

METHANE HYDRATE FORMATION IN ULLEUNG BASIN UNDER CONDITIONS OF VARIABLE SALINITY. REDUCED MODEL AND EXPERIMENTS

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ABSTRACT. In this paper we present a reduced model of methane hydrate formation in variable salinity conditions, with details on the equilibrium phase behavior adapted to a case study from Ulleung Basin. The model simplifies the comprehensive model considered by Liu and Flemings using common assumptions on hydrostatic pressure, geothermal gradient, and phase incompressibility, as well as a simplified phase equilibria model. The two-phase three-component model is very robust and efficient as well as amenable to various numerical analyses, yet is capable of simulating realistic cases. We compare various thermodynamic models for equilibria as well as attempt a quantitative explanation for anomalous spikes of salinity observed in Ulleung Basin. methane hydrate and flow and transport and subsea porous sediment and phase equilibria and salinity MSC 76S05 and MSC 76V05 and 35R35

1. INTRODUCTION

Gas hydrate is a frozen compound in which hydrocarbons are trapped in a water molecule lattice. Gas hydrates comprise a large and dynamic carbon reservoir; see [30, 12]. In continental margin settings with high methane concentrations, gas hydrates occur naturally in Hydrate Stability Zone, denoted by HSZ, at water depths H greater than 300-500 mbsl (meters below sea level), wherever enough methane is present. Numerous laboratory and field studies at gas hydrate bearing sites, including several drilling expeditions in the past decades, have provided critical background data on the conditions of gas hydrate stability, and have given an overall view of the composition and distribution of gas hydrates in nature. We refer to the recent review [7] and to the monograph [41] for an abundant list of references which illustrate the statements above.

Gas hydrate in these systems is known to occur in conditions of extreme variations in salinity. For example, gas hydrate in Ulleung Basin (offshore Korea) occurs in formations with salinities ranging from as low as 22 psu

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(practical salinity units) to brines with salinity values of 82.4 psu [44]. Similar large range in salinity values have been reported in naturally occurring deposits along continental margins [43, 44]. Because of the need to understand methane hydrate evolution, there is growing interest in easy and robust mathematical and computational models which can be calibrated to experimental data and account for, e.g., the variable salinity. This paper is the first of two in which we present an approximate reduced model of methane hydrate evolution in subsea sediments under conditions of variable salinity. Our two-phase three-component physical model is a simplification of comprehensive models in [25, 14, 8], and is simultaneously a significant generalization of the simpler models in [46, 31, 43], in which simplified kinetic or even simpler mechanisms for fluid equilibria were assumed. In contrast to [43] and consistently with [25], our model fits in the general framework of multiphase multicomponent models such as those in [22, 6], and implements bona-fide equilibrium phase constraints known from thermodynamics [41, 9], albeit in an approximate manner. In the companion paper [33] we present details of numerical discretization with a particular emphasis on the variants of the time stepping, which are enabled by the approximations proposed here. Model construction. Our model accounts for both transport modes of methane and of salt: advective and diffusive, and it is derived from that in [25] under the following simplifying assumptions.

- (I). The liquid and hydrate phases are incompressible.
- (II). The pressure is fixed, and is close to hydrostatic.
- (III). The temperature gradient is fixed. In particular, the energy equation is not solved and the latent heat is not accounted for.
- (IV). The depth BHSZ of bottom of HSZ is fixed, and is determined either from observations, or from phase equilibria using a fixed seawater salinity value. In addition, we consider NaCl as the only inhibitor and ignore the influence of other electrolytes.

After the simplifications, our model is still rich enough to allow the study of complex dynamics of hydrate formation over thousands of years ([kyr]) under the conditions of variable salinity, and yet is robust and very efficient compared to the published comprehensive approaches. In particular, it solves a system of two mass conservation equations for three variables, of which one is eliminated via an approximate phase equilibrium relationship. This relationship is fixed for the entire simulation but it allows the two-way coupling between the (transport of) salt and equilibria, and therefore the model can predict the occurrence of salinity anomalies. In contrast, the comprehensive models available to date solve four equations (mass conservation plus pressure and energy equations) for five variables, and must reevaluate the phase equilibria at every grid point, time step, and at every iteration of the nonlinear solver. We acknowledge that due to the simplification following

from (I-IV), the model presented here cannot be used when significant pressure or temperature changes occur. Thus, in particular, it is inadequate for simulations of gas production from hydrate.

The crux of our model rests on how the equilibrium phase behavior is formulated. The common approach in fully implicit comprehensive models is to use multivariate look-up tables for the thermodynamics constraints, and to apply variable switching [6, 25]. However, the complexity and sparsity of the phase equilibrium data published in the literature makes the simulation of even simple case studies quite delicate, as we have seen in [35]. Therefore, we use the assumptions (I-IV) and approximate the precise thermodynamics data to formulate a robust, reduced, physically consistent, phase equilibria model. We use the software CSMGem [41, 1] and compare its results to several empirical and semi-empirical algebraic approaches. These comparisons show general consistency but also differences.

Furthermore, we follow our recent work [15, 34] in which the methane-salinity phase behavior is realized as an (inequality) nonlinear complementarity constraint; we will refer to this elegant explicit construction as NCC-MS. NCC-MS allows to implement easily a range of models from fully comprehensive to the simpler approximate time-stepping variants in which one or more variables are assumed known. With the reduced approximate phase equilibria in the NCC-MS formulation, each part of our model can be carefully analyzed, specialized, tested, and validated, while such an endeavor is nearly impossible in the comprehensive models. In fact, rigorous analysis of the diffusive transport model of methane was first given in [15], followed by more general analysis in [34] for the advective/diffusive transport. The NCC-MS approach enables various variants of numerical discretization and of time-stepping discussed in the second paper [33].

Model application. To demonstrate the application of our model, we choose an extreme example of a site from Ulleung Basin where methane gas is known to migrate through the gas hydrate stability field and gas hydrate is present in near-seafloor sediments characterized by a presence of brine [44]. We compare the model results with the data from 2010 UBGH2 expedition in which salinity spikes were observed close to the ocean floor [18]. We use our model to hypothesize on what could have been the dynamics of hydrate formation that can explain these spikes. In accordance with [44] we argue that large fluxes of dissolved methane cannot explain these anomalies, and the Ulleung Basin data argues against the presence of a high salinity front as postulated by [24].

The outline of the paper is as follows. We present the model in Sec. 2, and describe how it is calibrated using CSMGem in Sec. 3. In Sec. 4 we describe the setup of simulations and in Sec. 5 compare their results to the experimental data from 2010 UBGH2 expedition and discuss the limitations of the current models to explain the salinity spikes. We close in Sec. 6

with conclusions. The Appendix provides details on some of the calculations which relate our model to that in [25].

2. REDUCED MODEL OF HYDRATE AND SALINITY TRANSPORT WITH METHANE HYDRATE FORMATION

We now describe our methane–salt transport model. The notation is summarized in Table 1. The transport takes place in the sediment reservoir Ω under the ocean bottom; $\Omega \subset \mathbb{R}^d$, $d = 1, 2, 3$. Each point $x = (x_1, x_2, x_3) \in \Omega$ is at some depth $D(x)$ below the sea surface. In this paper we assume that x_3 points in the direction of gravity upwards and that the origin $x = 0$ is somewhere in, or beneath the hydrate reservoir. In the general case of a 3D reservoir the bathymetry is variable, thus $D(x)$ is measured relative to the sea surface rather than to the seafloor. In 1D case $x = x_3$, and it is customary to consider a fixed reference depth $D_{ref} = H$ equal to the water depth H at seafloor, i.e., at the top of the reservoir.

In this paper we assume that the conditions in Ω are favorable for hydrate presence: i.e., the pressure is high enough and the temperature is low enough in Ω , and that there is a sufficient methane supply to the system. The latter may result from upward advection of methane gas originating at depth [44]; methane may also be generated in situ via microbial methanogenesis [16]. The high pressure and low temperature conditions are possible at large depths H , or in Arctic regions. At higher temperatures, such as those occurring at depth within the sediment, methane exist in the gas (“vapor”) phase. Upward methane transport in the gas phase has been documented, but transport in such conditions is not considered in this paper. We refer to the gas phase only when discussing phase equilibria.

The liquid and hydrate phases have respective densities ρ_l, ρ_h which, in general, are mildly dependent on the pressures and temperature, but in our model we assume (I),

$$(1a) \quad \rho_l \approx \text{const}, \quad \rho_h \approx \text{const}.$$

Similar incompressibility assumptions are commonly made in two-phase water-oil reservoir models [32, 26], and (1a) is entirely reasonable over the time scale considered here.

Per assumptions (II) and (III), the pressure $P(x)$ is usually assumed to be close to the hydrostatic pressure, and the temperature usually follows the geothermal gradient

$$(1b) \quad P(x) \approx P_{ref} + G_H(D(x) - D_{ref}).$$

$$(1c) \quad T(x) = T_{ref} + G_T(D(x) - D_{ref}).$$

The use of (1c) is common [9, 38]; in [35] we showed little influence of a particular energy model for variable $T(x)$ on methane fluxes over long time period. Instead of (1b) one can find $P(x)$ from the pressure equation defined in the Appendix.

