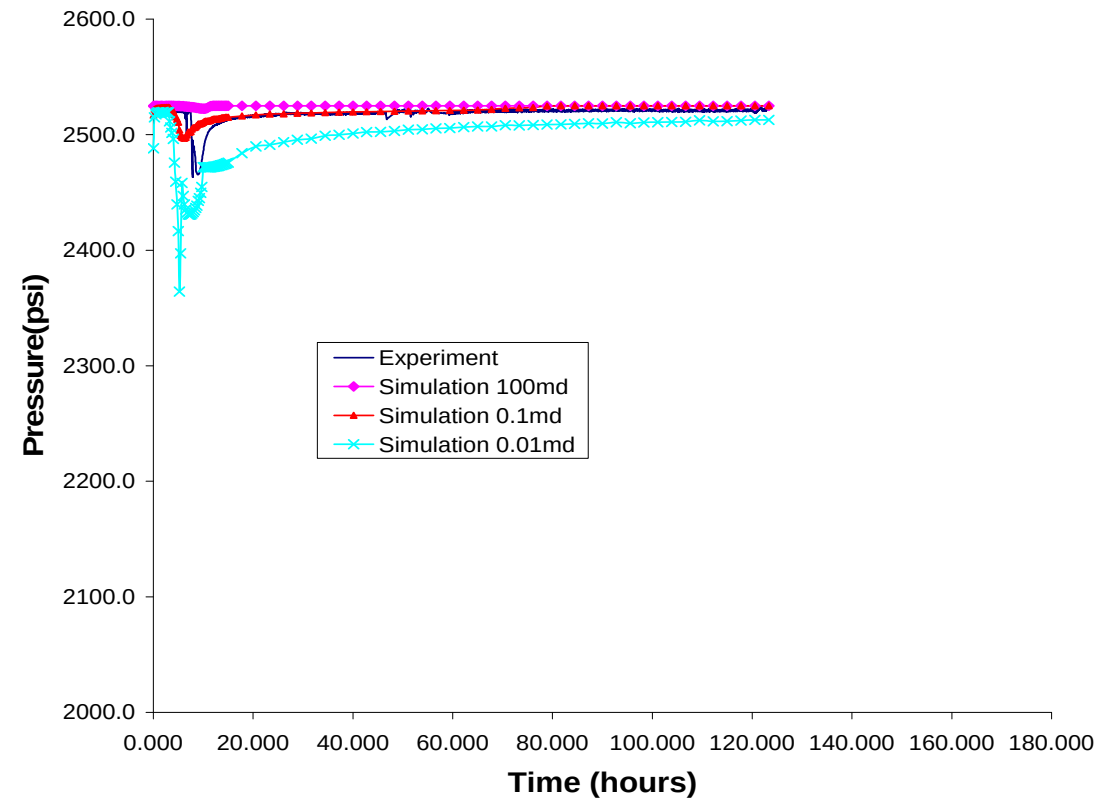


Figure 5(c): Pressure sensitivity with permeability for formation experiment

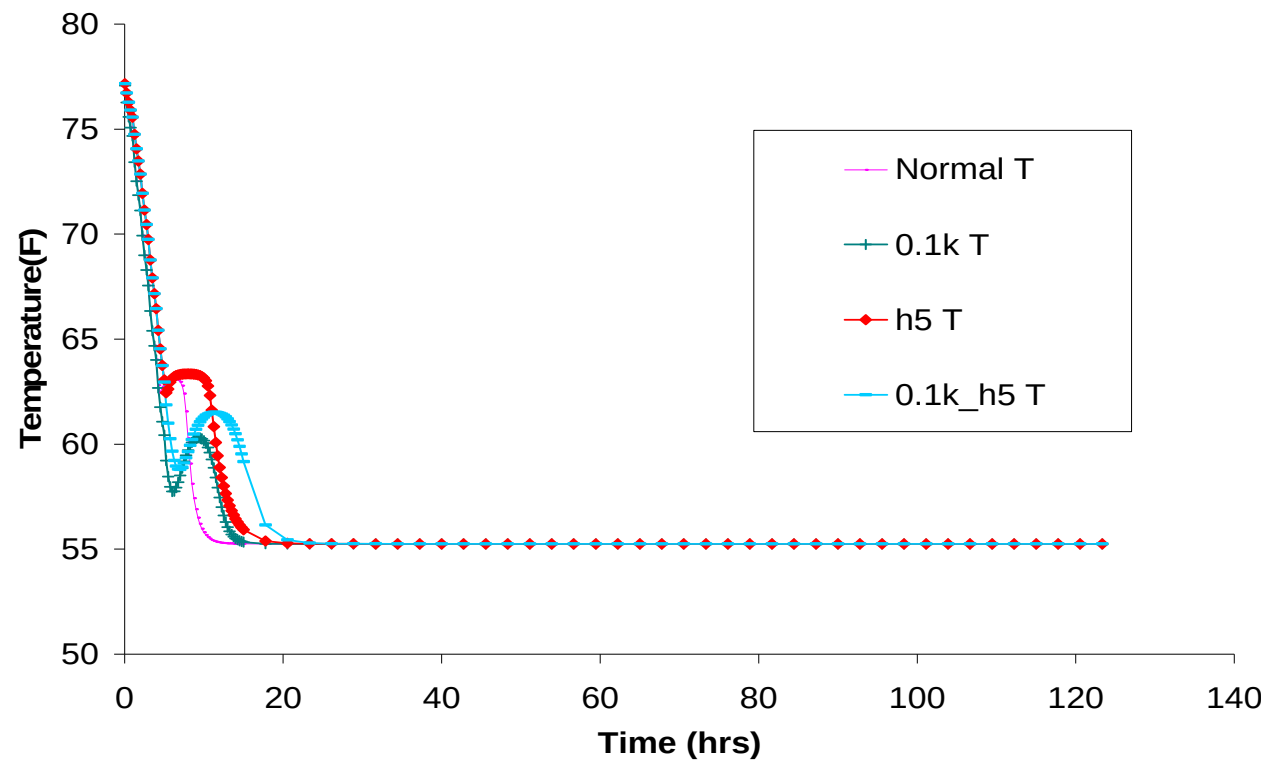


Figure 6(a): Sensitivity of temperature to kinetics constant and heat transfer coefficient

