

DISSOCIATION OF HYDRATED MARINE SEDIMENT

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Modelling of hydrate dissociation in a sediment bed is needed to understand the gas evolution characteristics. This will determine temperature profiles in the sediment bed at different times and also the rate of propagation of the dissociation front. The model would consider the subsidence of sediment bed during and after hydrate dissociation. Sediment collapse would affect the gas recovery from hydrated sediments and an understanding of the process is thus crucial to cost effective gas extraction from hydrate. The model gives us a picture of the collapse process in time. Sediment subsidence curves show that subsidence is a strong function of void ratio and compression index of the sediment. Lower void ratios resulted in almost linear dependence of subsidence on time, whereas higher void ratios produced a curvature in the plot. The effect was similar with lower compression indices producing gradual subsidence and higher values resulting in exponential curves. Total settlement plots illustrated a linear behaviour of settlement with time at low values of shear stress change. Larger values of both compression index and shear stress change caused markedly non linear relationship with time. Increasing iterations (in effect increasing the time of settlement) found settlements to taper off. The settlement curve obtained by the model was compared to the actual settlement curves of marine sediment under compression. It was found that when the model was set to the overburden pressure and other parameters of the experimental results, the prediction of settlement was acceptably close. The model will allow optimization of gas recovery efforts from hydrated sediments.

INTRODUCTION

Gas hydrates are crystalline compounds formed when gas molecules are trapped by water molecules, which form a cage like structure around the gas molecule. Hydrate formation is favoured at low temperatures and moderate to high pressures [1]. Gas Hydrates are different from stoichiometric hydrate compounds which occur, for example, when water combines with various salts. Hydrates first captured the attention of the hydrocarbon industry in 1934, by blocking pipelines.

Analytical and numerical models of diverse convolution have been developed to simulate hydrate dissociation. Some of these models have considered the kinetics of hydrate dissociation (e.g. Yousif et al., 1991) others have not (e.g. Selim and Sloan, 1990; Tsyarkin, 2000). While several workers have included heat transfer by conduction and convection and the flow (of the gas only, or gaseous and aqueous phases) in their models others have ignored these processes. In some models, e.g., Tsyarkin (2000), the formation of ice upon hydrate dissociation has also been considered. Yousif et al. (1991) developed a 1D model for the kinetics of hydrate dissociation in porous media

due to depressurization using the Kim–Bishnoi scheme for the rate of gas generation. The model solved continuity equations for each of the 3 phases (gas, liquid and hydrates) and used relations between the saturations of the phases and the rates of mass transfer of the phases. Darcy's Law was used to model the flow of water and gas separately. Porosity and permeability were updated as dissociation took place. Heat transfer was not considered and the dissociation was considered isothermal. Heat transfer was considered in a numerical model by Masuda et al. (2002).

A comprehensive model that simulates the kinetic or equilibrium dissociation of gas hydrates with heat transfer and multiphase fluid flow in porous media coupled to multi-component reactive transport code was developed by Moridis (2002). This simulator does not couple the mechanical deformation to these processes, i.e. the porous medium is assumed to be rigid. Hong et al. (2003), presented analytical and numerical solutions for gas production from the dissociation of hydrates employing the Clarke–Kim–Bishnoi kinetic model. Two-phase fluid flow and heat transfer in the porous media, due to gradients created by depressurization and dissociation, were coupled to the kinetic dissociation model. In their study they identified the kinetics of dissociation and the heat transfer mechanisms to be the rate-limiting factors (slow processes) for the gas production from hydrate dissociation.

Xu (2004) produced a numerical model for simulating dynamically changing marine gas hydrates systems due to temperature or pressure changes at the sea floor. The components considered were methane, salt and hydrates and a liquid phase with dissolved gas and salt. Darcy's Law was used to model the 2-phase flow of liquid and gas. The water and gas densities and enthalpies were coupled to temperature and pressure via the state equations and adjusted for the salt concentrations, which allowed for a dynamic feedback. The system was considered in thermodynamic equilibrium and no kinetic effects were included. The energy conservation equations are written with enthalpy as the state variable rather than the temperature. In this way, the model is able to keep track of the phase proportions, pressure and temperature, as hydrate converts to water plus gas.

A recent paper by Birchwood et al. (2005) models well bore stability using semi-analytical model and mechanical properties of THF hydrate bearing sediments which have cohesion hardening. Uncoupled with this model they constructed a thermal

simulator that investigates the effect of rate of circulation of the drilling fluid on the sediments temperature and hence the stability of the hydrate bearing sediments.

MODEL OF HYDRATE DISSOCIATION AND BED COLLAPSE

Natural gas recovery systems employing thermal decomposition of hydrate in submarine sediment is modeled here. Heat energy needed for hydrate decomposition is considered to be provided by pumping a hot fluid (usually steam) through a pipe. The cooler fluid flows back through another pipe placed concentrically inside the feed pipe. When the hydrate is heated up to the dissociation temperature T_e at the existing pressure in the sediment, it dissociates into gas and water by absorbing heat. Modeling of hydrate dissociation in a sediment bed is needed to understand the gas evolution characteristics. This will be done by determining the temperature profiles at different times and also the rate of propagation of the dissociation front. The model would consider both the phase change and bed collapse during hydrate dissociation.