Symbol	Definition	Units/value
$x = (x_1, x_2, x_3)$	Spatial coordinate	[m]
G	Gravitational acceleration	9.8 m/s ²
H	Water depth at seafloor	Model data, [mbsl] ^(a)
$D_{ref}(x)$	Reference depth	Model data, [m]
$D(x)$	Depth of point x from sea level	[m]
$z = D(x_3) - H$	In 1D case $x = x_3$, $D_{ref} = const = H$ Depth below seafloor	[mbsf] ^(b)
$\phi_0(x)$	porosity of the sediment	Model data
$K_0(x)$	permeability of sediment	Model data, [mD]
ρ_l	Liquid phase density ^(c)	1030 kg/m ³
ρ_h	Hydrate phase density ^(c)	925 kg/m ³
$G_H = G\rho_l$	Hydrostatic gradient	$\approx 10^4$ Pa/m
G_T	Geothermal gradient	Model data, [K/m]
P_{ref}	Pressure at the reference depth D_{ref}	Model data
T_{ref}	Temperature at the reference depth D_{ref}	Model data
P	Pressure, assumed given ^(d) ,	[Pa,MPa]
T	Temperature, assumed given ^(e)	[K]
S_l	Void fraction of liquid phase	
S_h	Void fraction of hydrate phase	
χ_{pC}	Mass fraction of component C in phase p	[kg/kg]
χ_{lM}	Mass fraction (solubility) of methane in liquid phase	[kg/kg]
χ_{lS}, χ_{lS}^m	Mass fraction of salt in liquid phase	[kg/kg], [mole/mole] ^(h)
$S = 10^{-3}\chi_{lS}$	Salinity	[g/kg]
S^{sw}	Seawater salinity	35 ^(f)
χ_{hM}	Mass fraction of methane in hydrate phase	0.134 kg/kg
$R = \chi_{hM}\rho_h/\rho_l$	Constant	0.1203 kg/kg
$\chi_{lM}^{max}(P, T, \chi_{lS})$	Maximum solubility of methane ^(g)	Model data, [kg/kg]
$\chi_{lM}^{max,0}(x), \alpha(x)$	Data needed for reduced model of χ_{lM}^{max}	

TABLE 1. Notation and definitions. (a) meters below sea level. (b) meters below seafloor, (c) assumed in (I) and (1a), (d) given by (1b), (e) given by (1c), (f) 31 if only NaCl is present, (g) given by phase equilibria model, (h) conversion from [kg/kg] to [mole/mole] is given in Sec. 7.3

The presence of the liquid and hydrate phase is accounted for by their void fractions, S_l, S_h , respectively, also called saturations [22, 6]. Since $S_l + S_h \equiv 1$, only one of these phase saturations is an independent variable.

The liquid phase (also called ‘‘aqueous phase’’) consists of water, salt, and dissolved methane components, and their corresponding mass fractions in the liquid phase are denoted by $\chi_{lW}, \chi_{lS}, \chi_{lM}$, respectively. In the hydrate literature the mass fractions χ_{lM}, χ_{lS} are also called the ‘‘solubilities’’. The hydrate phase is made of molecules of water and of methane, with the mass fractions denoted by χ_{hW}, χ_{hM} . Because of the physical nature of hydrate crystals built from a fixed proportion of methane and water molecules, it is common to assume the last two are constants, while $\chi_{lW}, \chi_{lS}, \chi_{lM}$ are variables. Since for mass fractions in the same phase we have $\chi_{lW} + \chi_{lS} + \chi_{lM} \equiv 1$ [[22], (2.2.8a)], therefore only two of the variables $\chi_{lW}, \chi_{lM}, \chi_{lS}$ can be independent. In what follows we choose the salt mass fraction χ_{lS} and one of methane related variables as the independent variables.

The porosity ϕ_0 and permeability K_0 of sediment typically decrease with overburden pressure, i.e., with increasing $D(x)$. If hydrate is present, then the actual porosity $\phi(x)$ available to the liquid phase is $\phi(x, t) = \phi_0(x)S_l(x, t)$. The actual permeability $K(x)$ in the presence of hydrate is an important property; however, it is only required when pressure equation is solved.

2.1. Mass conservation. In region Ω we write the mass conservation equations for methane and salt components as in [25]. Each equation includes a sum of mass fractions over all phases in which a given component is present. These equations can be derived from first principles as a simplification of the comprehensive model from [25].

$$(2a) \quad \frac{\partial \phi_0 N_M}{\partial t} - \nabla \cdot D_M \nabla \chi_{lM} + \nabla \cdot (q \chi_{lM}) = f_M,$$

$$(2b) \quad \frac{\partial \phi_0 N_S}{\partial t} - \nabla \cdot D_S \nabla \chi_{lS} + \nabla \cdot (q \chi_{lS}) = 0.$$

Here we have denoted by N_S , and N_M the (nondimensional) concentrations of methane and salt relative to water density

$$(2c) \quad N_M = S_l \chi_{lM} + R(1 - S_l),$$

$$(2d) \quad N_S = \chi_{lS} S_l.$$

where R is a positive constant made precise below.

The flux q is the volumetric Darcy flux of the liquid phase assumed known, and the source term f_M is given. The diffusivities D_M, D_S are functions of S_l

$$(2e) \quad D_C = D_C^0 \phi = D_C^0 \phi_0 S_l,$$

where D_C^0 is the (molecular) diffusivity of the component C in bulk brine, and $\phi_0 S_l$ account for the decrease of solubility due to presence of porous medium [[22], (2.2-20)]. For components with (small) molecules of similar size, $D_C^0 \approx D^0 = 10^{-9} \text{m}^2/\text{s}$. We note that more complicated formulas for

D_C involving, e.g., tortuosity, and Archie's exponent, can be found, e.g., in [5]Sec. 7.1C and [13]Sec.6.2.4.

In (2) we have four equations and five unknowns: $N_M, N_S, \chi_{lS}, \chi_{lM}$ and S_l . After we eliminate N_M, N_S using (2c) and (2d), we have the two mass conservation equations (2a)-(2b) with three unknowns. The additional relationship which closes the system is the phase constraint.

The quantity χ_{lM}^{max} determines how the methane N_M is partitioned between the liquid and hydrate phases. If $N_M(x, t) < \chi_{lM}^{max}$, then only the liquid phase is present, i.e., $S_l(x, t) = 1$, $N_M = \chi_{lM}$, and χ_{lM} is the independent variable which describes how much methane is dissolved in the liquid. On the other hand, when the amount present reaches the maximum amount that can be dissolved, i.e., $N_M \geq \chi_{lM}^{max}$, the excess forms the hydrate phase with $S_h = 1 - S_l > 0$. In this case S_l becomes the independent variable while $\chi_{lM} = \chi_{lM}^{max}$ fixed.

These constraints can be written concisely as a nonlinear complementarity constraint referred to as NCC-MS

$$(2f) \quad \begin{cases} \chi_{lM} \leq \chi_{lM}^{max}, & S_l = 1, \\ \chi_{lM} = \chi_{lM}^{max}, & S_l \leq 1, \\ (\chi_{lM}^{max} - \chi_{lM})(1 - S_l) & = 0 \end{cases} .$$

The companion paper [33] gives details on how (2f) is implemented in the numerical solver. Below we discuss the data for χ_{lM}^{max} .

The model (2) must be supplemented with boundary and initial conditions appropriate to a given case study.

2.2. Phase behavior: solubility constraints. From the hydrate literature [25, 41] it is known that *maximum solubility constraint* χ_{lM}^{max} depends on P, T, χ_{lS}

$$(3) \quad \chi_{lM}^{max} = \chi_{lM}^{max}(P, T, \chi_{lS}),$$

and there are tabulated data, or complex thermodynamics models, for χ_{lM}^{max} . Conversely, the variables P, T, χ_{lS} determine the circumstances in which $S_l < 1$ and $S_h > 0$, i.e., when the hydrate phase can be present. The dependence of χ_{lM}^{max} on the type of sediment from [8] will not be discussed here.

Per assumption (IV), we consider a particular approximation to (3)

$$(4) \quad \chi_{lM}^{max} \approx \chi_{lM}^{max}(x, \chi_{lS}) \approx \chi_{lM}^{max,0}(x) + \alpha(x)\chi_{lS},$$

calibrated for the case study in Ulleung Basin. To find $\chi_{lM}^{max,0}(x)$ and $\alpha(x)$ we use thermodynamics models and data from literature.

2.3. Numerical model. The numerical model corresponding to (2) is based on a nonuniform structured grid in 1D, and 2D/3D. Discretization is cell-centered finite differences (FD) with harmonic averaging and upwinding. We use operator splitting and treat advection explicitly and diffusion/equilibria

implicitly, in several variants of time stepping applied to the coupled methane–salt system. Details and sensitivity studies are provided in the companion paper [33].

3. MODEL CALIBRATION

In order to apply the model (2) to realistic cases, we need data, in particular, for χ_{LM}^{max} in (2f). In comprehensive models such as [25] the data for χ_{LM}^{max} are provided via multivariate look-up tables based on sparse data. The sparsity contributes to the roughness of the multivariate sampling, which in turn creates difficulties for a numerical solver. These difficulties can be exacerbated by switching of the primary unknowns as in [25], and by the use of numerical derivatives calculated from multivariate approximations, which can lead to further complications, even if the underlying case study is fairly simple.

In this section, we derive an approximate reduced model (4) for χ_{LM}^{max} which simplifies the phase behavior solver substantially but which honors the well known qualitative properties of χ_{LM}^{max} . In particular, it is known that the values of χ_{LM}^{max} in HSZ are most strongly controlled by the temperature [38, 9], with only a mild dependence on salinity, and with negligible dependence on the pressure.

We also compare various theoretical and experimental approaches to provide the context for our approximation. As one of the approaches, we consider the tabulated results of CSMGem. The code CSMGem was developed by Sloan and Koh [41, 1] and calculates χ_{LM}^{max} , also called methane hydrate saturation, based on the statistical thermodynamics models proposed in [4, 37, 3]. CSMGem is an extension of CSMHYD which is publicly available [1]. Since this model is most detailed and up-to-date, we select it for our numerical simulations in Sec. 4. We provide comparisons with the model by Tishchenko et al. [42] which uses a semi-empirical approach based on the theoretical work from [36] to derive χ_{LM}^{max} in conditions for $\chi_{lS} = 0$ (fresh water) to $\chi_{lS} = 2\chi_{lS}^{sw}$ (twice of seawater salinity). We also consider available experimental data. Some models for χ_{LM}^{max} require the knowledge of methane hydrate stability pressure P_{eq} . We note that in literature χ_{LM}^{max} is frequently called MHSAT, and P_{eq} is called MHEQ; we use these symbols in figures.