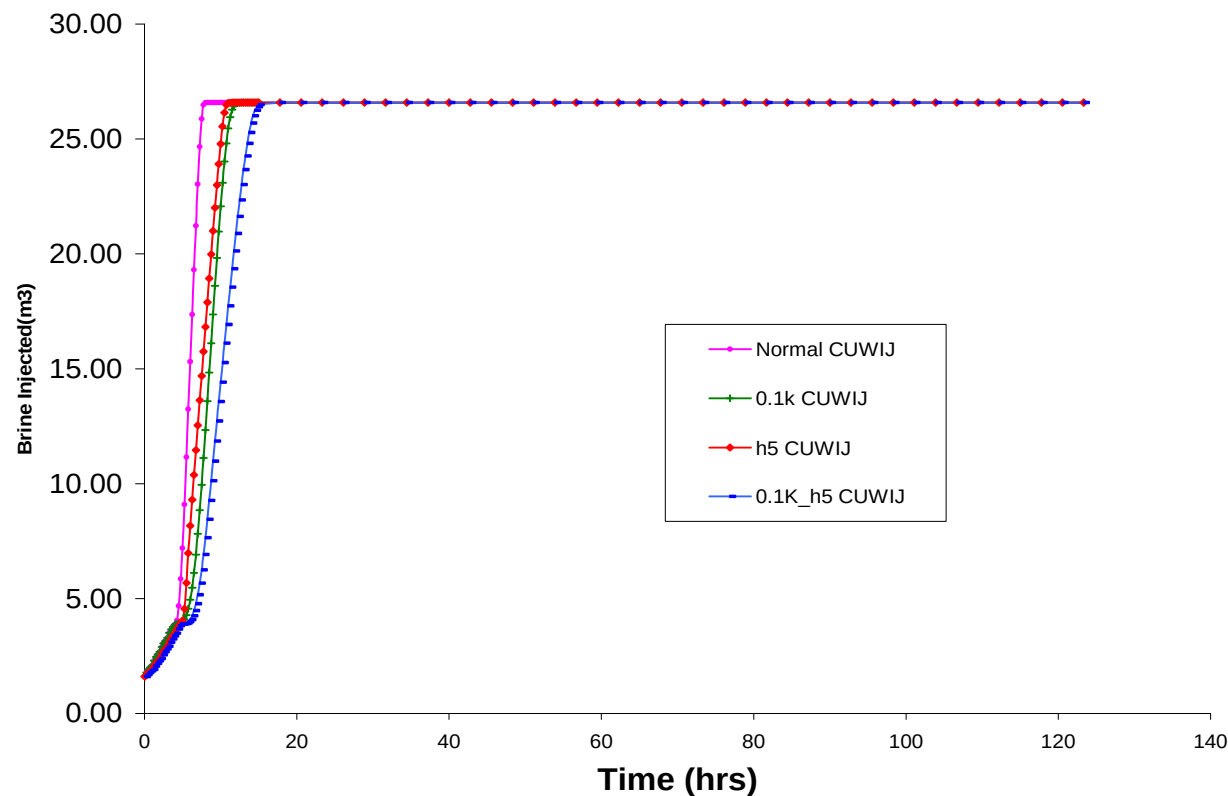


Figure 6(b): Sensitivity of brine injection to kinetics constant and heat transfer coefficient

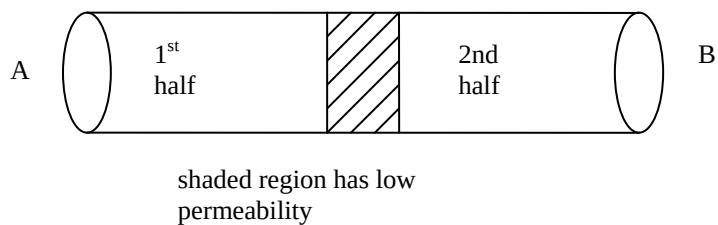


Figure 7: Schematic of a heterogeneous core with a low permeability region in the middle

