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Master's Thesis:

# **Modelling of Mine Gas Repositories**

submitted by :

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### Author's Statement

I hereby certify that I have prepared this master's thesis independently, and that only those sources, aids and advisors that are duly noted herein have been used and / or consulted.

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# **1** Introduction

Methane, the major component of natural gas, is a by-product of the coal formation process. In regions with abandoned underground coal mines, methane emission to the surface has to be controlled to ensure safe living conditions, since it is explosive and suffocative. The control of methane, a greenhouse gas, can reduce emissions into the atmosphere and the utilization of methane can provide an alternative energy source.

## 1.1 Coalbed Methane

Over millions of years coal seams are formed by so called "coalification" process, biochemical decay and metamorphic transformation of vegetable matter under high pressure. During the coalification process large amount of gases are produced. Most of the gases produced during this process escape to the atmosphere and some of them retain in the coal. Coalbed methane is the name given to methane found in coal seams (IEA [1994]).

Coal can be classified from lower to upper rank as (ACA [2004]):

- lignite
- subbituminious
- bituminous
- anthracite

The amount of gas retained in the coal depends on the rank of coal , depth of burial, geological anomalies, tectonic forces, and the temperature during coalification. In general, the higher the rank of coal and the greater the depth of seam, the higher is its gas content. The gas content of the coal seam differ between 0 to 25  $m^3$ /ton. In general, 90 to 95 % of the gas emission from coal seams are

methane and the rest are inert gases like  $N_2, CO_2, Ar$  and others like He,  $H_2$  (IEA [1994]).

## 1.2 Coalbed Methane Migration

In its natural state coalseams are under pressure deep in the subsurface. The mining of coal dramatically reduce the pressure of the coalseams, which eventually results in release of the coalbed methane via desorption. The desorption of the coalbed methane can take years to decades. During the active coal mining methane gas is discharged to the atmosphere through the mine shaft. Methane is less dense than air. The density difference between air ( $\varrho_a = 1.2 \ kg/m^3$ ) and methane ( $\varrho_m = 0.6 \ kg/m^3$ ) results in the upward movement of methane caused by buoyancy forces. After closing the coalmine the mine shaft is filled with cohesive material to prevent methane emission to the surface. However, methane finds its way through the overlying soil to the surface (Breiting et al. [2000]).



Figure 1.1: Schematic presentation of methane migration in the subsurface

Figure 1.1 shows methane migration in the subsurface. In the lower aquifer methane forms a gas phase. It passes through the lower aquifer and accumulates under the

aquitard. Methane passes through the aquitard by dissolving in the water phase. After passing through the aquitard some of the methane degasses in the the upper auqifer forming again a gas phase. The dissolved methane can also be transported in the water phase. Finally, it enters the unsaturated zone and reaches to the surface, where it can be dangerous. The problems with the methane migration to the surface are discussed in the next subsection.

### **1.3 Coalbed Methane Problem and Control**

Methane which is odorless can lead to serious problems to the people and environment (Breiting et al. [2000]):

- It is explosive if the concentration in air is in the range of 5 to 15 vol.-%.
- There is a risk of suffocation where methane is leaking near the surface of the households.
- It can be harmful to the vegetation growth.
- Methane is a greenhouse gas.



Figure 1.2: Permeable pavement for lowering methane concentration

Methane emission to the surface should be controlled in the regions with abandoned underground coal mines. Therefore, wells are drilled into the subsurface (figure 1.5a). Methane is controlled either via passive wells (1.5b) without applying extra pressure or via active wells with applying extra pressure (Ochs et al. [2003]). If the wells can not collect all the methane discharge, the pavement of the surface should be permeable enough to prevent any local increase in the methane concentration (figure 1.2).