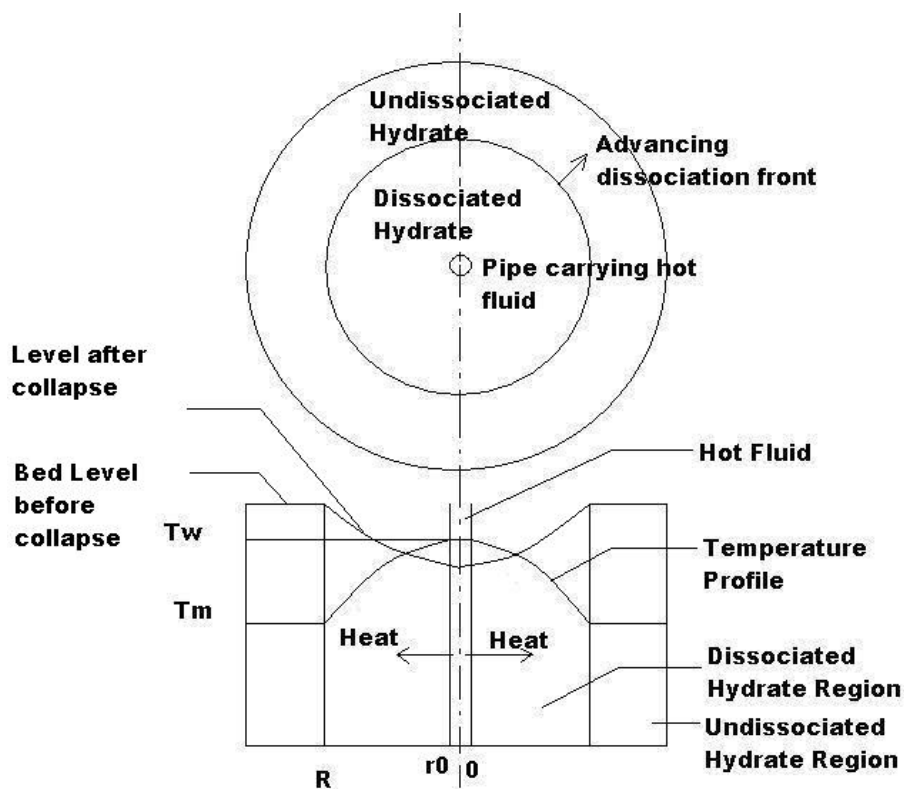


Figure 1. Temperature profile for hydrate dissociation by radial heating

As the hydrate gets dissociated, the dissociation front moves radially outward from the feed pipe. Figure 1 depicts the process of hydrate dissociation in a sediment bed.

As the hydrate dissociates into water and gas, the gas flows to the top and water flows downward. The movement of fluids is enhanced by the highly porous nature of the sediment. The formation of water during the hydrate dissociation will have profound effect on the movement of gas through the sediment.

Hydrate dissociation affects the bed stability. As the heat transfer occurs from center to the periphery of the hydrate bed, overall flow of gas and water released occurs in a direction perpendicular to it. Gas moves upward and water moves down. Loss of hydrate (due to dissociation) causes a reduction in the effective structural strength of the sediment. Hence the sediment tends to collapse during the hydrate dissociation. This in turn would affect the heat transfer and water and gas movements and thus the hydrate dissociation.

SEDIMENT COLLAPSE DURING HYDRATE DISSOCIATION

Literature informs us that the dissociation process will weaken the sediment structural strength to nearly half [1] by converting the solid hydrate to gas and water. As a result, the sediment will cave in and the heat transfer to the radial extremities will be hampered by the lowered thermal conductivity of the bulk sediment which now has no hydrate but only water and gas in its pores. After dissociation of the hydrate in the interstices of sediment skeleton, there is an immediate settlement and then dissipation with time of the excess pore-water and pore-gas pressures. The initial excess pore-water and pore-gas pressures can be considered as initial conditions. Modeling dissociation and collapse requires the following equations:

1. Energy balance equation for the thermal dissociation process.
2. Consolidation equations for sediment.

ASSUMPTIONS

- The temperature of pipe surface is uniform along the length of the pipe.
- The control volume is axi-symmetric.
- The temperature differential is much greater radially than it is axially.
- The hydrate region around the pipe is dissociated radially.

- Axial dissociation is neglected.
- Thermal properties of each phase (Sediment, hydrate and liquid) are assumed constant with temperature. This is an approximation holding good in the small temperature range namely 300K to 330K and pressure of 30Mpa [1].
- Temperature drop across the pipe wall is negligible.
- The gas phase is assumed to be continuous (implying homogeneous gas pore pressure everywhere in the sediment).
- Sediment porosity and the three saturations (S_h , S_g , S_w) of hydrate, gas and water are assumed to remain constant over time.

The above assumptions are not completely accurate for all cases; for example, in a real sediment bed, the thermal properties of each phase (hydrate and liquid) will vary with temperature. However, these assumptions are reasonable as a first attempt in understanding the dissociation characteristics of gas hydrate in a sediment bed.

MODEL EQUATIONS

Energy Balance for the control volume is given by:

Rate of accumulation = Rate transported in-Rate transported out + Rate of production,

Equation (1.1) will give the temperature profile in the sediment [19, 20]:

$$\left[(\phi \rho_h C_h S_h) + (\phi \rho_g C_g S_g) + (\phi \rho_w C_w S_w) + (1 - \phi) \rho_s C_s \right] \frac{\partial T}{\partial t} = k_m \left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} \right) + \dot{m}_h L \quad (1.1)$$

Where k_m is the mean thermal conductivity of sediment which takes either of the following two values depending on the value of r [19]:

$$k_m = \begin{cases} \phi S_h k_h + \phi S_w k_w + \phi(1 - S_h - S_w) k_g + (1 - \phi) k_s, & r > R^* \\ \phi S_w k_w + \phi(1 - S_w) k_g + (1 - \phi) k_s, & r \leq R^* \end{cases}, \quad (1.2)$$

where R^* is the radius of the expanding dissociation front.