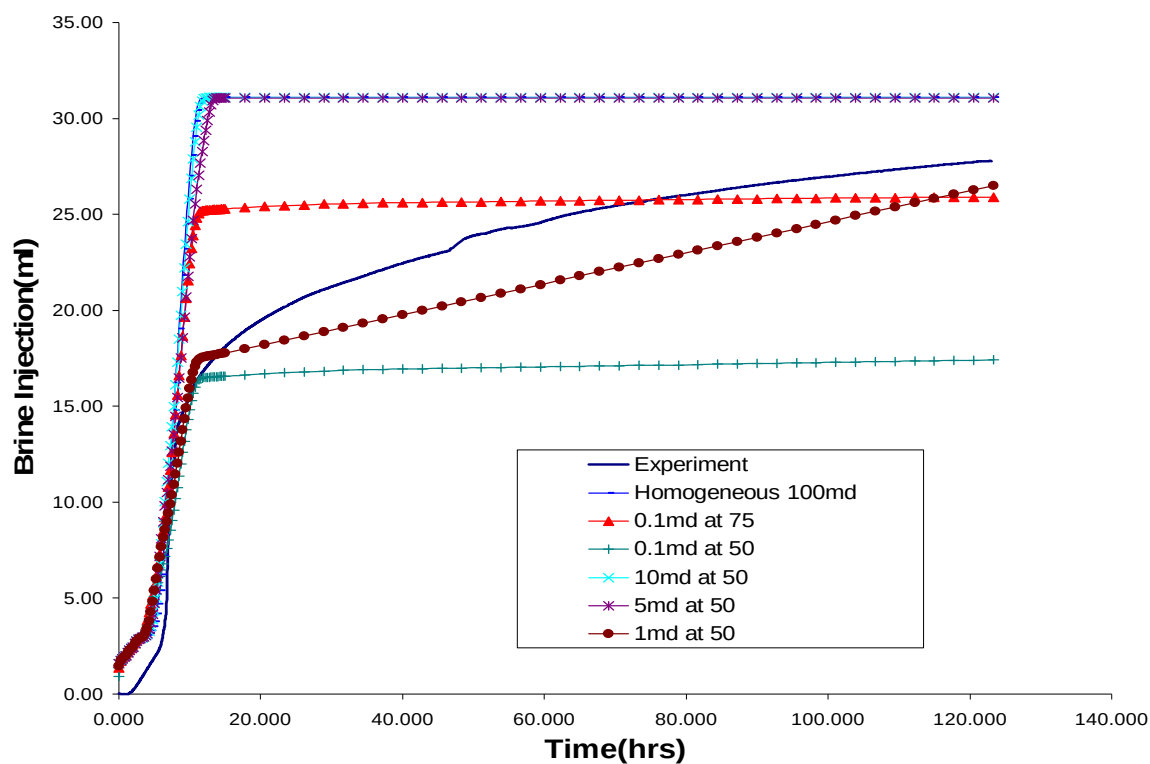


Figure 8(a): Sensitivity of brine injection to heterogeneity during formation experiment

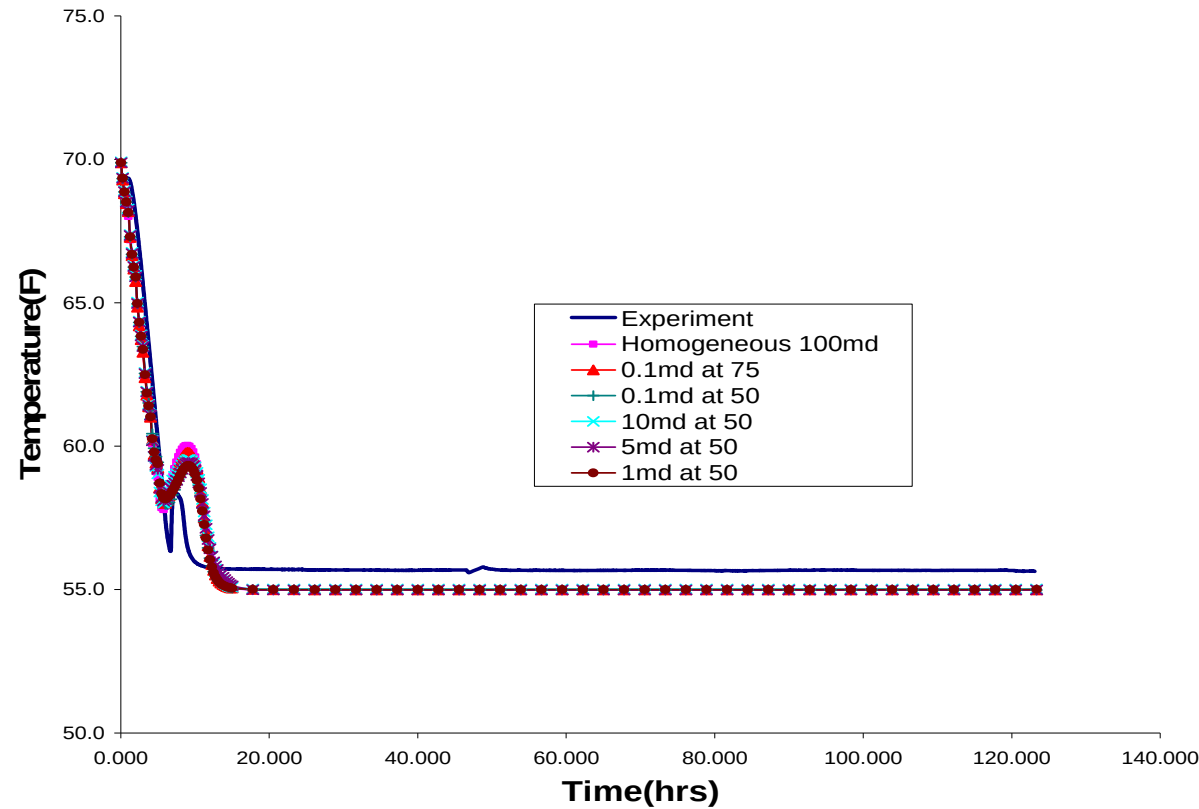


Figure 8(b): Sensitivity of temperature to heterogeneity during formation experiment