### 1.4 Co-generation Power Plants

Methane, which has to be controlled via wells, is either discharged to the atmosphere or is utilized as an energy source. Co-generation power plants are built on site to produce thermal and electrical energy from the extracted gas mixtures. Conventional power plants (for gas combustion) can only produce electricity and have an efficiency of 35%, the rest is released to the environment as heat energy. Whereas, in co-generation power plants excess heat can be reutilized for electricity production, which increases he efficiency up to 90% or excess heat can be utilized as thermal energy for the heating of the households (BHKW [2004]). Utilization is economically viable if the necessary minimum amount of methane ( $\approx 33-35$  vol.-%) can be extracted during the life time ( $\approx 20$  years) of the project. Co-generation power plants have a capacity range of 212 - 1942 kW for electricity production and a capacity range of 320 - 1974 kW for thermal energy production depending on the size of the power plant (Pro2 [2004]). In Europe energy need per capita per year is 6500 kWh in 2002 (VDEW [2004]). That means a co-generation power plant can meet the energy needs of up to 2600 persons in a year in Europe depending on the capacity of the power plant.

### 1.5 Task Description

In the regions with abandoned coal mines considerable amount of methane migrates to the surface. This methane can cause restricted use of land and is a potential risk for the residents. This fact resulted in the installation of extraction wells in many mining areas to be able to control the migration of methane and prevent the intrusion of methane into the basements of buildings.

If the amount and concentration of the extracted methane-air mixture is high enough, it can be utilized as an energy source. Co-generation power plants can be build on site to produce thermal and electrical energy from the extracted gas mixture. Co-generation power plants (figure 1.4) require a minimal methane concentration of around 33-35 vol.-%.

In Germany the utilization of methane primarily depends on the development of new technology which can make it possible to exploit lower concentrations of methane and to maximize methane output by locating the wells at correct position and depths.

For the development of mine gas repositories no reliable tests exist to evaluate the productiveness or the optimal operation of the extraction wells. Due to usual complex geology and physical behavior of mine gas repositories numerical simulations can help to get better understanding of these systems and to identify the important processes influencing the productiveness.

Methane migration in the subsurface can be modeled by using different numerical models. In the work of Ochs et al. [2003] single-phase (gas) single-component (methane) model was used to model gas-extraction in the unsaturated subsurface. In order to get better understanding of the methane migration in the subsurface more complex models are needed. In the work of Kobayashi [2004] twophase (water, gas) two-component (water, methane) model and two-phase (water, gas) three-component (water, methane, air) model were used to model methane migration in abandoned coal mining areas. Two-phase three-component model, which is developed by Kobayashi, is able to model mass transfer between the phases.

The goal of this thesis is to further develop the two-phase three-component model for the modeling of mine gas repository including the transport of the components water, air and methane. With this model several test cases will be set up in cooperation with the Deutsche Montan Technologie GmbH to investigate the behavior of mine gas repositories.

## **1.6 Global Potential of Coalbed Methane Recovery** during Active Coalmining

Global methane emissions from all sources, natural or man-made, are estimated in the range of 425 - 675 million tonnes/yr. Most of the methane emissions are from natural sources, such as swamps, decay of vegetation, termites and digestive tract of animals. Man-made sources are rice fields, landfills, oil and natural gas production and transmission, and coal mining. The total methane emission from the coal industry are estimated at 21.8 million tonnes/yr, which is about 4-6 % of total global emissions. The ten largest coalbed methane emitting countries, which comprises 90 % of worlds coal production, are U.S.A., U.K., Russia, Australia, China, Germany, Poland, Czech Republic, S.Africa and India (IEA [1994]).

Coal seams in shallow depth, which can be extracted by surface mining, do not contain significant amount of methane and they are low in rank, like lignite and subbituminous coals. Almost all methane emissions from the coal industry are produced by underground mining, and most of this gas is captured via mine ventillation and coal seam degasification, which can be done through drilling wells at the surface or horizontal boreholes at the base of the shaft (IEA [1994]).

Under ideal conditions; i.e deep gassy seams are available, institutional barriers are minimized, and required technology and knowledge are available; 70 % of coalbed methane, whereas under less favorable conditions, intermediate depth seams containing less gas, only 30 % to 40 % of the coalbed methane can be recovered. Table 1.1 represents the theoretical or technological potential for the coalbed methane recovery and the utilization in 1990 for the ten largest coalbed methane emitting countries (IEA [1994]).

