Formation & Dissociation of Methane Hydrates in Sediments
Part II : Numerical modelling

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The ForDiMHyS project is a program devoted to experimental studies and the model development of the kinetics of FORmation and Dissociation of Methane Hydrates in Sediments. The first part of the project which is presented in another paper (Bonnefoy and Herri, 2002) is designed to obtain experimental data on hydrate formation & dissociation under *in-situ* temperature and pressure conditions of methane hydrate in well constrained porous materials. The second part presented hereafter consists in modelling the flows inside the core; a specific numerical model has been developed to simulate the experimental set-up described in part one. The numerical model is 3D three phases and simulates the kinetics of hydrate dissociation and formation, taking into account the solubility of methane in water and the heat of phase transitions.

1. Introduction

The modelling of hydrate formation and dissociation concerns a great number of petroleum and geophysical applications e.g.:

- petroleum applications with the modelling of the behaviour of hydrate reservoirs in order to define a relevant scenario of production of hydrate fields or the study of hydrates in sedimentary bassins to reconstitute the history of the basins,
- geophysical applications as the study of landslide on a continental margin due to hydrate dissociation or the study of hydrate eruption.

These applications motivated the development of a simulator derived from a more conventional reservoir model. The aim of the modelling is to simulate experiments and to test different kinetic laws for formation and dissociation. These simulations take into account the thermal effect too, *i.e.* the temperature variation due to the heat of phase transitions : exothermic formation and endothermic dissociation. This model can be equivalently used in order to quantify the dynamic behaviour of hydrate fields and possible gas recovery.

Considering the formation process, the model requires to take into account the solubility of methane in water. In fact :

- Firstly, experiments proved recently that hydrates could form in the porous media under realistic conditions even if the gas is not present under its gas phase : hydrates can form from dissolved gas in water (Buffet *et al*., 1997, 2000) as the methane molar fraction x is greater than the molar fraction x_e corresponding to the hydrate equilibrium conditions at temperature T.

So, in this description, the thermodynamic variables are (x,T) and hydrate formation can appear as $x>x_e(T)$.

- Secondly, the modelling of water circulation at the core scale requires the modelling of methane solubility to take into account the quantity of methane which is transported in the water circulation.

Therefore, as a first step of this work, a kinetic model of order one has been retained for describing the hydrate dissociation and/or formation. The main assumption is that the formation kinetic is depending on the driving force $(x-x_e)$, where x is the molar fraction of methane in water and x_e is the equilibrium molar fraction at temperature T

Considering hydrate dissociation, methane concentration in hydrate corresponds to about 170 gas volumes per water volume in standard conditions. The quantity of methane given by hydrate dissociation is much higher that the methane quantity dissolved in water, when temperature and pressure conditions are those corresponding in hydrate accumulations. A common approximation consists in neglecting the solubility of methane in water at least for the dissociation study; but a kinetic of order one depending on the methane solubility in water can be equivalently used (see 2.3).

2.Model description

2.1.Governing equations The physical description of hydrate formation and dissociation in porous media is firsly based on equations of conservation for each component : water, hydrate and methane in gas and water phases. The velocity fields are based on the generalized Darcy Law.

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- *conservation of water (conservation equations are written in terms of mass fraction)*

$$\frac{\partial}{\partial t}\left[F\left(c_w S_w \rho_w\right)\right] + div\left(c_w \rho_w \vec{u}_w\right) + c_{w,q} Q_w + \gamma_w = 0$$

with $\vec{u}_w = -K \frac{k_{rw}}{\mu_w} \nabla P$ Darcy velocity of the water phase

γ_w is the mass net rate of water due to chemical reactions (dissociation and formation).