S_g , S_w , and S_h are the saturations of components of sediment bed such that

$$S_g + S_w + S_h = 1$$

\dot{m}_h is the rate of dissociation of hydrate in $kg/(s.m^3)$, L is the specific heat of dissociation/formation of hydrate in J/kg of hydrate due to hydrate dissociation and T represents the temperature of the bulk sediment at a distance r from the center.

INITIAL AND BOUNDARY CONDITIONS

At time $t > 0$, the external surface of the pipe is maintained at a temperature T_w .

The initial condition of this system is

$$\text{At } t = 0, \quad T = T_i, r \leq r_0. \quad (1.3)$$

The boundary conditions are

$$\begin{aligned} \text{At } r = r_0 & \quad T = T_w \text{ for } t > 0 \\ \text{At } r \rightarrow 0 & \quad T = T_i \text{ for } t > 0 \end{aligned} \quad (1.4)$$

r_0 being the outer radius of the pipe.

The source term in Eq. (1.1), \dot{m}_h is related to the gas and water production rates by the following equation [20]:

$$\dot{m}_h = \dot{m}_g + \dot{m}_w, \quad (1.5)$$

where \dot{m}_g is the rate of formation of gas and \dot{m}_w is the rate of formation of water.

And,

$$\dot{m}_h = \dot{m}_g M_h / M_g, \quad (1.6)$$

M_h and M_g being the moles of hydrate and gas respectively.

The local gas generation/depletion rate caused by hydrate dissociation or growth can be obtained by the Kim-Bishnoi model [21]:

$$\dot{m}_g = KA(P_e - P) \quad (1.7)$$

Where P_e is the hydrate equilibrium pressure, P is the ambient pressure, A is specific surface area of the pore volume occupied by hydrate, \dot{m}_g and \dot{m}_h are the rates of production/depletion rates of gas and hydrate respectively, in $\text{kg.m}^{-3}\text{s}^{-1}$ and the rate constant K is obtained by an Arrhenius type relation

$$K = K_0 e^{-\Delta E/RT} \quad (1.8)$$

Where K_0 is the intrinsic decomposition constant and ΔE is the energy change for the reaction [21].

Equation (1.1) may be written as:

$$\frac{\partial T}{\partial t} = \left[k_m \left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} \right) + \dot{m}_h L \right] \left(\frac{1}{[(\phi \rho_k C_k S_k) + (\phi \rho_g C_g S_g) + (\phi \rho_w C_w S_w) + (1 - \phi) \rho_s C_s]} \right) \quad (1.9)$$

Thus the energy equation of an axisymmetric cylindrical region is as follows:

$$\frac{\partial T}{\partial t} = A \left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} \right) + B, \quad (1.10)$$

where

$$A = \left(\frac{k_m}{\left[(\phi \rho_k C_k S_k) + (\phi \rho_g C_g S_g) + (\phi \rho_w C_w S_w) + (1 - \phi) \rho_s C_s \right]} \right),$$

and

$$B = \left(\frac{\dot{m}_k L}{\left[(\phi \rho_k C_k S_k) + (\phi \rho_g C_g S_g) + (\phi \rho_w C_w S_w) + (1 - \phi) \rho_s C_s \right]} \right).$$

We now present a preliminary model for collapse of the bed.

COLLAPSE OF SEDIMENT BED

Fine grained sea-floor sediments subjected to compressive vertical load, either from increased overburden or (in the case of hydrate dissociation in hydrated sediment) by sudden lowering of sediment strength, will compress over time. Analysis of such settlements is usually accomplished through one-dimensional analysis of three consecutive phases: (a) Immediate settlement also called plastic deformation (non time dependent); (b) primary compression or consolidation (compression that is time dependent because of hydrodynamic effects on pore water being squeezed out of the pore spaces); and (c) secondary compression (time-dependent compressions resulting from relative particle compressions, bending or reorientations) [22].

The non time dependent immediate settlement will not be considered here because it applies only to a sudden application of compressive vertical load.

Assumptions for sediment collapse model

- The gas phase is assumed to be continuous (implying homogeneous gas pore pressure everywhere in the sediment).
- The coefficients of volume change for the sediment remain constant during the consolidation process.
- The coefficients of permeability with respect to the gas and water phases are assumed to be a function of the stress state.

- The effect of gas diffusing through water, gas dissolving in water and the movement of water vapor, on gas pore pressure are ignored.
- The sediment particles and the pore-water are assumed to be incompressible.
- Strains occurring in the solid component of sediment during consolidation are small.
- Sediment porosity and the three saturations (S_h , S_g , S_w) of hydrate, gas and water are assumed to remain unchanged.

Dissociation of hydrate causes the voids, earlier filled by solid hydrate, to become filled with gas and water. This causes a drastic reduction in the structural strength of the sediment. This is because now, the load is borne by the empty sediment skeleton. Literature informs us that the drop in structural strength (in terms of shear stress of sediment) is nearly 50% [3].

The compression of sediment due to primary compression or consolidation ΔH_p , can be calculated from the following equation [22]:

$$\Delta H_p = H \cdot C_c \frac{\log \left(1 + \frac{\Delta \sigma}{\bar{\sigma}_v} \right)}{1 + e_0}, \quad (2.1)$$

where, H is the layer thickness, e_0 the initial void ratio, C_c the compression index, $\Delta \sigma$ the shear stress change and $\bar{\sigma}_v$ the effective overburden pressure.