China	1,053	976	7.7	35-45	3.1	0.1
Bussia	1,000 703	361	5.0	35 45	$\frac{5.1}{2.0}$	0.1
U.S.A	931	384	3.6	30-40	1.3	0.3
Poland	216	148	1.4	35 - 45	0.6	0.1
Germany	434	78	1.2	35-45	0.5	0.3
U.K.	95	79	0.9	35-45	0.4	0.1
S.Africa	206	124	0.8	25-35	0.2	-
India	212	64	0.5	25-35	0.2	-
Australia	163	53	0.4	30-40	0.1	0.1
Czech R.	119	25	0.3	35-45	0.1	0.1
Total	4,132	2,292	21.8		8.5	1.3

Table 1.1: Global methane emissions and potential recovery in 1990

As table 1.1 represents, only a small portion of recoverable methane is utilized by the coal producing countries. In Germany and in U.K., where coal production is stabilized or declining, coalbed methane recovery has reached a steady state. In the U.S.A, the industry is expanding as gassier coal seams are being mined. Although there are many sites in the U.S.A, they are not economical for coalbed methane utilization. In China the industry is developing fast but it is limited by the lack of necessary technology or technology transfer from the countries where coalbed methane is more established. Australia has good potential and the transfer of technology is leading to higher percentages in the utilization (IEA [1994]).

Currently, the primary reason for coalbed methane recovery from the active coal mines is mine safety. In general the obstacles to coalbed methane recovery and utilization are (IEA [1994]):

- Gas Ownership Issues: The conflicts concerning the ownership of the coalbed methane hindered many project in different countries. Owners of the surface, coal, oil and gas, and other minerals assert ownership of coalbed methane.
- Tax : Tax policies can boost the commercial utilization of methane
- Financial condition of industry: The small percentage in the profit of coal industry is leading the capital owners to invest to the other sectors of the industry with higher return value.
- Availability of technology: The development of turbines and combustors which can accept lower concentrations of methane as source will lead to higher utilization.

### 1.7 Situation in Germany

From 1980 to 2001 the volume of coal mined in Germany sank from 87 to 27 billion tons, and the number of those employed in the industry declined by 72 % to about 53,000 (UBA [2004]). The Ruhr and Saar basins are the most important coal and methane producing regions. Figure 1.3 shows active coal mines in the federal state of Nordrhein-Westfalen (DSK [2004]). As figure 1.3 shows, there is no active coal mines in the major cities of the Ruhr basin, i.e. Duisburg, Essen, Bochum and Dortmund. Almost all of the mines in this region have been abandoned, where bituminous coal seams exist in 800 meters deep (IEA [1994]). Coalbed methane recovery in Germany can be divided into two groups:

- Coalbed methane recovery from active coalmines.
- Coalbed methane recovery from abandoned coalmines.

### 1.7.1 Coalbed Methane Recovery from Active Coalmines

The recovery of coalbed methane is nearly 30 % of the total methane released from coal seams. Approximately 70 % of the recovered methane is utilized as heating or electricity production. The rest is released to the atmosphere. As the government officials suggest, 45 % of the methane could be recovered and utilized. Safety regulations in Germany does not allow any utilization if the methane content is less than 25 vol.-%, since it is explosive in the range of 5 to 15 vol.-%. If the recovery techniques are improved, a recovery efficiency of 35 to 45 % can be reached (IEA [1994]).



Figure 1.3: Active coal mines in the federal state of Nordrhein-Westfalen



Figure 1.4: Entrance shaft of an abandoned coal mine and a co-generation power plant in Bochum





Figure 1.5: a) A new drilling site in Essen, b) A passive methane extraction well in Dortmund

### 1.7.2 Coalbed Methane Recovery from Abandoned Coalmines

In the Ruhr-basin there are many coal mines which have been abandoned at the end of 19Å 'th century. The entrance shafts of these mines are closed to make the old mines inaccessible (figure 1.4). In the last decade the coalbed methane potential of these abandoned mines has been discovered. Coalbed methane is dangerous but valuable. Methane which is released from the existing coal seams is propagating to the surface. This situation endangers the households living near the abandonned coal mines. The solution of the problem is controling the coalbed methane by drilling wells from the surface (figure 1.5a). Methane is extracted either passive (figure 1.5b) without applying extra pressure or active with applying extra pressure. If available methane concentration is above 33-35 vol.-%, it can be used as an energy source too.