- *conservation of methane*

$$\begin{cases} \frac{\partial}{\partial t}\left[F S_g \rho_g\right] + div\left(\rho_g \vec{u}_g\right) \\ + \frac{\partial}{\partial t}\left[F\left(c_{ch_4} S_w \rho_w\right)\right] + div\left(c_{ch_4} \rho_w \vec{u}_w\right) + \\ c_{ch_4,q} Q_w + Q_g + \gamma_g + div(J_{ch_4}) = 0 \end{cases}$$

$\vec{u}_g = -K \frac{k_{rg}}{\mu_g} \nabla P$ Darcy velocity of the gas phase

J_{ch4} is the methane diffusion flux in water phase.

$J_{ch_4} = -D \nabla c_{ch_4}$

D is the methane diffusion coefficient in water phase expressed ($kg.m^{-1}.s^{-1}$)

c_{ch4} is the mass fraction of methane dissolved in water ($c_w + c_{ch4} = 1$). The Q term represents injection and production rates (or aquifers at the field scale). γ_g (resp. γ_h) is the mass net rate of methane due to chemical reactions (resp. hydrates).

- *conservation of hydrates*

$$\rho_h \frac{\partial}{\partial t}\left[F S_h\right] + \gamma_h = 0$$

- *conservation of energy*

$$\frac{\partial}{\partial t}\left[F\left(S_w \rho_w U_w + S_g U_g \rho_g + S_h \rho_h U_h\right)\right] + \frac{\partial}{\partial t}\left[(1-F)\rho_r U_r\right] + div\left(\vec{J}_q + \rho_w H_w \vec{u}_w + \rho_g H_g \vec{u}_g\right) + \gamma_H + H_w Q_w + H_g Q_g = 0$$

with H is the mass enthalpy and U is the mass energy. $\vec{J}_q$ is the flux associated to the thermal conduction.

γ_H is the energy net rate due to heat of phase transitions. (At first approximation, we consider here that the thermal conductivity law is independent of the saturations. This approximation is motivated by the lack of experimental data).

The volumetric saturation balance is added to the system of conservation equations.

$$S_g + S_w + S_h = 1$$

2. 2 Porosity evolution and relative permeabilities

- During the formation and dissociation processes, the "free" volume which is not occupied by hydrates depends on the hydrate saturation and defines the effective porosity $\phi_{eff} = \Phi(1-S_h)$. In our model, the absolute permeability and the porosity are linked through a logarithmic law :

$$\log(K) = a\phi_{eff} + b .$$

a and b have to be determined experimentally.

- The relative permeabilities are supposed to keep the same form and to be functions of the reduced saturation defined as follows. $S'_{w,g} = \frac{S_{w,g}}{1 - S_h}$

Remark:

- Capillary pressure was not considered in the numerical tests but can be considered in the simulator

2.3 Kinetic equations: The kinetic description of the formation or dissociation rate is a subject of main interest and depends on rate of the processes involving during the growth of the hydrate surface : diffusion at the hydrate/water interface**,** surface absorption, surface diffusion towards a singularity (corner, step…) and integration to the surface.

In our description, we assume that diffusion at the hydrate/liquid interface is the limiting step and thus the kinetic rate is directly depending on the hydrate surface A, and on the driving force (x-x_e).

- The local mass rate of methane generated by dissociation is given by the following relation

$$x < x_e(T) : \gamma_g = \phi S_h M_g k A \ (x_e - x) .$$

x_e is the molar fraction of dissolved methane in water at equilibrium in the presence of hydrate at temperature T, k is a kinetic constant and A is the specific surface, which can be estimated using the K-ϕ_{eff} relation (Youssef et al.,1991)

This approach must be compared to the Kim model (Kim et al., 1987).

$$g_g = FS_h M_g k_{K-B} A_{K-B} (P_e - P)$$

Physical data are available for this model (k_{K_B} = $K_o \exp(-Ea/RT)$

Physical data		value	unit
K_0	Kinetic constant	15.64	m/Pa.s
E_o	Energy of activation	78152	J/mol
M_g	CH4 molar mass	0.016	Kg/mol
DH	Energy of dissociation	54000	J/mol

Tab. 1: Physical data

The molar fraction of methane dissolved in water in physical equilibrium (without hydrate) with gas phase at pressure *P* can be written :

$$x(T,P) = K_{eq}(T,P).P$$

(K_{eq} is the equilibrium constant of methane solubility in water with is greatly dependent of temperature *T*, and at second order to pressure *P*).