In case secondary compression is considered then the secondary compression is assumed to start once the primary compression had reached completion, which for practical purposes is taken as Degree of Consolidation $U = 95\%$. The amount of secondary compression at any given time t , subsequent to the completion time of primary compression, (t_0), is determined from the following equation:

$$\Delta H_s = H \cdot C_\alpha \frac{\log \left(\frac{t}{t_0} \right)}{1 + e}, \quad (2.2)$$

where C_α is the coefficient of secondary compression. The values of layer thickness H, and the void ratio e, are determined at the completion of primary compression.

SOLUTION OF DISSOCIATION FRONT EQUATIONS

We had derived the energy equation of an axisymmetric cylindrical region as:

$$\frac{\partial T}{\partial t} = A \left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} \right) + B \quad (2.3)$$

Using method of central finite differences, we can have the explicit form of the approximation to Eq. (1.1) as follows:

$$T_i^{j+1} = T_i^j + A \frac{\Delta t}{(\Delta r)^2} \left[\left(1 - \frac{1}{2i} \right) T_{i-1}^j - 2T_i^j + \left(1 + \frac{1}{2i} \right) T_{i+1}^j \right] + B \quad (2.4)$$

T_i^j is the temperature at $r = i\Delta r$ and time $t = j\Delta t$.

Since r_0 is very small compared to the size of the reservoir we can take $r_0 \approx 0$

So at $r = r_0 \approx 0$, we have [19],

$$\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} = 4 \left\{ \frac{T_1 - T_0}{(\Delta r)^2} \right\} \quad (2.5)$$

So we can write the finite difference expression at $r = 0$ as

$$T_0^{j+1} = T_0^j + 4A \frac{\Delta t}{(\Delta r)^2} (T_1^j - T_0^j) + B, \quad (2.6)$$

where $T_0 = T_w$ at all times.

The foundation of this model is to relate the numerical value of temperature at the nodes of the mesh to the position of boundary between solid and liquid phases: as the phase change frontier passes a node, a temperature jump is observed. It means that the temperature value remains in the range T_w to T_e . When the temperature value of a node passes T_e , the solid phase at this node is totally dissociated. Then we can estimate the time to dissociate hydrate x meters from pipe by determining the moment at which the phase change boundary passes by the position $R = x$.

RESULTS AND DISCUSSION

The plots give us a picture of the collapse process in time. The temperature Vs time plot shows that the temperatures at the regions close to the pipe are most affected by the hot fluid. Sediment temperature does not reach the pipe temperature because of the effect of cooling which the dissociation process has on the sediment. If higher number of iterations are used (All Figures were produced with just 25 iterations), it is

found that the temperature does tend to reach the maximum possible Viz, pipe temperature. In order to stabilize the simulation, the stability parameter $\frac{\text{thermal diffusivity} \cdot \Delta t}{\Delta x^2}$ was fixed at 0.45. This allowed us to provide varying spatial increments and the program calculated the optimum temporal increments for a stable run.

Sediment subsidence curves show that subsidence is a strong function of void ratio and compression index of the sediment. Lower void ratios resulted in almost linear dependence of subsidence on time, whereas higher void ratios produced a curvature in the plot (figures 4, 5). The effect was similar with lower compression indices producing gradual subsidence and higher values resulting in exponential curves.

Total settlement plots illustrated a linear behavior of settlement with time at low values of shear stress change as evident from figs 7 and 8. Larger values of both compression index and shear stress change caused markedly non linear relationship with time. Increasing iterations (in effect increasing the time of settlement) found settlements to taper off (not shown). The program as coded had problems when dealing with the larger time limits (above 1000 hours) with the plots oscillating between unlikely extremes. This will be corrected in the later model.

The settlement curve obtained by the model was compared to the actual settlement curves of marine sediment under compression [22]. The curves are given in figure 9. it was found that when the model was set to the overburden pressure and other parameters of the experimental results, the prediction of settlement was acceptably close (figure 10). In fig 10, the points are the experimental values and the curve is the prediction by the model. Considering all the simplifying assumptions made in the model, the predictions are acceptable for a first attempt.

CONCLUSION

A temperature time formulation is presented to solve the problem of sub sea hydrate thermal dissociation in cylindrical geometry. A compression subsidence formulation models bed collapse after dissociation of the hydrate. The subsidence model is validated by data on marine sediment subsidence from literature.