### 1.8 Coalbed Methane Utilization

Coalbed methane utilization highly depends on the methane concentration of the recovered gas mixture. Table 1.2 represents the four forms of recovery and the quality of the coalbed methane gas.

Туре	Origin	$Ch_4Content$
Low Quality	Ventilation Air (Active Mines)	${<}1$ vol $\%$
Medium Quality	Unsealed Gob Wells (Active Mines)	30 to $95$ vol $%$
Medium Quality	Passive and Active Wells (Abandoned Mines)	6 to $60$ vol $%$
High Quality	Sealed Gob Wells & Horizontal Boreholes (Active Mines)	$>\!\!95$ vol%

Table 1.2: Four forms of capture and the quality of the coalbed methane gas

Methane recovery is prerequisite for utilization. However, it is not a sufficient condition. Coalbed methane recovery is mainly applied to control the methane emission or to maintain safety in coal mines. In order to utilize methane it should be financially attractive, which depend on evaluation of (IEA [1994]):

- the quantity and quality of the gas
- the cost of gas gathering and processing
- the physical accessibility of markets

The utilization of coalbed methane is either realized on-site or off-site (IEA [1994]):

- On-site utilization, i.e generating electricity or heating of the households or industry, normally does not require purification (separation of  $CO_2$ , water vapor). Therefore, medium quality gas can be used. Additionally, it requires gathering systems like wells and utilization plants (combustor, generator).
- Off-site utilization is mainly done by selling methane to the housholds or industry as substitute of natural gas. It is only possible if the needs of the pipeline owners, high quality and quantity, can be met. Methane concentrations of pipeline gas must have at least 96% of methane and not more than 4% of inert gases. Therefore, it requires an investment on pipelines, compression process and treatment facility. Additionally, pipeline operators' low tolerance on fluctuation may limit the amount which can be supplied.

In the regions with abandoned coal mines methane migration in the subsurface has great importance both for public safety and for economical reasons (co-generation power plants). Complex numerical models are needed to get better understanding of the methane migration in the subsurface. The goal of this thesis is to further develop two-phase (water,gas) three-component (water,methane ,air) model and to set up several test cases to invesigate the behaviour of mine gas repositories. In the next section two-phase three-component model (2p3c model) and the modifications to this model which are applied in this work are described in detail.

# 2 Two-Phase Three-Component Model (2p3c Model)

## 2.1 Conceptual Model

### 2.1.1 Definitions of Phase and Component

For the understanding of a multi-phase system like the migration of methane in the subsurface, some preliminary definitions have to be given. The terms phase and component are defined as follows:

- Phase: The term phase is used to differentiate between two or more fluid contuinia, seperated by a sharp interface, across which discontinuities in fluid properties exist (Helmig [1997]). A phase has a homogeneous chemical composition and physical state. Solid, liquid and gaseous phases can be distunguished while there can be several liquid phases present in a porous medium, only one gas phase can exist (Class et al. [2002]).
- **Component**: The term component stands for the constituents of the phases which can be associated with a unique chemical species. The number of the components in a system is the minimum number of independent chemical species necessary to define the composition of all phases present in the system (Kobayashi [2004]).