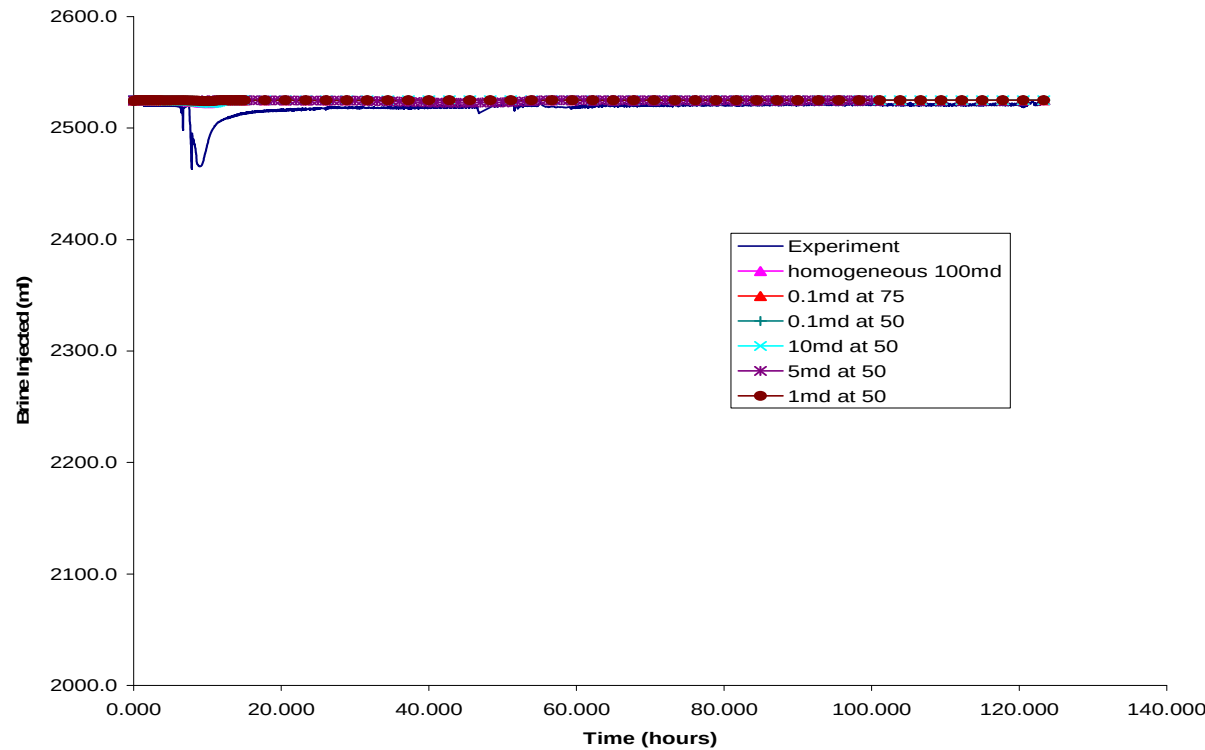


Figure 8(c): Sensitivity of pressure to heterogeneity during formation experiment

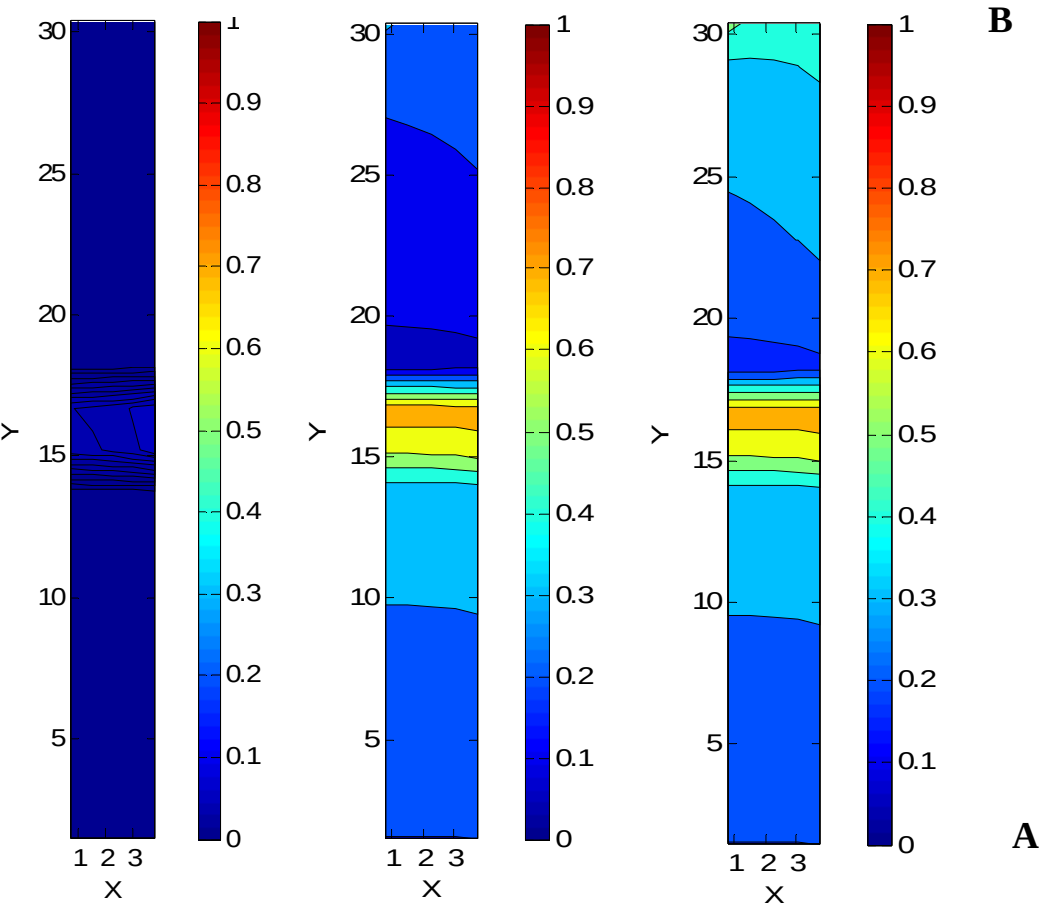


Figure 9(a) Hydrate saturation profiles after 4, 12 and 120 hours of formation time for ‘1md at 50’ case

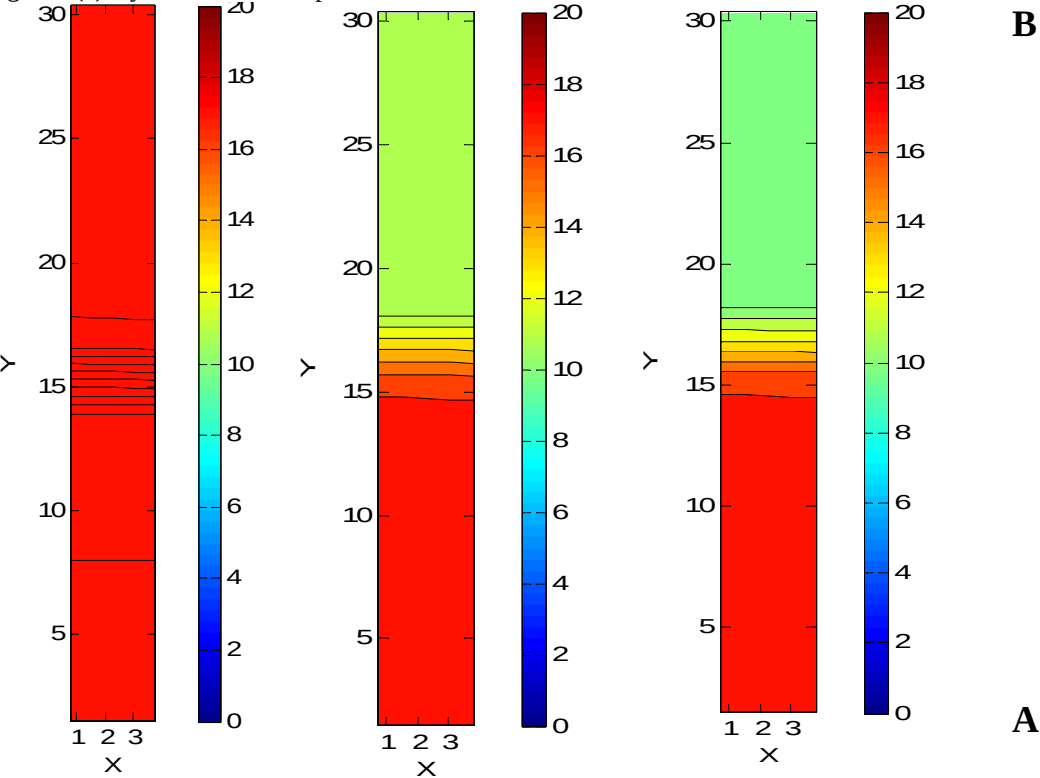


Figure 9(b) Gas pressure profiles after 4, 12 and 120 hours of formation time for ‘1md at 50’ case