In our model, we assume that this equilibrium is instantaneously reached.

$x_e(T)=x(T,P_{eq}(T))$ is the molar fraction of methane at the three phase equilibrium point hydrate - water - gas.

Consequently, a value of the kinetic constant can be deduced for this model.

$$(x - x_e) = K_{eq}(P,T)P - K_{eq}(P_{eq},T)P_{eq}$$

$$\propto \left[K_{eq}(P_e,T) + \left(\frac{\partial K_{eq}}{\partial P} \right)_{P_{eq}} P_{eq} \right] (P - P_{eq})$$

- A kinetic of order one is also assumed for formation process in the domain of stability of hydrates (Herri *et al.*, 1999):

$$x>x_e: \; g_g = FS_w M_g k' A' (x_e - x)$$

In the near future, the validity of such a kinetic formation model will be confronted to experimental results and k' value will be adjusted. Such a experimental data acquisition is the objective of the work which is presented in Bonnefoy and Herri (2002).

- γ_w and γ_h are deduced from γ_g using stoechiometric coefficients and molar masses.

3. Numerical Resolution

The equations of mass-conservation of water, methane dissolved in water or gas phase, energy and hydrate are numerically solved. Each equation of conservation is integrated on a control volume and discretised according to finite volume schemes. This system of coupled non-linear parabolic-hyperbolic equations is solved using a finite volume scheme on a cartesian grid. A fully implicit scheme in time has been used.

4. Simulations of hydrate formation and dissociation of laboratory experiments

In order to validate the numerical approach, two sets of tests were carried out.

The depletion of a core has been simulated assuming different boundary conditions.

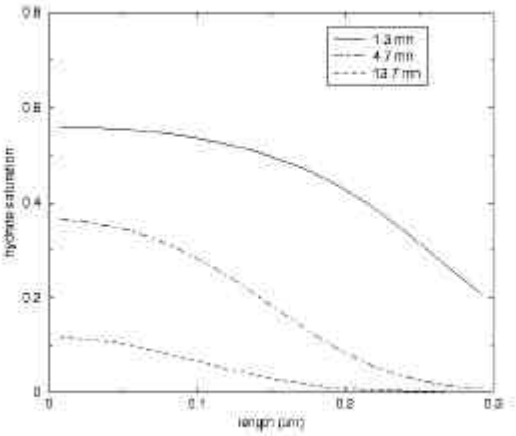


Figure 1: Distribution of hydrate saturation in an isothermal experiment of dissociation

The first experiment is assumed isothermal (Isothermal boundary conditions are applied on the boundary of the core). The laboratory core is 0.3 meter long. The porosity is 25% and its permeability 200 mD. The core contents intially 60% of hydrates at a pressure of 60 bars and a temperature of 8°C. A depressurisation process of 5 bars is initiated at one end of the sample. The core is represented by a 1D grid of 20 cells. Figure 1 shows the distribution of hydrate saturation during the dissociation at different times.

A second experiment is simulated using adiabatic boundary condition; the temperature decreases due to the endothermic feature of the dissociation process and the reaction stops at thermodynamic conditions located on the stability curve of hydrates. Only a few percent of the methane present in the hydrate phase is produced (see Fig 2); temperature decreased by less than 0.5°C during the experiment.

A second set of numerical tests concerns the process of hydrate formation. Water containing the dissolved

methane circulates in the core; isothermal conditions (Fig 3.) are assumed. With the kinetic parameters used (same value of kinetic constant), hydrate forms near the injection area and finally forms a plug. For a lower value of the kinetic constant, the hydrate saturation distribution has a smoother shape and almost uniform at the middle of the sample. This shows the great sensibility of the model towards the k' value.