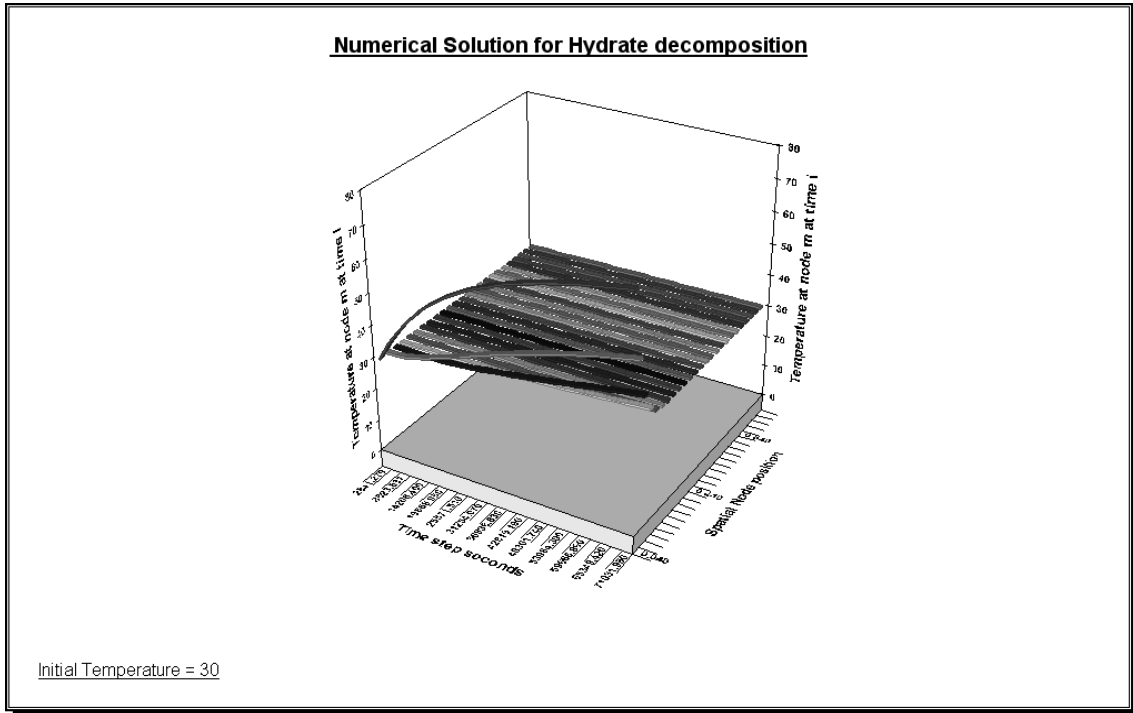
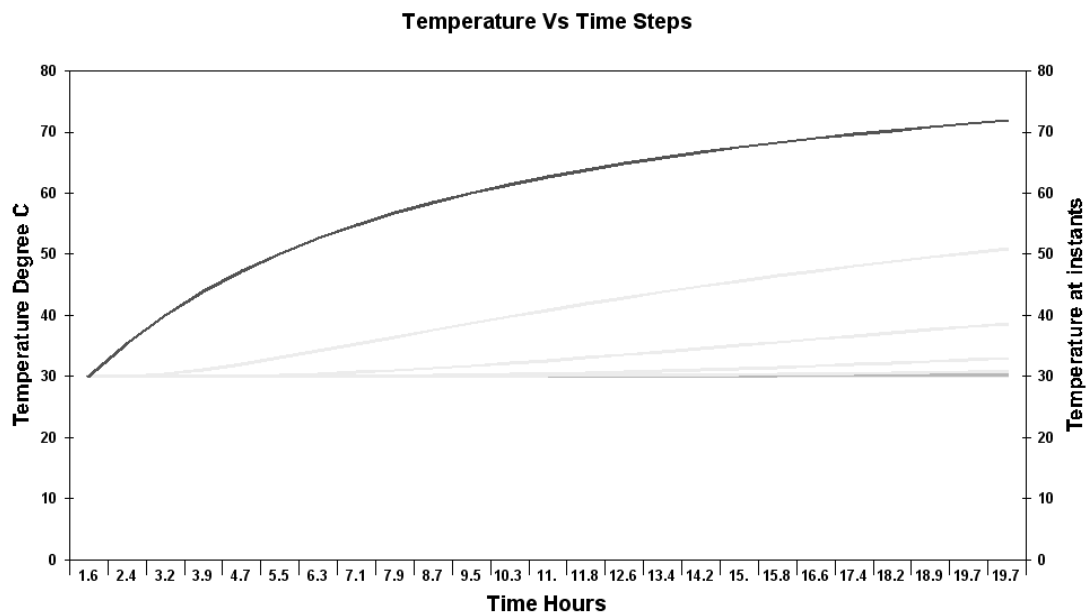