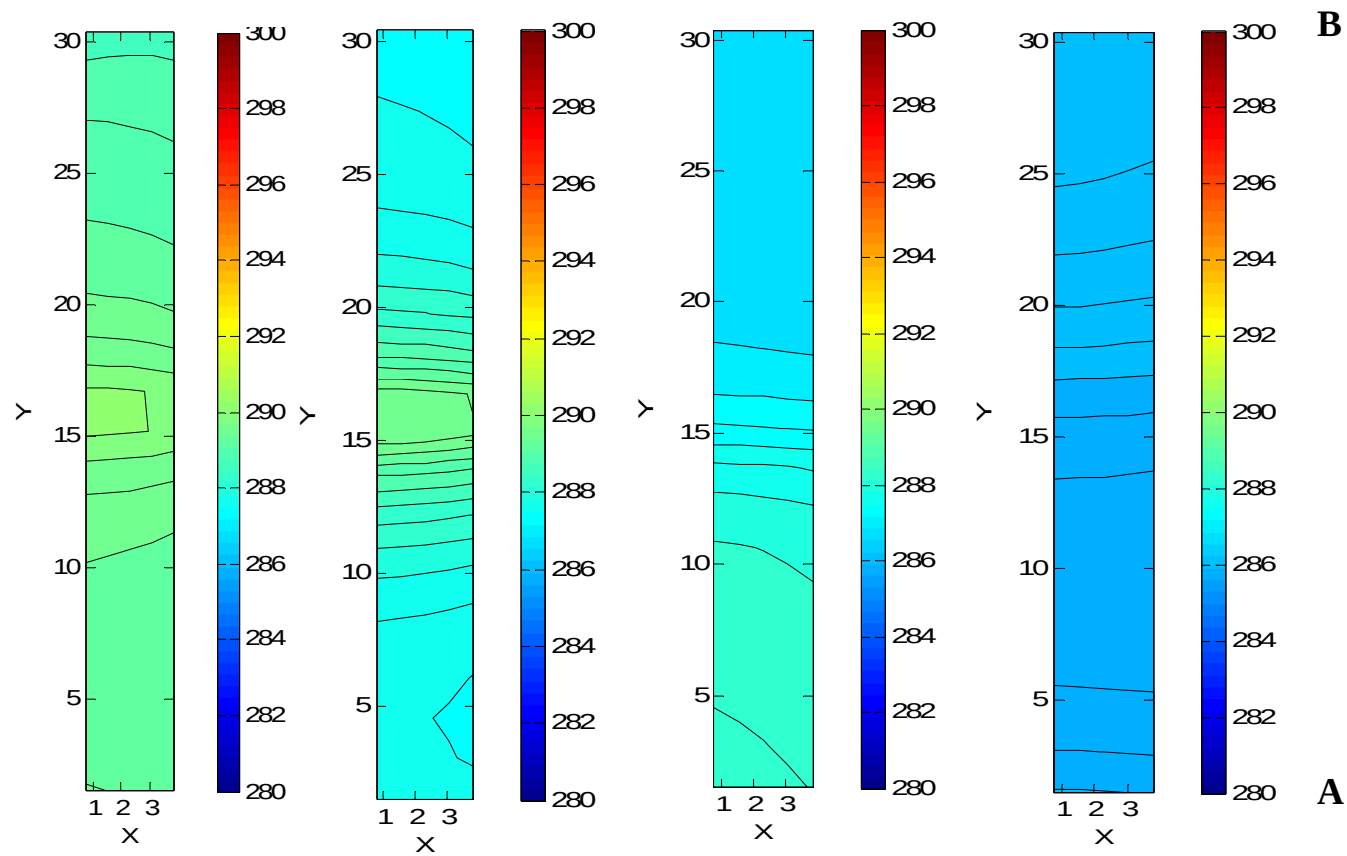


Figure 9(c) Temperature profiles after 4, 6, 9 and 120 hours of formation time for '1md at 50' case