In practice, to get a model for χ_{LM}^{max} , we first determine the HSZ where hydrate can coexist with liquid phase. Our main simplifying assumption (IV) is that the salinity at large depths is close to the seawater value as suggested in [9]. With this we calculate the pressure P_{eq} at the three phase equilibrium (aqueous-hydrate-vapor). The knowledge of P_{eq} fixes the depth BHSZ of the bottom of HSZ. Alternatively, as was done for Ulleung Basin, we determine BHSZ from seismic-inferred observations.

Next, above BHSZ we only consider the two-phase aqueous-hydrate equilibria, and for this we prepare (offline) the tabulated data on χ_{LM}^{max} depending

on (T, P, χ_{lS}) within the range realistic for Ulleung Basin. We recognize that in some settings within the Ulleung basin and elsewhere, there is evidence for methane transport in the gas phase within the HSZ. In this paper, however, we do not consider the gas transport. The presence of gas phase within the HSZ is the exception, in most systems there is no gas within the HSZ.

In general, the data for $\chi_{lM}^{max}(T, P, \chi_{lS})$ is trivariate. However, we can simplify further, since for a given position x within HSZ we recall that $T(x), P(x)$ are known. In the end, our reduced model is a fit to (4) of the tabulated data against χ_{lS} .

In this paper, we consider the stability and saturation of only structure I (sI) hydrate, with methane as the only guest component in the clathrate structure. Also, as included in assumption (IV), we consider NaCl as the only thermodynamic inhibitor. More generally, other electrolytes such as KCl or CaCl_2 also serve as inhibitors [41, 11]; however, their effect is by an order of magnitude smaller than that of NaCl, and will be neglected.

3.1. Calculation of P_{eq} . The equilibrium pressure P_{eq} is the pressure at which the three phases: liquid, hydrate, and vapor, can coexist. In general, P_{eq} increases with the temperature T and decreases with the salinity χ_{lS} .

Various estimates of the dependence of P_{eq} on T and χ_{lS} are shown in Fig. 1 including those from CSMGem, [28], and [42]. The model for $P_{eq}(T, \chi_{lS})$ from CSMGem is obtained by running CSMGem for tabulated values of T, χ_{lS} .

The algebraic model for P_{eq} from [28] is obtained by fitting the lab measurements of P_{eq} with the following relationship

$$(5) \quad \ln\left(\frac{P_{eq}}{P_0}\right) = -926.815 + \frac{31979.3}{T} + 144.909 \ln(T) \\ + 5847.92\chi_{lS}^m + 322.026(\chi_{lS}^m)^2 + 5840.5 \ln(1 - \chi_{lS}^m).$$

Here P_{eq} [MPa], T [K], and $P_0 = 0.101$ MPa is the atmospheric pressure, and χ_{lS}^m [mole/mole] is the mole fraction of NaCl in the aqueous phase. The relationship (5) is valid in conditions with salinity up to ~ 8.5 times higher than seawater value and is in good agreement with laboratory data obtained under high salinity conditions [10, 21].

As shown in Fig. 1, CSMGem values are close to those given by (5) and to those given by the semi-empirical model from [42]. However, for fluids with high salinity, the P_{eq} estimated in [42] is greater than that estimated by CSMGem and the empirical relationship derived in [28].

However useful and accurate, the model from [28] is not accompanied by a χ_{lM}^{max} model. Thus in what follows we use CSMGem as the model for P_{eq} with largest validity range providing both χ_{lM}^{max} and P_{eq} .

3.2. Three phase equilibrium point(s) and the depth D_{eq} of BHSZ. The knowledge of D_{eq} and P_{eq} and $T_{eq} = T(x_{eq}(t))$, is needed in the estimates of χ_{lM}^{max} .

Source	Model	P range [MPa]	T range [K]	S range [g/kg]
Experiments [28]	P_{eq}	$P < 18$	$T < 290$	[0, 20]
Parametric approach [9]	χ_{lM}^{max}	[10, 30]	[273, 300]	[0, S^{sw}]
Semi-empirical approach [42]	P_{eq}, χ_{lM}^{max}	$P < 50$	[273, 297]	[0, 70]
CSMGem [41]	P_{eq}, χ_{lM}^{max}	$P < 100$ (a)	[273, 306](b)	

TABLE 2. Range of validity of P_{eq} and χ_{lM}^{max} models in Sec. 3.3.1. (a-b) Data from [3], (b) from Fig. 7.4 in [3].

From (5), since $T = T(x, t)$ and $\chi_{lS} = \chi_{lS}(x, t)$, we see that $P_{eq} = P_{eq}(x, t)$. If $P = P(x, t)$, then at a given time t there may be a point or points $x = x_{eq}(t)$ at some depth $D_{eq} = D(x_{eq}(t))$ at which

$$(6) \quad x : P(x) = P_{eq}(T(x), \chi_{lS}(x, t)).$$

In general, this means that χ_{lM}^{max} can vary in time t ; this is allowed in the comprehensive models in [24, 25, 35, 8]. Further, the depth of points x_{eq} needs not be unique. These considerations must be taken into account when modeling nonhydrostatic pressure, dynamically changing temperature, and in particular when modeling the production of gas from hydrates. Unfortunately these general considerations also make the numerical model very complex, since a recalculation of P_{eq} and χ_{lM}^{max} must be done at every point, at every time step, and/or even within every iteration of an iterative solver. Furthermore, if χ_{lM}^{max} varies in time, the model is not amenable to even the general mathematical analysis of well-posedness in [34].

However, in basin modeling it is reasonable to make some approximations. Following the main assumptions (II, III) we adopted, with hydrostatic pressure and a linear temperature profile as in (1b) and (1c), we see that P, T are monotone in x . If, in addition, the salinity $\chi_{lS} \approx const$, there is at most one such depth D_{eq} where (6) holds; this is the base of HSZ. For depths above D_{eq} (or temperatures lower than T_{eq}), liquid in Ω can coexist with hydrate phase.

If the salinity within HSZ is nonconstant, the conundrum is that we do not know $\chi_{lS}(x)$ when calculating D_{eq} from (6). However, we can assume, as suggested in [9], that the salinity at the depths close to D_{eq} equals that of χ_{lS}^{sw} . This means that the base D_{eq} of HSZ is calculated only once, and is fixed; we identify BHSZ as the set of points x_{eq} for which

$$(7a) \quad x_{eq} : P(x_{eq}) = P_{eq}(T(x_{eq}), \chi_{lS}^{sw}).$$

This approximation is clearly reasonable given the fact that it only determines BHSZ.

Alternatively, one may have additional information about D_{eq} from the seismic-inferred depth of hydrate stability zone. Such was the case of Ulleung Basin where we know the depth of BHSZ.

3.3. Model for χ_{lM}^{max} . Once we know D_{eq} , the values P_{eq} and T_{eq} are fixed. With these, one calculates the maximum methane mass fraction at the three

phase equilibrium, which is used in turn to get $\chi_{LM}^{max}(T(x), \chi_{lS}(x, t))$ at a given x, t .

We recall first the parametric model from [9] which provides a linear fit to data generated by the theoretical thermodynamics calculations from [47]; see also Tab. 1 in [9]. The model

$$(7b) \quad C_3(T, P) = C_3(T_0, P_0) + \partial_T C_3(T_0, P_0)(T - T_0) + \partial_P C_3(T_0, P_0)(P - P_0),$$

provides the solubility of methane at the three phase equilibrium point [9] based on an estimate of $C_3, \partial_T C_3, \partial_P C_3$ at some given (T_0, P_0) . We provide these for completeness in Tab. 3.

In particular, knowing D_{eq}, P_{eq}, T_{eq} we can calculate from (7b) the solubility $C_3(T_{eq}, P_{eq})$ at the base of HSZ. To correct for the influence of salinity, and to find χ_{LM}^{max} at a given depth $D(x)$ within HSZ, we follow [9] and use

$$(7c) \quad C_{eq}(T(x), \chi_{lS}) = C_3(T_{eq}, P_{eq}) \exp\left(\frac{T(x) - T_{eq}}{a}\right) (1 - \beta \chi_{lS}^M).$$

Here $a = 14.4$ K, $\beta = 0.1 \text{ mol}^{-1}$ are the parameters determined from the theoretical calculation of Zatsepina and Buffett [47], Eq. (7). The variable χ_{lS}^M is the salinity in the unit of molality. See also [38], Eq. (11), for (7c) calculated for pure water in heterogeneous sediments. Finally, we obtain χ_{lS}^{max} via the conversion factor

$$(7d) \quad \chi_{LM}^{max} [\text{kg/kg}] = C_{eq} [\text{mM}] 10^{-3} \frac{16.04}{1030}.$$

Here we have used molecular weight of methane equal 16.04 g/mole, the seawater density 1030 g/L, and recalled that 1mM = 10^{-3} mole/L.

Combining (7d) with (7c) we see that the dependence of χ_{LM}^{max} on χ_{lS} is linear, which is consistent with the model postulated in (4).

We compare the model (7d) and various other parametrizations and experiments of χ_{LM}^{max} including CSMGem, [42, 41, 9, 19] in Fig. 2. Estimates using fresh water and low pressure in [42] and [41] agree well with each other and with experimental results. As salinity increases, the estimates from both [42] and [9] suggest a reduction in χ_{LM}^{max} (i.e., the reduction of the maximum methane mass fraction in equilibrium with hydrate), in agreement with the laboratory results from [19]. CSMGem, however, suggests an increase in χ_{LM}^{max} , consistent with the theoretical calculation of [48], which also suggest an increase in χ_{LM}^{max} at salinities higher than about 0.1 mole/kg of water, or 7g/kg. Finally, since only few experimental data for high salinity are available [19], the evaluation of accuracy of theoretical analyses for high salinity is difficult.