Figure 2. Temperature-Bed radius-Time surface



Time in hours

Figure 3. Temperature Vs Time plot

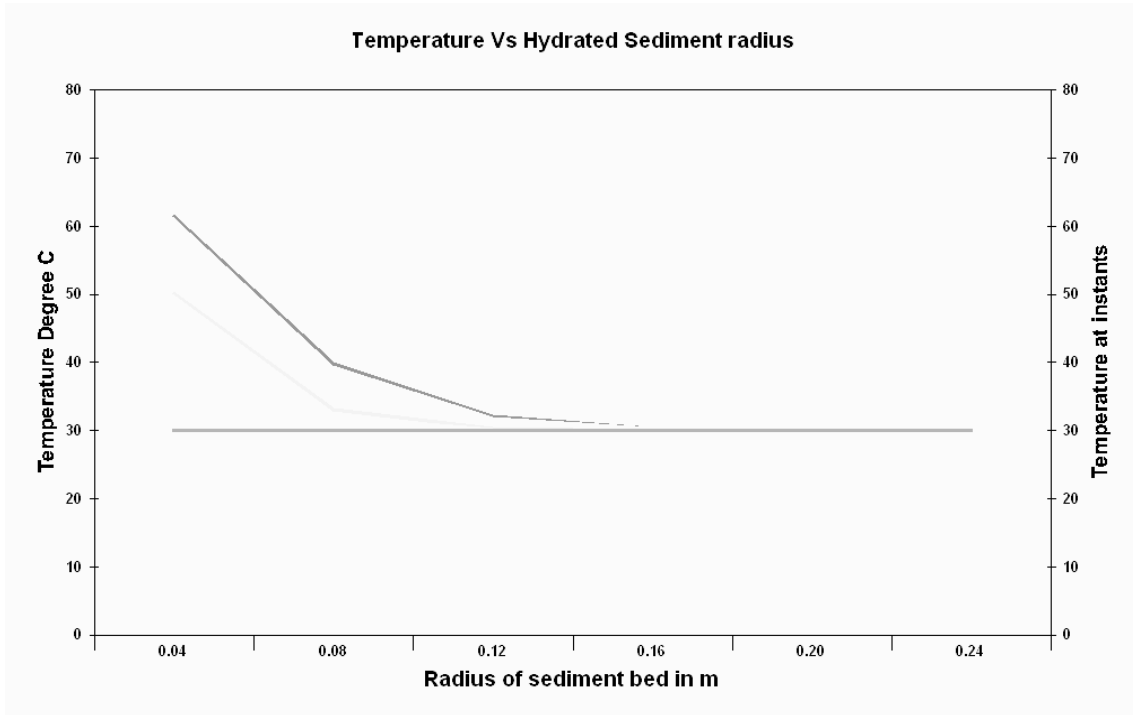
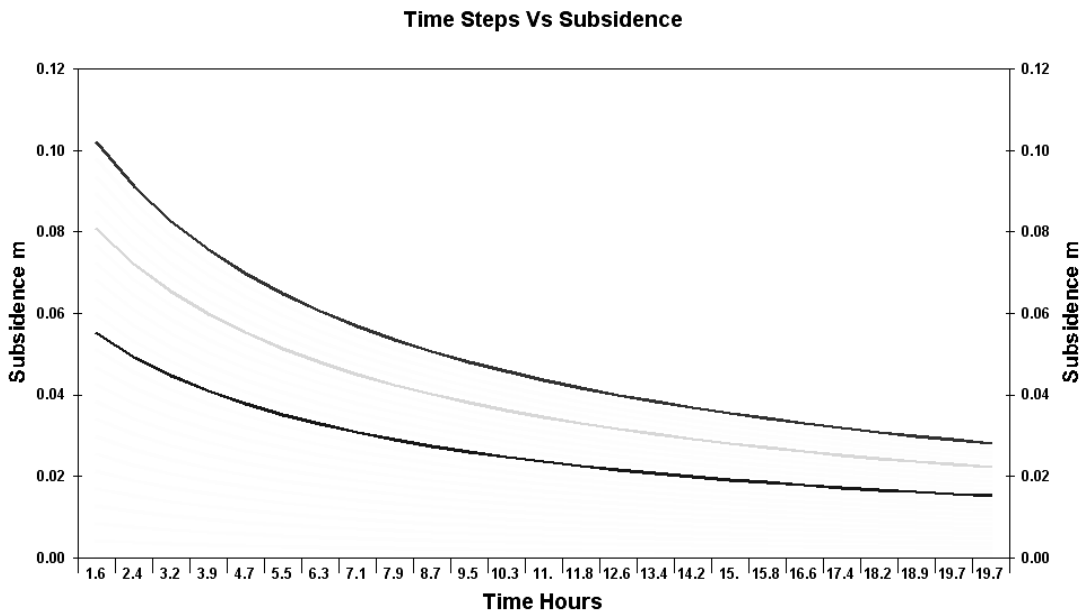
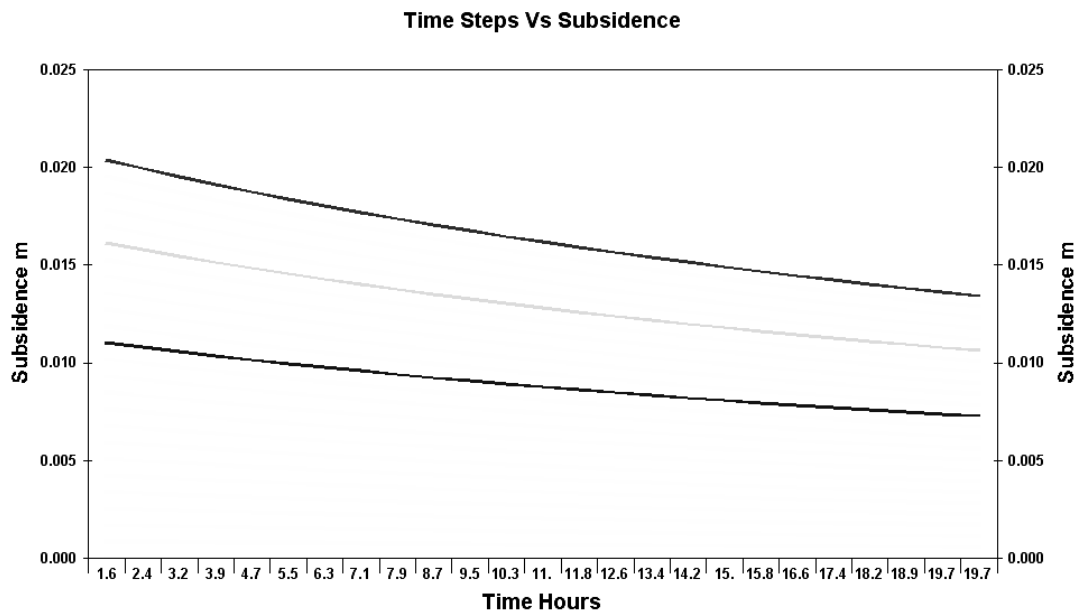


Figure 4. Temperature Vs Bed radius plot



Time in hours

Figure 5. Subsidence Vs Time Plot (Void ratio 1.5, compression index 0.5)