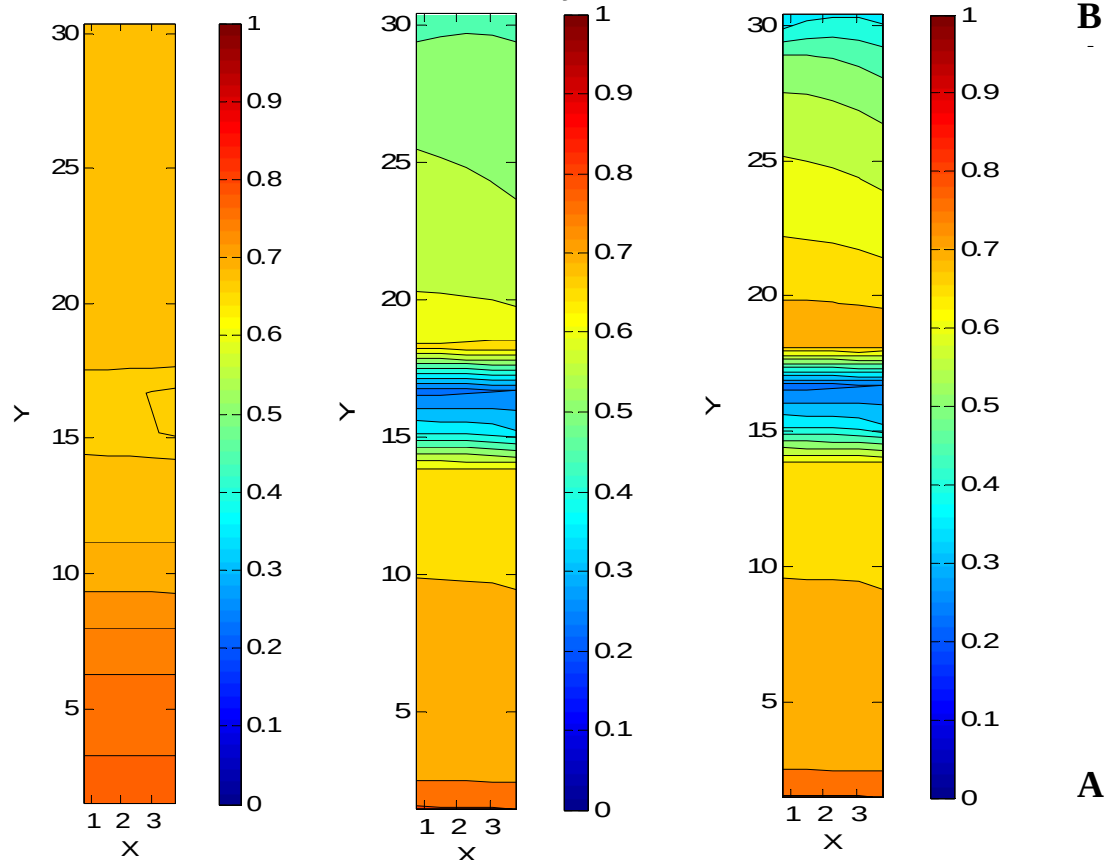


Figure 9(d): Aqueous saturation profiles after 4, 12 and 120 hours of formation time for '1md at 50' case

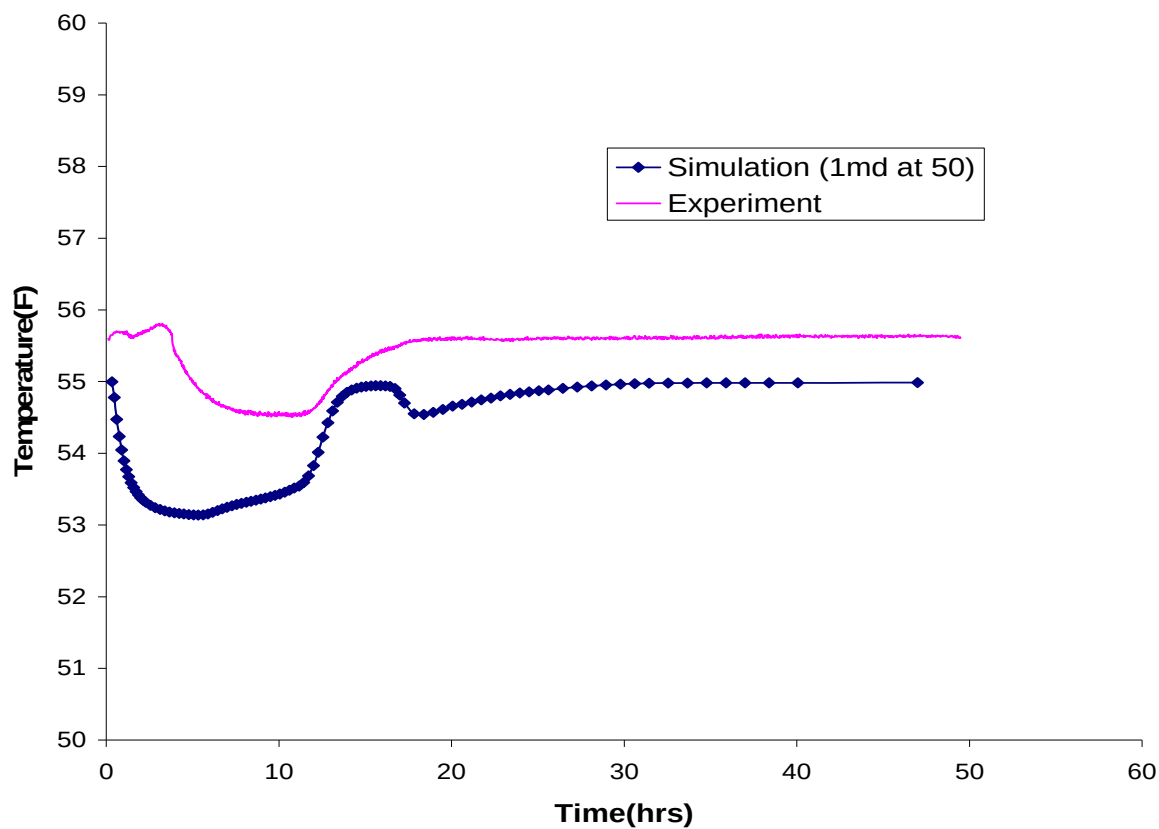


Figure 10(a): Comparison of dissociation temperature for '1md at 50' case with experimental results