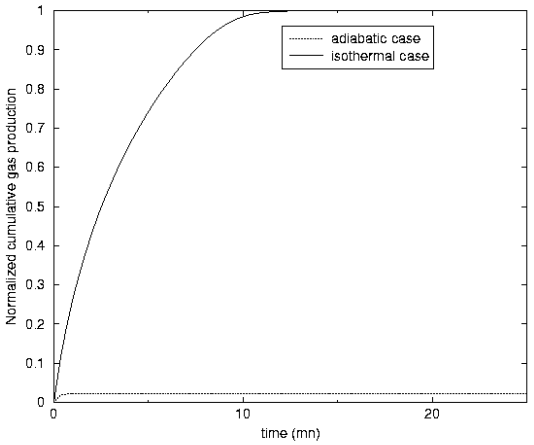


Figure 2: Normalized cumulative gas production for adiabatic and isothermal experiments of dissociation

So, the next step of this work will be to carry out a sensitivity analysis on the kinetic parameters and then to compare the results to experimental ones from the apparatus which is described in part I [Bonnefoy and Herri (2002)]. At that time, the ForDiMHyS program has just begun and by lack of experimental results we could not propose such a comparison. This will be the subject of our next work.

Conclusions

A general model for hydrate formation and dissociation was developed. This model was tested at core scale with physical values available in the literature. In a close future, the experimental set-up which is described in part one will allow us to get the physical data and to simulate the formation and dissociation of methane hydrate, firstly at a core level, and after at a field scale.

In fact, it should be underlined that this model is able to simulate three-phase flow in 3-D porous media. So, we are able to simulate the behaviour of an hydrate field which is submitted to a variation of its thermodynamical condition, *i.e.* pressure and temperature. It will allow us to simulate the production of hydrate fields or to quantify the influence of variation of the sea bottom temperature on the stability of continental slopes.

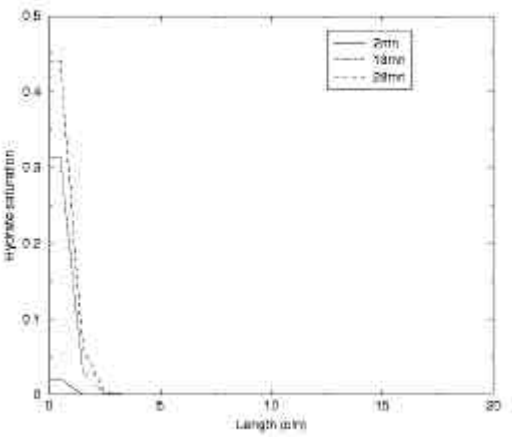


Figure 3: Distribution of hydrate saturation during a hydrate formation experiment

Nomenclature

c_w mass fraction of water in water phase
$c_{w,q}$ mass fraction of water produced or injected in water phase
c_{ch4} mass fraction of methane in water phase
$c_{w,q}$ mass fraction of methane produced or injected in water phase
D diffusion coefficient of methane in water
Φ porosity
Φ_{eff} effective porosity
γ_w net rate of mass of water due to chemical reactions
γ_g net rate of mass of gas due to chemical reactions
γ_h net rate of mass of hydrate due to chemical reactions
γ_H net rate of energy due to chemical reactions
H_i enthalpy of the phase i
K permeability
kr_w relative permability of water
kr_g relative permability of gas
P Pressure
Q_i source terms in i phase
$x(T,P)$ molar fraction of methane
μ_w water viscosity
μ_g gas viscosity

ρ_w water density
ρ_g gas density
ρ_h hydrate density
S_w water saturation
S_h hydrate saturation
S_g gas saturation
U_i mass enery of the phase i
$\mathbf{u}_w$ filtration velocity of water phase
$\mathbf{u}_g$ filtration velocity of gas phase

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