We remark that, if the position D_{eq} of BHSZ changes, one should recalculate C_3 and C_{eq} in (7b) and (7c). This is done in comprehensive models, but has not been included in our model.

T_0	P_0	α	β	$C_3(T_0, P_0, 0)$	$\partial_T C_3(T_0, P_0, 0)$	$\partial_P C_3(T_0, P_0, 0)$
292	20	14.4	0.1	153.36	6.34	1.11
K	MPa	°C	mol ⁻¹	mM	mM/K	mM/MPa

TABLE 3. Parameters required in Equation (7b) to calculate methane hydrate stability and saturation following [9]. Recall that the unit of C_3 is mM, where M (molarity) is mole/L.

3.3.1. *Use of CSMGem to get χ_{LM}^{max} .* First, for a given $T(x)$ we calculate P_{eq} . Then we use $P(x)$ to find the depth D_{eq} of BHSZ assuming seawater salinity at BHSZ. Next we use CSMGem to estimate χ_{LM}^{max} . We first construct a look-up table in which the input values of pressure P_i , temperature T_j , and salinity $\chi_{LS,k}$, cover the range of interest. For the pressures we consider the range between the seafloor pressure and that at BHSZ. Since pressure has relatively small effect on χ_{LM}^{max} , we only use these two values $P_1 = P_{ref}$ and $P_2 = P_{BSR}$ as the grid points. The temperature dependence is very significant, and we consider the interval $T_j \in [273\text{K}, 291\text{K}]$, with $\Delta T = 2$ K. We also consider salinity values $\chi_{LS,k} \in [0, 0.125]\text{kg/kg}$, where the right endpoint is four times the seawater salinity χ_{LS}^{sw} , with $\Delta\chi_{LS} = 0.0156$ for the total of nine grid points.

Next we use CSMGem to estimate χ_{LM}^{max} for each of the grid points $(P_i, T_j, \chi_{LS,k})$. This is done by trial and error: we provide CSMGem with some guess of χ_{LM} , and CSMGem predicts the phase conditions for $(P_i, T_j, \chi_{LS,k}, \chi_{LM})$. We try different values of χ_{LM} until we locate the maximum methane mass fraction $\chi_{LM}^{max}|_{(P_i, T_j, \chi_{LS,k})}$ for which methane is only in two phases, i.e., as dissolved methane and methane hydrate. This process gives a table of values

$$(P_i, T_j, \chi_{LS,k}, \chi_{LM}^{max}|_{(P_i, T_j, \chi_{LS,k})})$$

with $1 \leq i \leq 2, 1 \leq j \leq 20, 1 \leq k \leq 9$.

Next, for each grid point (P_i, T_j) we estimate the regression between $\chi_{LS,k}$ and $\chi_{LM}^{max}|_{(P_i, T_j, \chi_{LS,k})}$. The regression provides us, for each (P_i, T_j) in the gridded table, with the coefficients A_{ij} and B_{ij} of the linear model so that

$$\chi_{LM}^{max}|_{(P_i, T_j, \chi_{LS,k})} = A_{ij} + B_{ij}\chi_{LS,k}.$$

As shown in Fig. 3, the values A_{ij}, B_{ij} are not very sensitive to the pressure, thus we approximate further

$$(8) \quad \chi_{LM}^{max}|_{(P_i, T_j, \chi_{LS,k})} = \bar{A}_j + \bar{B}_j\chi_{LS,k}.$$

where $\bar{A}_j = A_{1j}, \bar{B}_j = B_{1j}$.

For the cases where $P(x), x \in \Omega$ changes by more than 1-2 MPa, one may consider a more accurate multivariate model than (8).

In the last step we connect (8) to the model (4). With constant geothermal gradient according to (1c), each T_j corresponds to a unique depth D_j , thus we set-up a look-up table extending (8) to

$$(9) \quad \chi_{LM}^{max}(x, t) = \bar{A}(D(x)) + \bar{B}(D(x))\chi_{LS}(x, t)$$

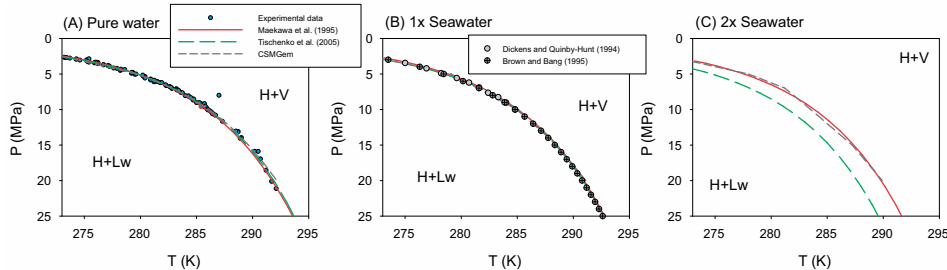


FIGURE 1. Methane hydrate stability P_{eq} denoted by MHEQ for different salinity, pressure, and temperature estimated by various models. Available experimental data were shown for comparison. For salinity values below that of seawater, all models agree well with each other and the experimental data. The stability field estimated by Tishchenko et al (2005) in [42] strays away from the theoretical estimation by CSMGem and from the estimation by Maekawa in [28] based on interpolation of experimental data.

where $\bar{A}(x), \bar{B}(x)$ are the appropriate piecewise linear functions built from (D_j, A_j) and (D_j, B_j) , respectively.

We observe that there is qualitative agreement between the approximation (4), the parametric model (7c), and the regression (9). In particular $\chi_{LM}^{max,0}(x) := \bar{A}(D(x))$ is the temperature dependent coefficient, and $\alpha(x) := \bar{B}(D(x))$ is the salinity dependent coefficient.

However, we note that \bar{B} found from tabulated data can have any sign. In fact, we find that it is positive, in contrast to the model (7c). In the companion paper [33] we discuss the sensitivity of simulations to the particular value and to the sign of \bar{B} .

4. APPLICATION TO THE ULLEUNG BASIN CASE

In this section we describe how the model (2) was calibrated using data from Ulleung Basin. The second drilling expedition to the Ulleung Basin (UBGH2) [2] offshore South Korea (Fig. 4) drilled four sites that targeted the acoustic blanking chimneys in the seismic reflection data. These acoustic features extend from below the HSZ to near the seafloor, where they are usually accompanied by the presence of pockmarks or mounds on the seafloor bathymetry [17]. The seismic blanking zones have been interpreted to image conduits for gas migration, because of the low impedance of seismic waves as they travel through gas. Gas hydrates with different modes of occurrence were recovered from all four sites. From three of the sites (UBGH2-3, UBGH2-7, UBGH2-11), massive gas hydrates related to fracture filling (or grain displacing) morphology were observed at depths shallower than 6 mbsf [2]. Disseminated gas hydrates related to either fracture filling or pore filling modes were recovered from UBGH2-2_1 [2]. Finally, the porosity values

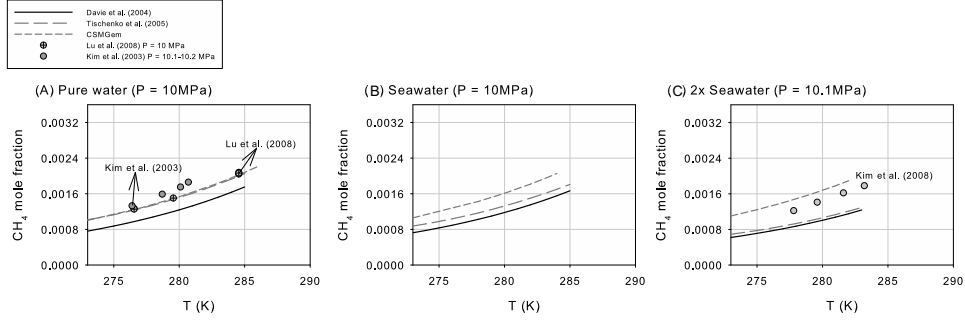


FIGURE 2. Methane hydrate saturation χ_{IM}^{max} for different salinity, pressure, and temperature estimated by various models. Note that only few experimental data for pure water and $\chi_{IS} \approx 2\chi_{LS}^{sw}$ are available. The value χ_{IM}^{max} estimated by CSMGem is always higher than the one estimated by Davie et al (2004) in [9], while χ_{IM}^{max} estimated by Tishchenko et al (2005) in [42] overlaps with one or the other approaches. The experimental data is from Lu et al (2008) [27] and Kim et al (2003) [20]. More figures are available as supplementary material.

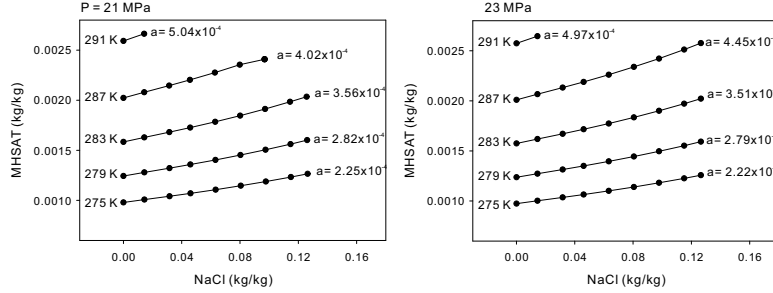


FIGURE 3. The dependence of χ_{IM}^{max} on the salinity χ_{IS} estimated from CSMGem as in (9). Positive value of the slope α indicates that the methane hydrate is more difficult to form at higher salinity. Higher temperature elevates χ_{IM}^{max} and makes methane hydrate more difficult to form. χ_{IM}^{max} decreases only slightly when increasing pressure at the same temperature and salinity.

were found to be

$$(10) \quad \phi_0 \in [0.6, 0.87],$$

with a few local anomalies down to 0.4. In the simulations we use the actual non-constant porosity data for this site.