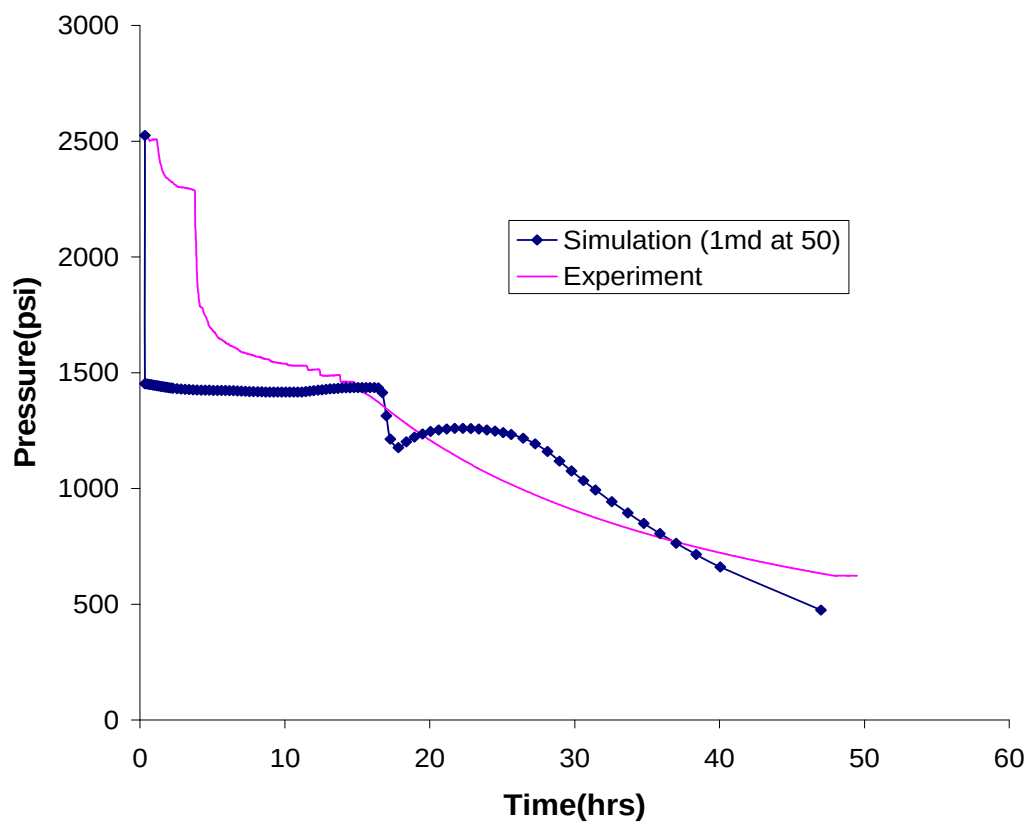


Figure 10(b): Comparison of dissociation pressure for '1md at 50' case with experimental results

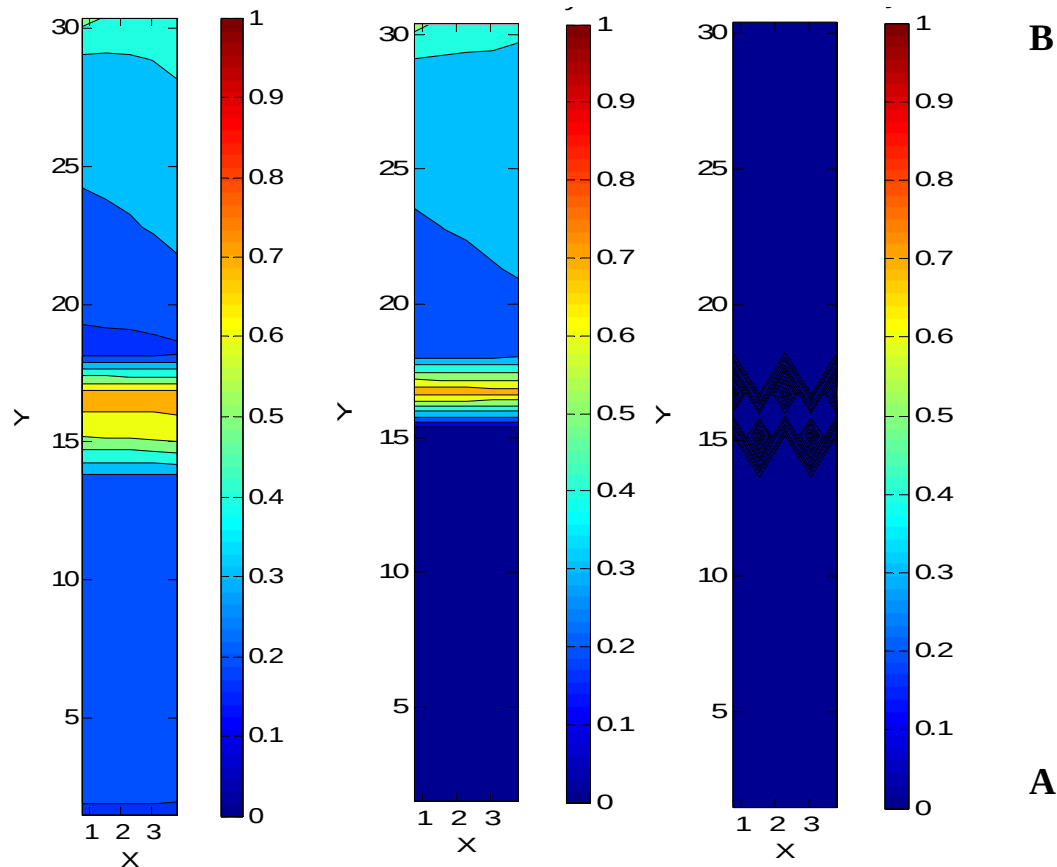


Figure 11(a) Hydrate saturation profiles after 1, 12 and 15 hours of dissociation for '1md at 50 case'