# 2.1.2 Numerical Models for the Methane Migration in the Subsurface

Methane migration in the subsurface can be modelled by using different models. In the work of Ochs et al. [2003] single-phase (gas) single-component (methane) model is used to model gas-extraction in the unsaturated subsurface. Although this model could give valuable tips for an efficient operation of passive and active methane wells, its application is limited to the unsaturated zone. In order to get better understanding of the methane migration in the subsurface more complex models are needed. In the work of Kobayashi [2004] two-phase (water, gas) twocomponent (water, methane) model and two-phase (water, gas) three-component (water, methane, air) model are used to model methane migration in abandoned coal mining areas. Two-phase three-component model, which is developed by Kobayashi, is able to model mass transfer between the phases. In this work two-phase threecomponent model is further developed to describe the solubility of methane in the water phase as a function of temperature and pressure, the mixture viscosity of the gas phase as a function of temperature, the effect of tortuosity on the diffusion of the components, the diffusion of methane in the water phase as a function of temperature.

### 2.1.3 The Phases and the Components in 2p3c Model

Methane propagation in subsurface is modeled with 2-phase 3-component isothermal multiphase multicomponent model. Two phases are water phase and gas phase. Each phase comprises of three components water, methane and air. The mass transfer between the phases can happen via evaporation and condensation of component water or via dissolution and degassing of components air and methane.(fig.2.1)



Figure 2.1: Two-phase three-component model concept (modified after Class et al., 2002)

### 2.1.4 Constitutive and Closure Relations

#### **Mole Fractions**

The sum of the mole fractions of of each component in a phase should be one.

$$X_{w}^{w} + X_{w}^{a} + X_{w}^{m} = 1 \qquad [-]$$

$$X_{g}^{w} + X_{g}^{a} + X_{g}^{m} = 1 \qquad [-]$$
(2.1)

#### **Partial Pressures**

According to DaltonÂ's law the sum of partial pressures of each component in gas phase should give total gas phase pressure (equation 2.2). For the components methane and air the ideal gas law is valid (equation 2.3).

$$P_g = P_g^w + P_g^a + P_g^m \qquad [Pa] \tag{2.2}$$

$$P_g^{\alpha} = \frac{n_{\alpha} \cdot R \cdot T}{V} \qquad [Pa] \tag{2.3}$$

Partial pressure of water in gas phase can be calculated according to RaultA's law (equation 2.5). Since the mole fraction of water in the water phase is almost one  $(X_w^w \simeq 1)$ , vapour pressure of water in the gas phase is equal to the saturation vapour pressure of water  $(P_g^w \simeq P_w^{sat})$ .

$$P_g^w = P_w^{sat} \cdot X_w^w \qquad [Pa] \tag{2.4}$$

$$X_g^w = \frac{P_w^{sat}}{P_g} \qquad [-] \tag{2.5}$$

#### Henry's Law

In order to calculate the mole fractions of components air and methane in the water phase RaultA's law can not be used, because the concentration of the air and methane is very low in water. Instead HenryA's law is used, since it is valid for the solutions of low concentrations. Henry constant for air can be computed according to equation 2.6 (Helmig [1997]).

$$X_w^a = P_g^a \cdot H_w^a \qquad [-]$$

$$H_w^a = (0.8942 + 1.47 \cdot e^{-0.04394 \cdot T}) \cdot 10^{-10} \qquad [1/Pa]$$
(2.6)

where T is in  $[^{o}C]$ .

Mole fraction of the methane in water  $(X_w^m)$  is not calculated using HenryÂ's law, since it is not available for methane as a function of temperature and pressure. In this work  $X_w^m$  is directly calculated using the solubility function of methane in water (figure 3.1 right), which is a function of total gas pressure  $(P_g)$ , mole fraction of methane in the gas phase  $(X_g^m)$  and temperature (T) (equation 2.7). In this work solubility function of methane in water is implemented into a 2-phase 3-component model. See chapter 3 for more details concerning the solubility of methane in the water phase.

$$X_w^m = S_w^m(P_g, T, X_g^m) \qquad [-]$$
(2.7)

#### Density

$$\varrho_{mass,g} = \varrho_{mol,g} (X_g^a M^a + X_g^m M^m + X_g^w M^w) \qquad [kg/m^3]$$

$$\varrho_{mass,w} = \varrho_{mol,w} (X_w^a M^a + X_w^m M^m + X_w^w M^w) \qquad [kg/m^3]$$
(2.8)

$$\varrho_{mol,g} = \frac{P_g^a + P_g^m + P_g^w}{BT} \qquad [mole/m^3]$$
(2.9)

The computation of  $\rho_{mol,w}$  can be found in S.Panday et al. [1995].