4.1. Salinity data. Salinity, pressure and temperature conditions are fundamental in constraining the stability of gas hydrate. For the Ulleung Basin,

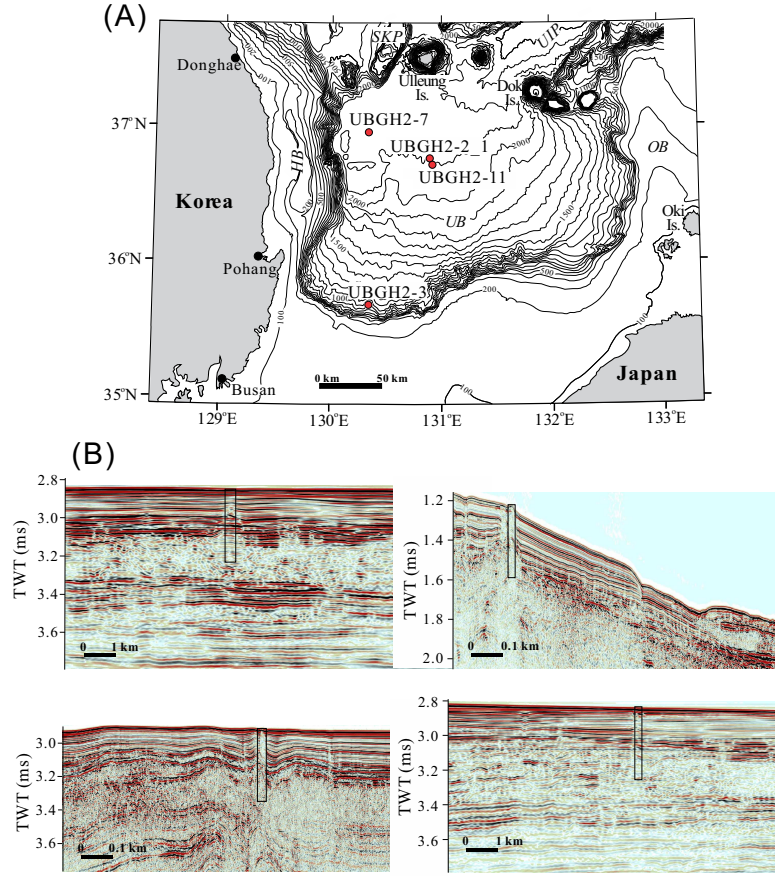


FIGURE 4. (A) Bathymetric map of the Ulleung Basin, offshore Korea, showing the location of the four drilled sites in this study. (B) Seismic profiles across the drilled sites. The rectangles are the location and the depth covered by drilling. These locations were chosen inside the seismic blanking zone in the chimneys. (From KIGAM)

the salinity data obtained shipboard is of less precision than dissolved chloride [40]. We therefore use the chloride data and convert it to salinity (see Fig. 5) using the empirical relationship obtained by fitting all data from UBGH2 sites with

$$(11) \quad S = 61.6Cl_M + 1.4301,$$

where Cl_M [M] is chloride concentration in mol/L (M).

Pore water chloride profiles from these four sites reflect gas hydrate kinetics and fluid origins; see Fig. 5. Chloride concentrations at the bottom of the recovered sections are always lower than seawater, which have been interpreted as reflecting input of fresh water from clay mineral dehydration

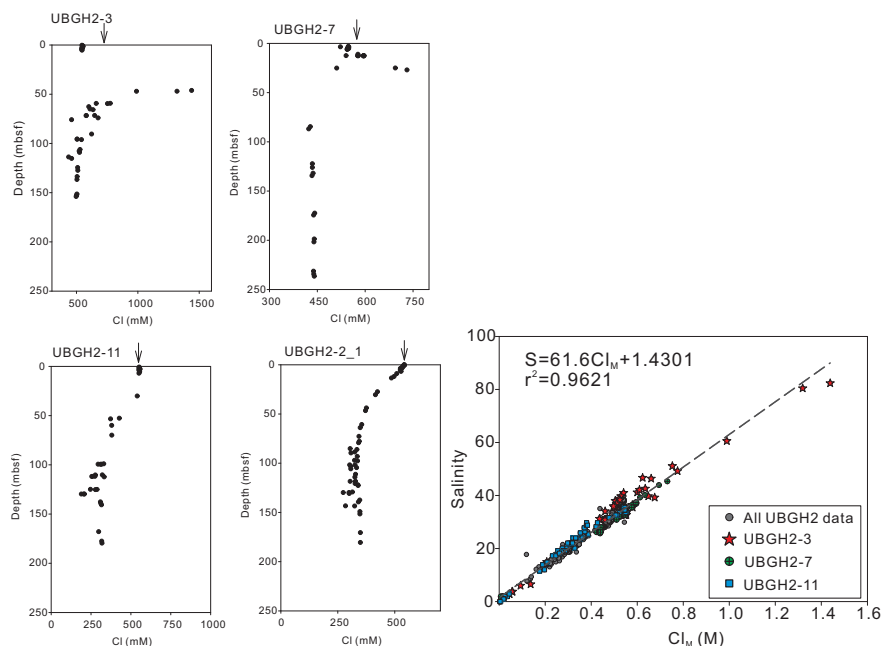


FIGURE 5. Left: profiles of Cl in pore water for the four study sites. Right: empirical relationship between salinity and chlorinity for UBGH2 data. The arrow denotes seawater values. The freshening observed at depth precludes inferences for the presence of a high salinity front as the mechanism to support methane transport in the gas phase as postulated by [25]

reactions at depth [18]. The shallower sediment sections show different degrees of chloride enrichment at each site. At UBGH2-3 we have the most prominent chloride peak, with concentrations almost three times the seawater value. At UBGH2-11 and UBGH2-7, the enrichments range from a few millimolar to ≈ 180 M above seawater concentration, respectively. The site UBGH2-2_1 show the strongest signal of deep-sourced fresh water input, but has no enrichments in chloride. It is worth noticing that these enrichments in chloride concentration are minimum values, since they may be affected by gas hydrate dissociation during core recovery [40]. We also refer to [29] for more discussion.

Finally, the salinities we infer from shipboard measurements were not measured in-situ. Indeed, the "real" Cl and salinity are likely higher than what we measured, because of gas hydrate dissociation during recovery lowers the pore fluid salt and chloride concentrations, but none of our conclusions drawn in Sec. 5 will be different if using the "real" salinity.

	UBGH2-2_1	UBGH2-3	UBGH2-7	UBGH2-11
Seafloor depth $D_{ref} = H$ [m]	2092	898	2145	2082
Pressure P_{ref} [MPa] at seafloor (a)	21.13	9.06	21.65	21.02
Temperature T_{ref} [K](b) at seafloor	273.35	273.45	273.55	274.35
BHSZ depth [mbsf]	176.0	131.6	124	159
P at BHSZ [MPa] (a)	22.89	10.39	22.90	22.62
T at BHSZ [K] (c)	292.7	286	294.8	292.2
χ_{IS} at BHSZ [kg/kg]	0.0229	0.0323	0.0273	0.0210
FGH depth [mbsf] (d)	76.4	6.2	7	7
P at FGH [MPa] (a)	21.89	9.13	21.71	21.09
T at FGH [K](c)	281.6	274	274.6	275.1
Geothermal gradient G_T [K/m] (e)	0.108	0.095	0.171	0.120

TABLE 4. Basin parameters of the four study sites in Ulleung Basin. FGH is the depth of first observed hydrate appearance. (a) Pressure was calculated assuming (1b). (b) Seafloor temperature was measured at each of the drilling site [23]. (c) Temperature is estimated from seafloor temperature and geothermal gradient with (1c). (d) The depth of hydrate first appearance was determined by visual observations of hydrate or by pore water anomalies. (e) Geothermal gradient G_T determined from linear regression of downhole temperature measurements at all UBGH2 drill-sites [39]

4.2. **Temperature and pressure data.** The data from Ulleung Basin includes temperature T_{ref} at the seafloor and downhole temperature measurements from which we estimate G_T , see Tab. 4.

Further, with known hydrostatic gradient G_H , the pressure at the seafloor, at the first gas hydrate appearance, and at the base of the HSZ are listed in Tab. 4. In a typical reservoir of thickness of 100 to 200 m, the pressure difference in the hydrostatic distribution is about $\Delta P_H \leq 2$ MPa, and it significantly exceeds the contributions to pressure difference that may occur due to advective fluxes that have been observed. Thus it makes sense to assume hydrostatic relationship (1b).

5. MODEL RESULTS AND DISCUSSION

In this Section, we apply our model to the case from UBGH2-7 in an effort to illustrate applicability of the model to a natural system and to explain the coupled methane and salinity dynamics resulting in salinity spikes accompanying hydrate deposits. We provide background with motivation, details on the set-up of the cases, and we discuss the results.

Background. Based on purely thermodynamic considerations, water and gas hydrate will co-exist in the sediment section that lies within the HSZ. As the temperature in the sediment increases according to the attendant geothermal gradient, a depth is reached where gas hydrate becomes unstable. Below this depth, water and free gas co-exist, but as long as there is water available in the formation, free gas should not be present within the HSZ. There is, however ample evidence of methane migration through the HSZ at gas-hydrate provinces worldwide. Observations of methane discharge at the seafloor, pressure core sampling imaging and analyses of methane concentrations at in situ pressures, acoustic blanking in seismic data, and logging data all support the vertical migration of gas through the HSZ, which in most cases result in formation of massive gas hydrate deposits at or near the seafloor [44].