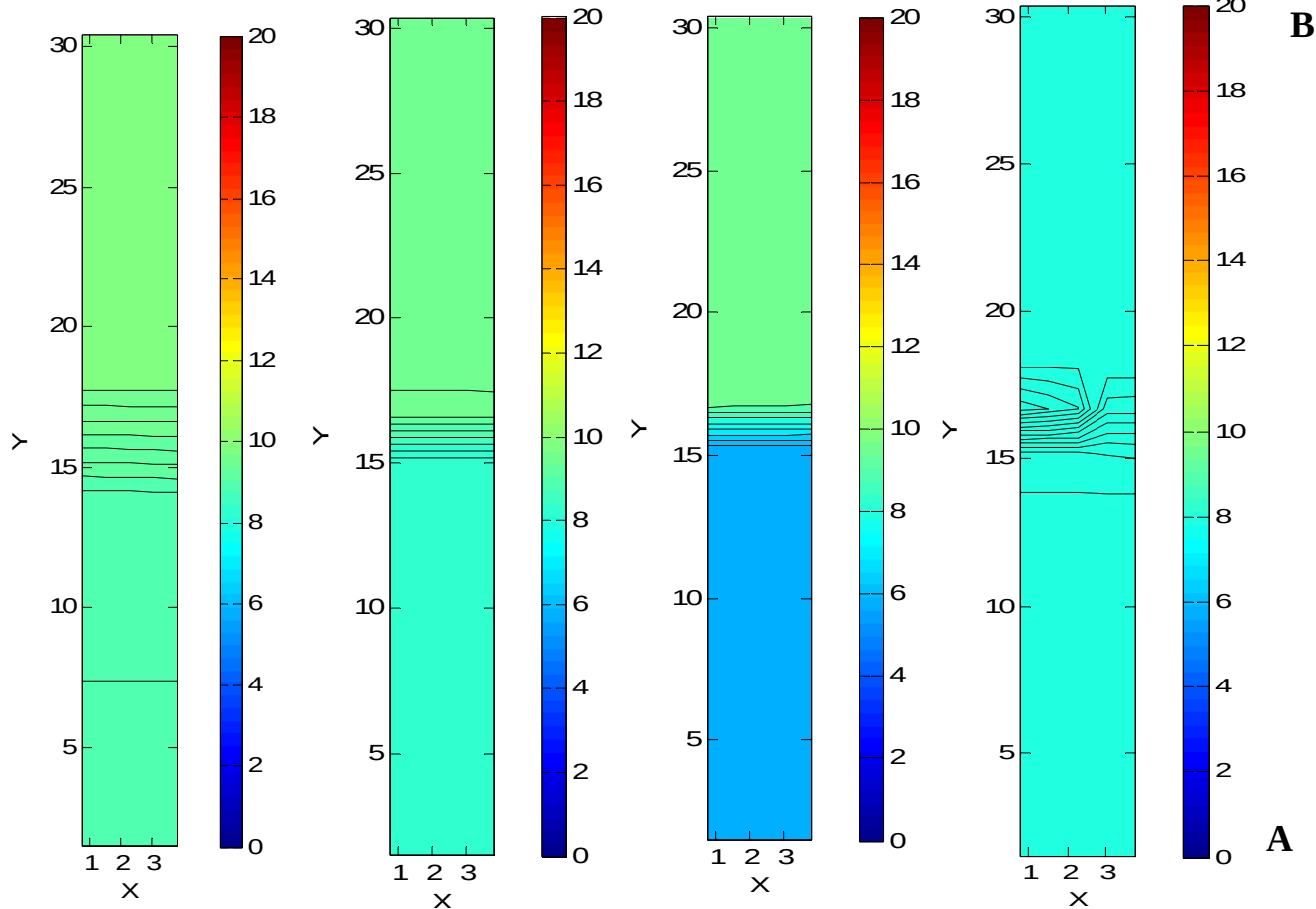


Figure 11(b) Gas pressure profiles after 1, 12, 15 and 17 hours of dissociation for '1md at 50 case'

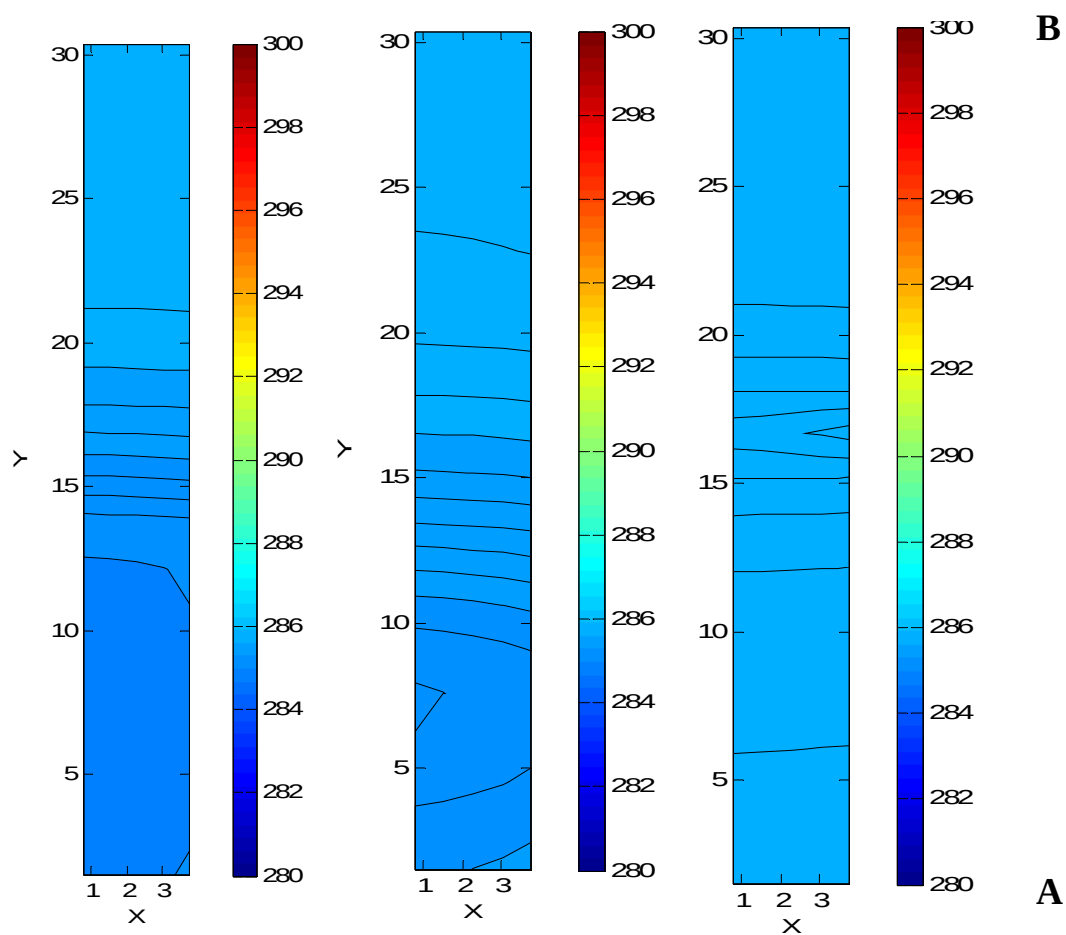


Figure 11(c) Temperature profiles after 2, 12 and 16 hours of dissociation for '1md at 50 case'