Time in hours

Figure 6. Subsidence Vs Time Plot (Void ratio 1.5, compression index 0.1)

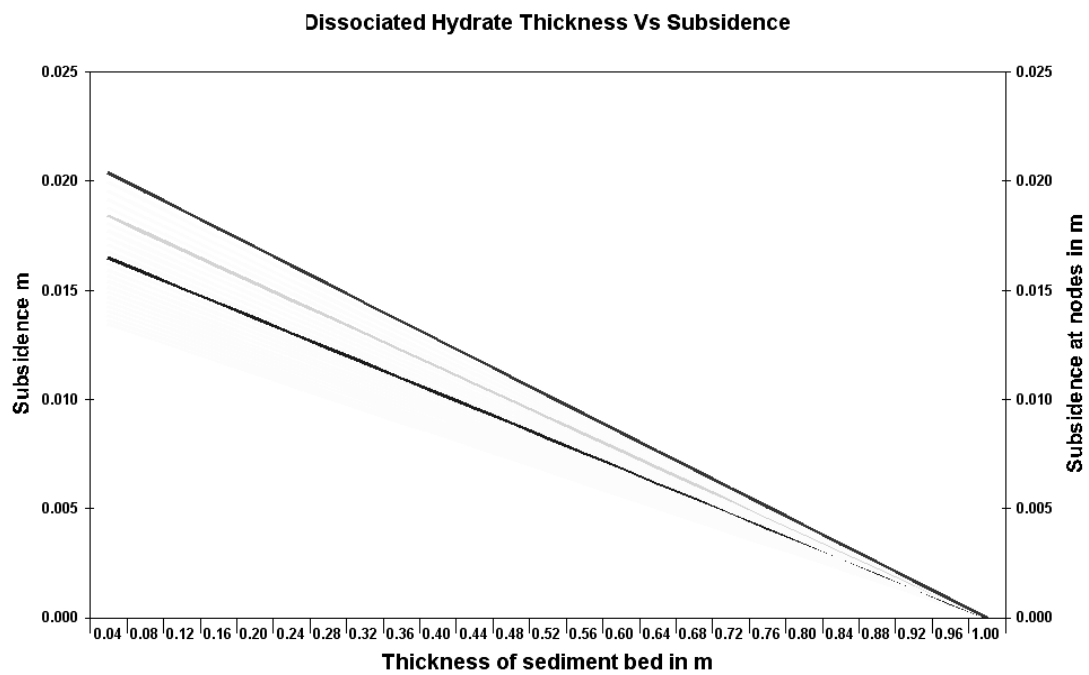
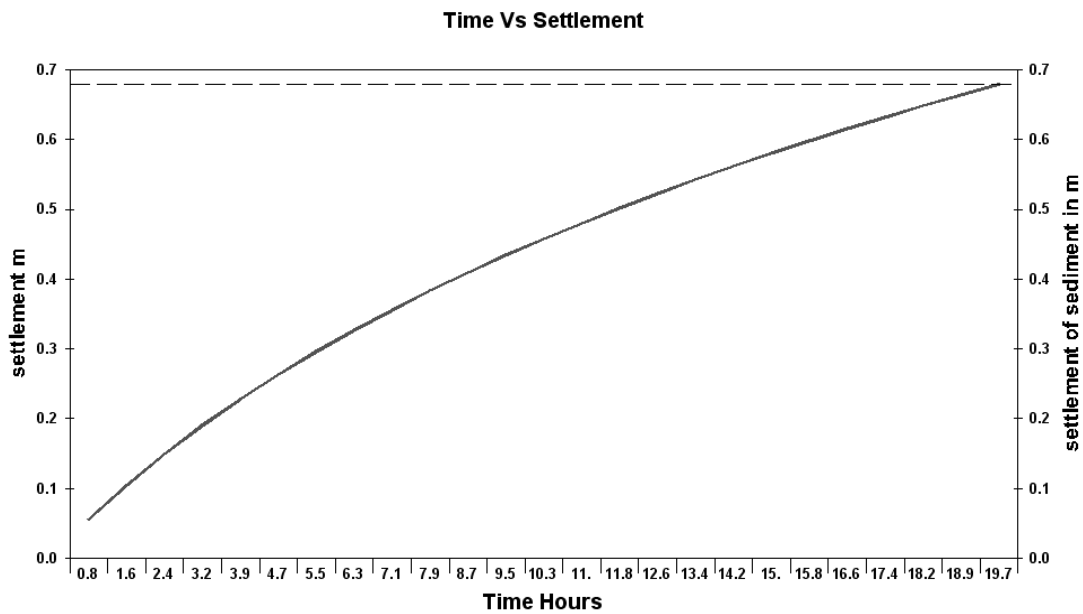
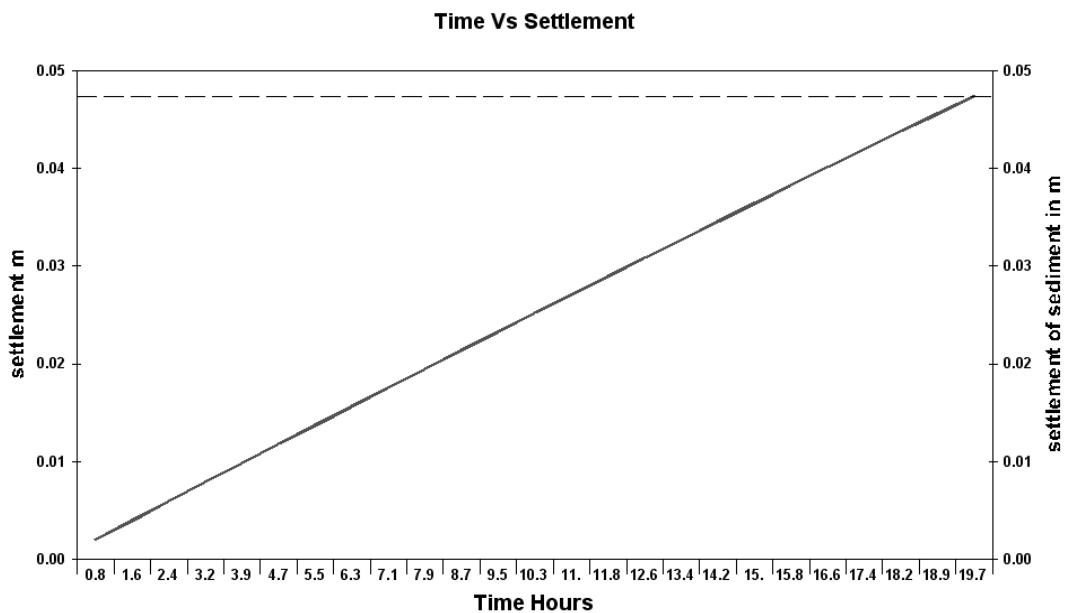