RT

Figure 2.2 shows mass density of the gas phase v.s. mole fraction of methane in the gas phase  $(X_g^m)$  for atmospheric pressure. Figure 2.3 shows mass density of the gas phase v.s.  $X_g^m$  for a pressure range of 1 [bar] - 30 [bar] with 5 [bar] intervals.



Figure 2.2: Mass density of the gas phase v.s. mole fraction of methane in the gas phase  $(X_q^m)$  for 1 [bar]

As figure 2.2 shows the density of the gas phase is between the density of the air and methane. It varies depending on the mole fraction of the components. As figure 2.3 shows mass density of the gas phase is increasing with increasing pressure. There is always water in the gas phase depending on the temperature and pressure. Therefore,  $X_g^m$  never equals to 1.



Figure 2.3: Mass density of the gas phase v.s. mole fraction of methane in the gas phase  $(X_a^m)$  for different pressures

### Viscosity

Viscosity is a property of material that is governed by intermolecular forces. The viscosity of gases at low pressures is independent of pressure and increases with increasing temperature. In liquid state, viscosity depends on pressure or density as well as on the temperature (VDI-Gesellschaft [1992]).

The viscosities of the single gases  $(O_2, N_2, CH_4)$  at low pressure can be calcultaed as a function of temperature. In order to calculate the air viscosity, it is necessary to calculate the viscosities of  $O_2$  and  $N_2$ . In the following equations, all the viscosity values are dynamic viscosities in [kg/m\*s] and temperature is in [<sup>o</sup>K]. **Viscosity of Nitrogen**: The viscosity of nitrogen at low pressures for a temperature range of 63.1  $[{}^{o}K] < T < 5048 [{}^{o}K]$  can be calculted according to equation 2.10, which has approximately 3 % error (VDI-Gesellschaft [1992]).

$$\mu_{N2} = 5.6957 \cdot 10^{-7} \cdot T^{0.618} - 5.0095 \cdot 10^{-6} \cdot e^{-3.5578 \cdot 10^{-3} \cdot T} + 4.7710 \cdot 10^{-6} \cdot e^{-3.2155 \cdot 10^{-2} \cdot T} + 2.5258 \cdot 10^{-7} \qquad [kg/m * s] \quad (2.10)$$

**Viscosity of Oxygen**: The viscosity of oxygen at low pressures for a temperature range of 77.3  $[{}^{o}K] < T < 6184 [{}^{o}K]$  can be calculted according to equation 2.11, which has approximately 3 % error (VDI-Gesellschaft [1992]).

$$\mu_{O2} = 6.771 \cdot 10^{-7} \cdot T^{0.618} - 6.7514 \cdot 10^{-6} \cdot e^{-2.9043 \cdot 10^{-3} \cdot T} + 6.4299 \cdot 10^{-6} \cdot e^{-26248 \cdot 10^{-2} \cdot T} + 3.4041 \cdot 10^{-7} \qquad [kg/m * s] \quad (2.11)$$

**Viscosity of Methane**: The viscosity of methane at low pressures for a temperature range of 95.3  $[{}^{o}K] < T < 7624 [{}^{o}K]$  can be calculted according to equation 2.12, which has approximately 3 % error (VDI-Gesellschaft [1992]). In this work viscosity function of methane is implemented into the 2-phase 3-component model.

$$\mu_{CH_4} = (0.807 \cdot (\frac{T}{190.6})^{0.618} - 0.357 \cdot e^{-0.449 \cdot \frac{T}{190.6}} + 0.340 \cdot e^{-4.058 \cdot \frac{T}{190.6} + 0.018}) \cdot \frac{1}{82296.56} \qquad [kg/m * s] \quad (2.12)$$

#### Wilke Method

For the calculation of the mixture viscosity of gas phase at low pressures Wilke Method is used. Equation 2.13 describes Wilke-method for three components in the gas phase (Poling et al. [2001]). In this work Wilke-method is implemented into the 2-phase 3-component model.