The report of the presence of near-surface brines associated with massive gas hydrate deposits on Hydrate Ridge (Oregon), led to the development of hypotheses to explain this observation. Torres et al [43] used a one dimensional transient model to simulate the observed chloride enrichment and show that in order to reach the observed high chloride values, methane must be transported in the gas phase from the depth of the BSR to the seafloor. Methane transport exclusively in the dissolved phase is not enough to form methane hydrate at the rates needed to generate the observed chloride enrichment. As shown by [45], when enough free gas accumulates below the HSZ, the excess (non-hydrostatic) pressure at the top of the gas layer may be sufficient to fracture the sediments and drive gas towards the seafloor. Alternatively, Liu and Fleming argue in [24] that as gas migrates from below the HSZ, gas hydrate formation depletes water, and elevates salinity enough to shift the local three-phase equilibrium to the point where the aqueous water, hydrate and vapor (free gas) coexist, thus allowing vertical migration of free gas through the HSZ. The role of salinity in the thermodynamics of hydrate is important here, since there is a 1.1°C offset in dissociation temperature of methane hydrate in 33%NaCl, relative to that for pure water. Rapid increase in salinity due to recent gas hydrate formation poses negative feedback on hydrate crystallization by shifting the phase boundary.

There have been additional observations of pore fluids highly enriched in dissolved chloride at sites of massive gas hydrate occurrence in northern Cascadia accretionary margin (Canada), the Krishna-Godavari Basin (India) and the Ulleung Basin (Korea). The sites drilled on seismic acoustic chimneys indicative of free gas transport in the Ulleung Basin, all show chloride enrichments of up to 1440 mM from near-seafloor to depths of 100 meters below seafloor (mbsf). Below the depth of chloride maxima, however, chloride values approach concentrations that are lower or equal to seawater values, with minor negative chloride anomalies superimposed on baseline that reflect discrete gas hydrate bearing horizons [44]. None of these sites, however, show any evidence for the elevated salinity values beneath the shallow lens of massive hydrate formation [44]. Extreme high salinity values (of up to

3 times seawater values, [25]) have been postulated by current models, as these high values are needed to create a shift in the gas hydrate thermodynamic equilibrium and sustain gas transport from the base of the gas hydrate stability front to the seafloor.

Below we apply our model in an effort to explain the observed salinity anomalies. It turns out that we are only partially successful.

Model set-up. We use fully implicit numerical solver implementation of (2), with $dx = 1\text{m}$, $dt = 1\text{yr}$; see details in [33].

The data from UBGH2-7 is along the vertical transect and thus the case is essentially 1D, and we set up $\Omega = (0, L)$ where $L = 124\text{m}$ is the reservoir thickness. The bottom of the reservoir is at $x = 0$ and is at BHSZ. We assume T and P as in Sec.4.2. We use relatively small advective flux q and thus, solving pressure equation is not necessary.

We set up the following boundary and initial conditions. The boundary conditions for methane and salt components are needed at $x = 0$ and $x = L$. For the top of reservoir $x = L$, i.e., sea bottom, we use seawater salinity and zero methane concentrations

$$(12) \quad \chi_{IM}(L, t) = 0, \quad \chi_{IS}(L, t) = \chi_{IS}^{sw}.$$

At $x = 0$, we assume conditions above BHSZ and set up boundary condition for methane to be given by χ_{IM}^{max} at the corresponding depth. For salinity at $x = 0$ we use the observed salinity values $\chi_{LS}^0 = 0.0273 \text{ kg/kg}$ shown in Fig. 5 following [18]

$$(13) \quad \chi_{IM}(0, t) = \chi_{IM}^{max}(0, \chi_{IS}^0), \quad \chi_{IS}(0, t) = \chi_{IS}^0.$$

The initial conditions are

$$(14) \quad \chi_{IM}(x, 0) = 0, \quad \chi_{IS}(x, 0) = \chi_{IS}^I(x),$$

where $\chi_{IS}^I(x)$ is a linear function between $\chi_{LS}(0, 0)$ and $\chi_{LS}(L, 0)$.

We use reservoir parameters listed in Tab. 4 and set up five different scenarios to investigate how the profiles of dissolved methane concentration, salinity, and gas hydrate saturation respond to different modes of aqueous fluid transport. The cases are summarized in Tab. 5.

5.1. Scenarios with different advection rates and sources. Cases 1, 2, and 3 compare simulation scenarios with different Peclet numbers as in Fig. 6-8. Advection transports the fluids with abundant methane from sources below HSZ, which facilitates the formation of hydrate, see Fig. 8. With a strong advective flux (Case 3), gas hydrate saturation reaches more than 30% after 100 kyr of simulation. This is in contrast to Cases 1 and 2 with Peclet numbers smaller or equal to 1.

However, even with very strong advection in Case 3, no brine is formed at any depth in the sediments. On the contrary, due to the strong fluid advection prescribed in this scenario, the whole sediment column is flushed with the fresh water. Such result contradicts the observations from our study sites, where shallow brine coexists with the abundant gas hydrate in the

Case #	Diffusion rate D^0 (a) [m ² /yr] (a)	Advection rate q [m/yr] (b)	Peclet number	Methane source f_M (c) [kg/kg/kyr]	Time T [kyr]
1	$3 \cdot 10^{-2}$	$1.2 \cdot 10^{-9}$	$4 \cdot 10^{-6}$	0	25, 50, 100
2	$3 \cdot 10^{-2}$	$2 \cdot 10^{-4}$	0.83	0	25, 50, 100
3	$3 \cdot 10^{-2}$	$2 \cdot 10^{-2}$	82.7	0	2.5, 10, 25, 100
4	$3 \cdot 10^{-2}$	$1 \cdot 10^{-9}$	$4 \cdot 10^{-6}$	$4 \cdot 10^{-2}$	0.5, 1, 2
5	$3 \cdot 10^{-2}$	$2 \cdot 10^{-3}$	8.3	$4 \cdot 10^{-2}$	0.5, 1, 2

TABLE 5. Parameters of the five simulation cases. (a) corresponds to the standard molecular diffusivity $10^{-9}\text{m}^2/\text{s}$. (b) 1 m/yr corresponds to $\approx 3 \cdot 10^{-5}$ mm/s. (c) kg of dissolved methane in 1 kg of seawater for every thousand years. Peclet number $Pe = qL/D$ where $L = 124\text{m}$ is the reservoir depth.

sediments in the upper 100 mbsf as in Fig. 5. A similar case study applied in [43] to Hydrate Ridge led the authors to conclude that the methane transport exclusively by advection is not sufficient to sustain the hydrate formation rate required to produce the observed salinity enrichment. A different source of methane other than aqueous transport from depth was postulated in [43] to be required.

In Case 4 we postulate therefore the existence of a source of methane $f_M \neq 0$ in the sediment section where abundant gas hydrate was observed (17 mbsf at UBGH2-7). In this simulation, we use minimum advective flux (Peclet number $\ll 1$ as in Tab. 5), and show that in response to the strong methane input, gas hydrate saturation exceeds the highest saturation obtained in Case 3 within 5 kyr. Because of the rapid formation of methane hydrate, dissolved ions accumulate in the pore fluids faster than are lost by diffusion to the overlying bottom water, leading to a brine patch above 50 mbsf. After running the model for 10 kyr, the hydrate saturation exceeds 60% and the salinity is 1.5 times higher than χ_{15}^{sw} in bottom seawater, a value that is similar to what we observed in the pore water profiles in Fig. 9.

In Case 5 shown in Fig. 10 we include both large advective flux q and an arbitrary methane source $f_M \neq 0$. Similarly as in Case 4, gas hydrate saturation increases rapidly around the depths where methane source is present. However, the salinity enrichment in Case 5 is different than that observed in Case 4: the highest value is smaller and the profile is nonsymmetric because some of the salt is transported towards the seafloor by strong fluid advection.

We note that in Cases 4 and 5 one might argue that pressure equation (21) should be solved to account for the local value of $\nabla \cdot q = f = f_M$ instead of assuming $\nabla \cdot q = 0$. However, the methanogenesis represented by f_M turns carbon from solid phase (organic matter) to dissolved phase (dissolved methane in pore fluid) and does not introduce new carbon into the overall system, thus $f = 0$.

5.2. Discussion. The model (2) appears to reproduce the two-way coupled dynamics, and the hydrate and salinity profiles, in a manner consistent with the intuition. Furthermore, Case 4 gives results which are close to the profiles recorded in experiments. However, the presence of large source of methane f_M is needed to create the shallow brine patches, and the magnitude of f_M is not fully explained.

Limitations of the model in its ability to explain the experimental data. As shown in [16], microbial methane production through organic matter degradation initiates at the depth where sulfate in the pore water is depleted and methane concentration starts to increase, i.e., in sulfate-methane transition zone (SMTZ). The depth of microbial methane production may correspond to the location of the brine patches observed in Ulleung Basin. Therefore in Case 4 we tested whether in situ methanogenesis could provide the methane required to sustain the rapid hydrate formation. Methanogenesis rates in Ulleung Basin, estimated from one chimney and one non-chimney site using a kinetic model constrained by pore water data, range from a few to ≈ 25 mmol/m³/yr [16]. Using the unit conversion (22) we see that the rate f_M assumed in Case 4 is significantly higher than the realistic rate of methanogenesis estimated in [16]. In other words, the rate f_M proposed in [16] is not large enough to account simultaneously for rapid gas hydrate formation and the associated shallow brine observed in Ulleung Basin.

As another possible explanation, one might argue that there might be a lateral advective transport of gas which might provide the source of methane. However, the seismic and chemistry analyses presented in [18, 16] suggest that most of the methane is generated below the SMTZ, or even deeper, and move upwards as imaged in seismics, with no lateral advection.