Figure 7. Subsidence Vs Sediment Depth Plot. Each curve represents a time step



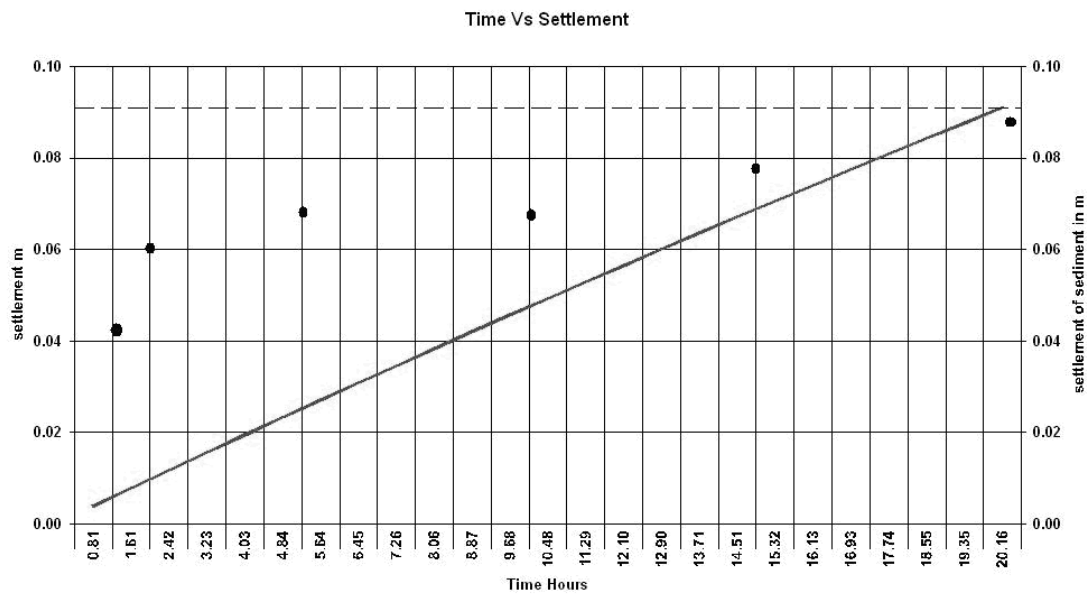
Settlement of sediment over time

Figure 8. Settlement-Time Plot for a Void ratio 1.5, compression index 0.5, shear stress change 7 kPa and effective overburden pressure 10 kPa



Settlement of sediment over time

Figure 9. Settlement-Time Plot for void ratio of 1.5, compression index 0.1, shear stress change of 1 kPa and effective overburden pressure of 10 kPa



Settlement of sediment over time

Figure 10. Model compared with actual settlement data [22]. Void ratio of 1.5, compression index 0.2, shear stress change of 1 kPa and effective overburden pressure of 10 kPa

NOMENCLATURE

A, B	Constants
C	Specific heat, various coefficients
D	Various Constants, Coefficient of Transmission
E	Energy
H	Layer thickness of sediment
K	Rate Constant
L	Heat of dissociation of hydrate
M	Molar Density in Moles/m ³
N	Hydration Number
R	Radius of dissociation front
S	Saturation of component
T	Temperature
V	Volume
d	Thickness of hydrate bearing sediment
e	void ratio
h	Hydraulic Head
k	Thermal conductivity
m	Mass
p	Pore-pressure
r	Radius
t	Time
v	Velocity
z	Elevation Head

Subscripts and superscripts

*	Phase change boundary, Dissociation front
0	At the start of space increments, initial value
1	First space increment from pipe
A, a	Pertaining to gas
D	Dissociated Hydrate skeleton
c	Critical, consolidation
e	Equilibrium
g	Pertaining to gas
h	Pertaining to Hydrate
i	Spatial step, initial state
j	Temporal step
J	Mass flow rate (gas)
k	Corresponding to net normal stress (used in coefficient of volume change)
m	Mean
s	Sediment
v	Volume
w	Pertaining to water
y	Along the Y axis

Greek

β	Constant
γ	Constant
ρ	Density
ϕ	Porosity
σ	Stress
τ	Shear stress
ψ	Pressure head, Coefficient of component volume change
ω	Molecular mass, specific weight

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