$$\mu_{g} = \sum_{i=1}^{3} \frac{x_{g}^{i} \mu_{g}^{i}}{\sum_{j=1}^{3} x_{g}^{j} \phi^{i,j}}$$

$$\phi^{i,j} = \frac{\left(1 + \sqrt{\frac{\mu_{g}^{i}}{\mu_{g}^{j}}} (\frac{M^{j}}{M^{i}})^{(1/4)}\right)^{2}}{\sqrt{8(1 + \frac{M^{i}}{M^{j}})}}$$

$$\phi^{j,i} = \frac{\mu_{g}^{j} M^{i}}{\mu_{g}^{i} M^{j}} \phi^{i,j}$$
(2.13)

For non-polar mixtures Wilke Method gives very good results. For binary systems Wilke method gives an average deviation of less than 1 %. Therefore, for the calculation of the air viscosity, this method can be used (major components of the air are nitrogen (non-polar) and oxygen (non-polar). After computation of the air viscosity, gas phase viscosity can be computed by using Wilke method. Among the 3 components (air, methane and water vapor) of the gas phase, only water is polar. Taking low temperatures and small mole fraction of water in the gas phase into account Wilke method can be used (Poling et al. [2001]). Figure 2.4 shows gas phase viscosity (wilke method) v.s. mole fraction of methane in the gas phase  $(X_g^m)$  for a temperature range of 273.15 [°K] - 303.15 [°K] with 5 [°K] intervals under atmospheric pressure.

#### Water Phase Viscosity

For the water phase viscosity pure water viscosity is used. In this work it is assumed that water phase viscosity is not effected from the very low dissolutions of methane and air in the water.

$$\mu_w = e^{-24.71 + \frac{4209}{T} + 0.04527 \cdot T - 3.376 \cdot 10^{-5} \cdot T^2} \cdot 10^{-3} \qquad [kg/(m*s)] \tag{2.14}$$



Figure 2.4: Viscosity of the gas phase v.s. mole fraction of methane in the gas phase  $(X_g^m)$  for 1 [bar]

#### **Dispersion and Diffusion**

Hydrodynamic dispersion is the sum of molecular diffusion and mechanical dispersion. The mechanical dispersion is a result of velocity fluctuations. Since the velocities are small in pore space, the mechanical dispersion is neglected. Diffusivity in the gas phase can be calculated by using binary diffusivities (Falta et al. [1992]). Binary diffusivities  $D_g^{aw}, D_g^{mw}, D_g^{am}$  can be calculated via equations 2.15 according to Poling et al. [2001]. Table 2.1 shows the notations in equations 2.15.

$$D_{g}^{i,j} = \frac{0.00266 \cdot T^{1.5} \cdot \sqrt{M^{r}}}{P_{g} \cdot (\sigma^{i,j})^{2} \cdot \Omega}$$
$$M^{r} = \frac{M^{i} + M^{j}}{M^{i} \cdot M^{j}}$$
$$\sigma^{i,j} = (\sigma^{i} + \sigma^{j})/2$$
(2.15)

$$\Omega = \frac{1.06036}{(T^*)^{0.15610}} + \frac{0.193}{e^{T^* \cdot 0.47635}} + \frac{1.03587}{e^{T^* \cdot 1.52996}} + \frac{1.76474}{e^{T^* \cdot 3.89411}}$$

$$T^* = \frac{T}{\left[\left(\varepsilon^i/k\right) \cdot \left(\varepsilon^j/k\right)\right]^{0.5}}$$

Abbreviation	Full name	Value
$\sigma^{a}$	characteristic lenght of air	3.711 [ <sup>o</sup> A]
$\sigma^m$	characteristic lenght of methane	$3.758 [^{o}A]$
$\sigma^w$	characteristic lenght of water	$2.641 [^{o}A]$
$\varepsilon^a/k$	characteristic energy of air over Boltzmann constant(k)	78.6 [ <sup>o</sup> K]
$\varepsilon^m/k$	characteristic energy of methane over Boltzmann constant(k)	$148.6 \ [^{o}\text{K}]$
$\varepsilon^w/k$	characteristic energy of water over Boltzmann constant(k)	809.1 [ <sup>o</sup> K]
Ω	diffusion collision integral	-
$P_{g}$	total gas pressure	in [bar]
T	temperature	in $[^{o}K]$
$M^i$	molecular weight of component	in [kg]