Thus, while the simulation gives results consistent with the data, further hypotheses are needed to explain the observations.

Inclusion of gas phase. Similarly to the reasoning used in [43] for the Hydrate Ridge case, we are led to conclude that the methane in the Ulleung Basin sites discussed here must be advecting in the gas phase from below the model domain. The methane solubility is too low for fluid advection to supply enough methane, with advection rate slow enough not to erase the positive salinity lense. Most likely, there is a source of gas below the HSZ, as imaged in seismic data, but free gas cannot travel through HSZ in the model (2) nor in the comprehensive models [25] since these assume that water is abundant. Liu and Flemings in [24] hypothesized that the positive salinity anomaly that results from rapid hydrate formation at the base of the HSZ sustains a local three-phase equilibrium that allows methane gas to migrate upward and extends the saline tongue throughout the HSZ. Such extended positive salinity anomaly is, however, not observed in Ulleung Basin. Rather, the observed profiles as in Fig. 5 show that the brine is confined to shallow depths less than 50 mbsf, and to salinities lower than seawater salinities at depths greater than that.

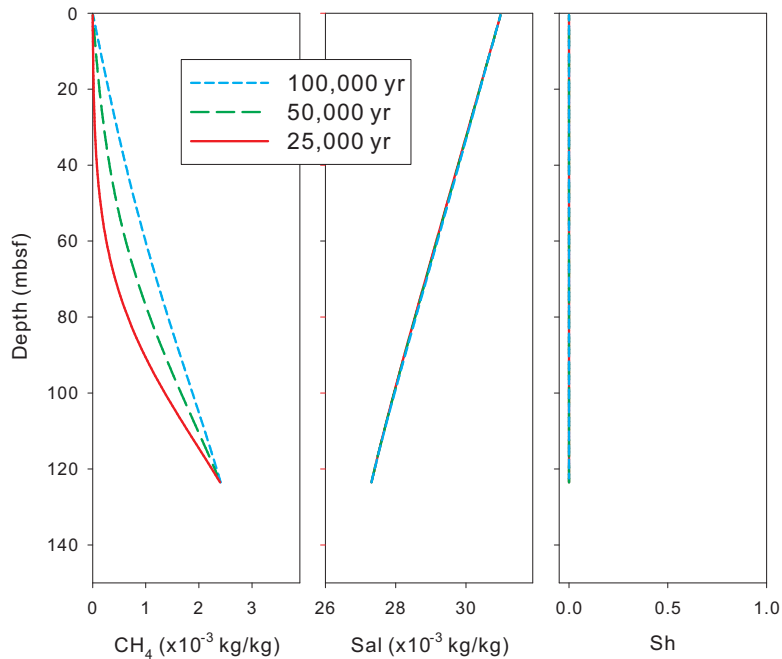


FIGURE 6. Model results of Case 1 for the fluid system with a small Peclet number ($4E-6$). In this case, diffusion alone is not sufficient to deliver enough methane to form gas hydrate.

Salinity dependence. Furthermore, according to the P_{eq} calculations for UBGH2-7 in the pressure range [21.65-22.90] and the temperature range [273.55-294.8], at the depth of the salinity spikes between 20-30 mbsf, we cannot have free gas phase, even if salinity equals double the seawater value. Therefore, our conclusions from simulation results are not affected by the particular approximations made to obtain the reduced phase equilibria model. In addition, the difference in salinity data that can be attributed to the measurements shipboard versus in-situ does not change our conclusions.

Further extensions of the model, and in particular, the inclusion of methane transport in the gas phase, are therefore needed to explain the particular salinity spikes, and are outside the present scope.

6. CONCLUSIONS

In this paper we presented a reduced model of transport of methane and salt dissolved in liquid phase, with accompanying methane hydrate formation. The model was obtained from the comprehensive model in [25] after several simplifying assumptions were made. These assumptions are easily justified for basin modeling, and make our reduced model very compact, efficient, and easily amenable to the various analyses. The model is easily calibrated using phase behavior described in literature, and we described in detail good agreement between various empirical and algebraic models.

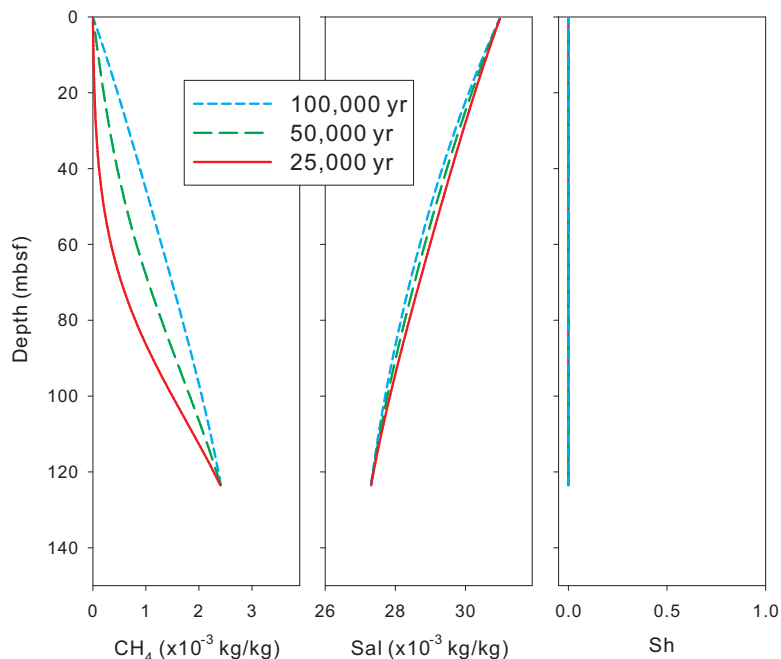


FIGURE 7. Model results of Case 2 for the fluid system with Peclet number close to 1. Even though the advection component is stronger in this case compared to Case 1, still not enough methane delivered for gas hydrate formation within the simulation time.

Thus our paper provides a bridge between the practical and useful models and the rigorous mathematical model and computational analyses, and thus represents a useful tool for modeling the dynamic gas hydrate evolution in marine systems. In addition, it opens the door to various new computational simulations while it can be calibrated with experimental data.

We were able to obtain good quantitative agreement between the model results and the data from Ulleung Basin by providing an additional methane source within the modeled domain, but note that in situ methanogenesis is not sufficient to generate the needed methane. In addition, the presence of fresh fluids at depth in Ulleung Basin sites that host near-seafloor brine patches argue against the development of a large positive salinity anomaly rising from the base of the HSZ to the seafloor, which could support methane transport through the HSZ as proposed by others, e.g., [24]. Our results are consistent with previous work by [43] and [44]. However, we stress that since neither in situ methanogenesis nor transport within a salinity front are consistent with Ulleung Basin data, there must be a separate process supplying enough methane, so that the salinity spikes that accompany near-surface gas hydrate patches can be sustained.

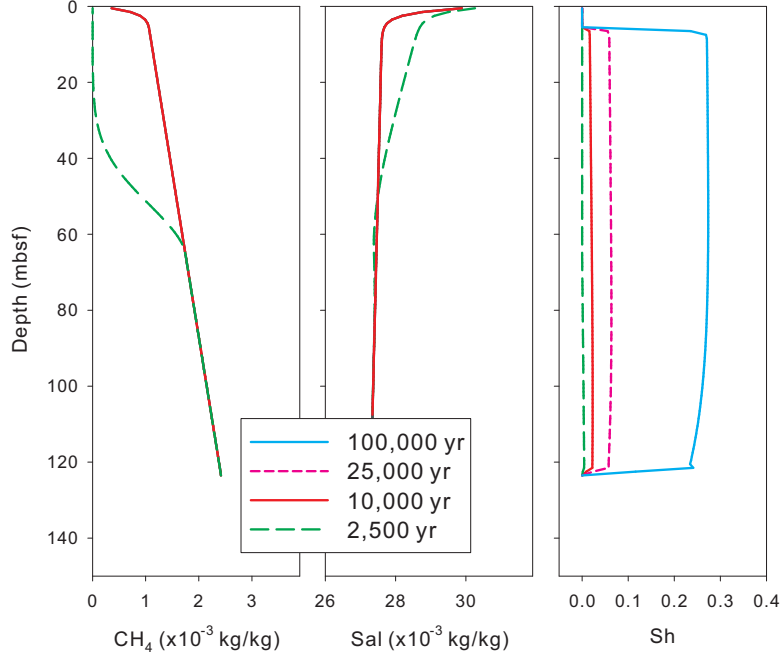


FIGURE 8. Model results of Case 3 for the fluid system with larger Peclet number. Methane is rapidly delivered by advection to form the gas hydrate in the entire sediment column. Salinity, however, decreases due to the effective delivery of fresh fluid from the bottom. This salinity trend is different from the observations.

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7. APPENDIX

For completeness we recall here the details on modeling as well as certain auxiliary conversion factors.

7.1. Derivation of reduced model. The conservation of mass for the methane component in hydrate zone [25] takes the form

$$\left(\frac{\partial}{\partial t}\right)(\phi_0(S_l\rho_l\chi_{lM} + S_h\rho_h\chi_{hM})) + \nabla \cdot (q\rho_l\chi_{lM}) - \nabla \cdot (D_{lM}\rho_l\nabla\chi_{lM}) = \bar{f}_M.$$

In this equation \bar{f}_M is an external source of methane, e.g., due to bacteria-induced methanogenesis.

The accumulation part (the term under the time derivative) can be rewritten with $N_M = \frac{\bar{N}_M}{\rho_l}$ as

$$N_M\rho_l = \bar{N}_M = S_l\rho_l\chi_{lM} + S_h\rho_h\chi_{hM} = S_l\chi_{lM} + (1 - S_l)R.$$

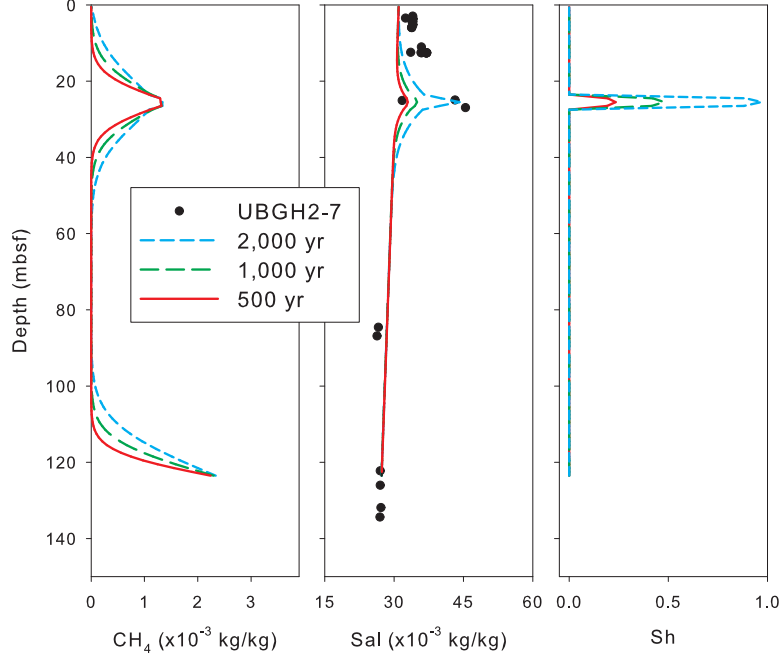


FIGURE 9. Model results of Case 4 for the fluid system with a small Peclet number and a methane source term at 25 mbsf. The observed salinity enrichment is similar to that for experimental data by adding an arbitrary source of methane. The source term contributes large quantity of methane in a short time sufficient for rapid hydrate formation which in turn creates the salinity spike. Due to the insignificant advection component assigned in this case, diffusion is not strong enough to erase such salinity spike.

where the (dimensionless) quantity R is

$$(16) \quad R := \frac{\rho_h \chi_{hM}}{\rho_l} \approx \text{const},$$

Note that \bar{N}_M is the total mass of methane per unit volume which accounts for the methane present both in the liquid and hydrate phases, and N_M is its dimensionless counterpart, relative to brine density.

Finally, it is useful to see that $S_l(x, t; N_M)$ is a function

$$(17) \quad S_l = \frac{N_M - R}{\chi_{lM} - R} = \begin{cases} 1, & N_M \leq \chi_{lM}^{max}(x, t), \\ \frac{N_M - R}{\chi_{lM}^{max}(x, t) - R}, & N_M > \chi_{lM}^{max}(x), \end{cases}$$

Upon $f_M := \frac{\bar{f}_M}{\rho_l}$, and rescaling, we rewrite (15) in the form (2a).

Next, mass conservation for salt has the form

$$(18) \quad \frac{\partial}{\partial t}(\phi_0(S_l \rho_l \chi_{lS})) + \nabla \cdot (q \rho_l \chi_{lS}) - \nabla \cdot (D_{lS} \rho_l \nabla \chi_{lS}) = \bar{f}_S.$$

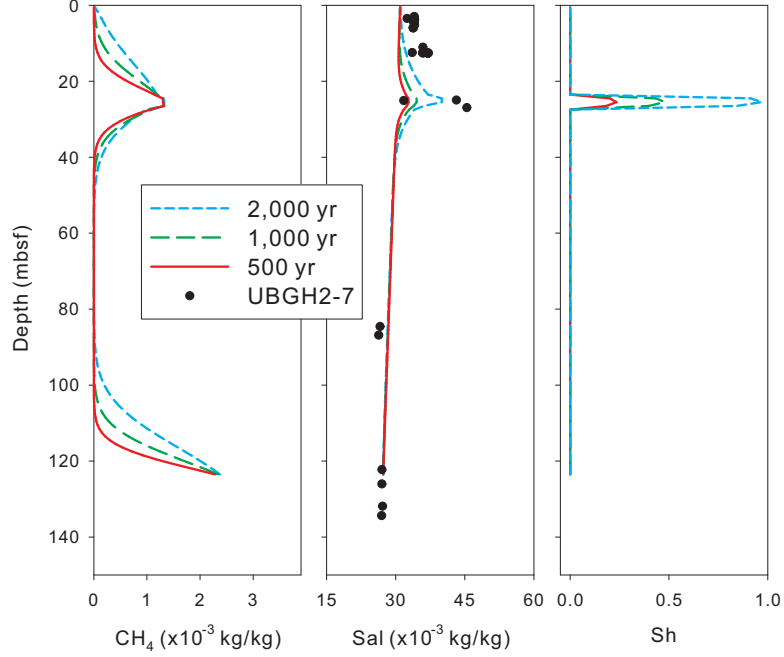


FIGURE 10. Model results of Case 5 and the fluid system with a large Peclet number and a methane source term. Similar to the results from Case 4, large quantity of gas hydrate forms in less than 2000 years. The salinity enrichment is smaller compared to Case 4 and its profile is nonsymmetric due to the more effective fluid transport by larger advection.

and that for water

$$(19) \quad \frac{\partial}{\partial t} \phi_0 (S_l \rho_l \chi_{lW} + S_h \rho_h \chi_{hW}) + \nabla \cdot (q \rho_l \chi_{lW}) - \nabla \cdot (D_{lW} \rho_l \nabla \chi_{lW}) = \bar{f}_W.$$

The structure of these equations is similar to that of (15) except that the salinity component is not present in the hydrate phase. Based on (1a) we can divide (18) by ρ_l ; remaining $\chi_{lS} = \chi_{lS}$ we obtain the salinity part of (2).

7.2. Pressure equation. To derive the pressure equation, we add (15), (18), (19). Collecting terms and taking into account volume constraints $S_l + S_h = 1$ as well as $\chi_{lM} + \chi_{lS} + \chi_{lW} = 1$ and $\chi_{kM} + \chi_{hW} = 1$ we see that the accumulation term becomes $\frac{\partial}{\partial t} \phi_0 (S_l \rho_l + S_h \rho_h)$. The advection term becomes $\nabla \cdot (q \rho_l)$, and the diffusion term

$$(20) \quad \begin{aligned} R_D &:= -\nabla \cdot (S_l \rho_l \phi_0 (D_M^0 \nabla \chi_{lM} + D_W^0 \nabla \chi_{lW} + D_S^0 \nabla \chi_{lS})) \\ &= -\nabla \cdot (S_l \rho_l \phi_0 (D_M^0 \nabla \chi_{lM} + D_W^0 \nabla (1 - \chi_{lM} - \chi_{lS}) + D_S^0 \nabla \chi_{lS})) \\ &= -\nabla \cdot (S_l \rho_l \phi_0 ((D_M^0 - D_W^0) \nabla \chi_{lM} + (D_S^0 - D_W^0) \nabla \chi_{lS})). \end{aligned}$$

Assuming that all diffusivities are equal, $\nabla \sum_{C=M,W,S} \chi_{lC} = \nabla(1) = 0$ and the diffusion term R_D vanishes. After further simplifications based on (1a) we obtain

$$\frac{\partial}{\partial t} \left(\phi_0 \left(S_l \left(1 - \frac{\rho_h}{\rho_l} \right) + \frac{\rho_h}{\rho_l} \right) \right) + \nabla \cdot q = f,$$

where $f = f_M + f_S + f_W$. If furthermore ϕ_0 is assumed constant in time, and $\rho_h \approx \rho_l$, then, after some algebra, we obtain the steady state pressure equation

$$(21a) \quad \nabla \cdot q = f.$$

The equation (21a) is coupled with Darcy's law

$$(21b) \quad q = -\frac{K}{\mu} (\nabla P_l - \rho_l G \nabla D(x))$$

In the absence of sources and $f \equiv 0$, q is divergence free. In the 1D case, $q = \text{const}$ and is equal to the flux across the boundary $\partial\Omega$. In fact, due to low fluxes q , the pressure is usually close to the hydrostatic $P_l^0(x)$ pressure defined by (1b).

7.3. Conversion factors. The conversion factor between χ_{lS} and χ_{lS}^m is computed as follows. Assume we have 1L seawater with weight 1.03kg=1030g. Let the salinity be $\chi_{lS} = 0.035\text{kg/kg}$. In the volume of 1L this corresponds to $0.035 * 1030 = 36.05\text{g}$. Using molecular mass of 58.44g/mole of NaCl, we see that this gives $36.05/58.44 = 0.62$ moles of NaCl. The same volume 1L of seawater has $N = 1030/18.02 = 57.2$ moles, since 18.02g/mole is the molecular weight of water. Thus the mole fraction corresponding to $\chi_{lS} = 0.035\text{kg/kg}$ and $S = 35\text{g/kg}$ is therefore $\chi_{lS}^m = 0.62/(0.62 + 57.2) = 0.01$.

Further conversion factors are needed. In particular, for f_M , we have

$$(22) \quad 1 \frac{\text{mmol}}{\text{m}^3\text{yr}} \\ = 10^{-3} \frac{\text{mol}}{\text{m}^3\text{yr}} \times 16 \frac{\text{g}}{\text{mol}} \times 10^{-3} \frac{\text{kg}(\text{CH}_4)}{\text{g}} \times \frac{1}{1030} \frac{\text{m}^3}{\text{kg}(\text{SW})} \times 1000 \frac{\text{yr}}{\text{kyr}} \\ = 1.55 \times 10^{-5} \frac{\text{kg}(\text{CH}_4)}{\text{kg}(\text{SW})\text{kyr}}$$

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