Table 2.1: Notations in equations 2.15

Equations 2.16 and 2.19 are modified for air, methane and water after Class et al. [2002].

$$D_{g}^{w} = \frac{1 - X_{g}^{w}}{\frac{X_{g}^{a}}{D_{g}^{aw}} + \frac{X_{g}^{m}}{D_{g}mw}} \qquad [m^{2}/s]$$

$$D_{g}^{m} = \frac{1 - X_{g}^{m}}{\frac{X_{g}^{a}}{D_{g}^{am}} + \frac{X_{g}^{w}}{D_{g}mw}} \qquad [m^{2}/s]$$
(2.16)

Figure 2.5 shows diffusion of the methane in the gas phase v.s. mole fraction of methane in the gas phase $(X_g^m)$  for a pressure range of 1 [bar] - 30 [bar] with 5 [bar] intervals at 288.15 [<sup>o</sup>K].

The effect of porous medium is taken into account by implementing tortuosity and porosity, since diffusion only occurs in the void space and not in the grains. Tortuosity is the ratio between the true path length and the smallest distance between two points (Cirpka [2004]). Tortuosity for multi-phase flow can be defined as a function of effective porosity and saturation of the phases (equation 2.18) (Class [2001]):

$$D_{pm_g}^w = T \cdot \phi \cdot S_g \cdot D_g^w \qquad [m^2/s]$$

$$D_{pm_g}^m = T \cdot \phi \cdot S_g \cdot D_g^m \qquad [m^2/s]$$

$$D_{pm_w}^m = T \cdot \phi \cdot S_w \cdot D_w^m \qquad [m^2/s]$$

$$D_{pm_w}^a = T \cdot \phi \cdot S_w \cdot D_w^a \qquad [m^2/s]$$
(2.17)

where T is tortuosity,  $\phi$  is porosity.

$$T_{g} = \frac{n_{e} \cdot S_{g}^{\frac{7}{3}}}{n_{e}^{2}}$$

$$T_{w} = \frac{n_{e} \cdot S_{w}^{\frac{7}{3}}}{n_{e}^{2}}$$
(2.18)

The diffusion mole-flux of the components can be calculated according to equation 2.19.



Figure 2.5: Diffusion of the methane in the gas phase v.s. mole fraction of methane in the gas phase  $(X_q^m)$  for different pressures at 288.15 [<sup>o</sup>K]

$$J_{g}^{w} = -\varrho_{mol,g} \cdot D_{pm_{g}}^{w} \cdot grad(X_{g}^{w}) \qquad [mole/(m^{2}/s)]$$

$$J_{g}^{m} = -\varrho_{mol,g} \cdot D_{pm_{g}}^{m} \cdot grad(X_{g}^{m}) \qquad [mole/(m^{2}/s)]$$

$$J_{w}^{m} = -\varrho_{mol,w} \cdot D_{pm_{w}}^{a} \cdot grad(X_{w}^{a}) \qquad [mole/(m^{2}/s)]$$

$$J_{w}^{m} = -\varrho_{mol,w} \cdot D_{pm_{w}}^{m} \cdot grad(X_{w}^{w}) \qquad [mole/(m^{2}/s)]$$

$$(2.19)$$

In this work diffusion of methane in water phase is computed as a function of temperature (figure 2.6). Diffusion of methane in water phase can be get from Lide [2004]. After second degree polynomial regression analysis equation 2.20 is obtained. Table 2.2 shows the regression function values and the values from Lide [2004].

Temperature (C)	$D_{mw} \cdot 10^{-9} \ [m^2/s]$	$D_{mw} \cdot 10^{-9}$ $[m^2/s]$ regression
10	1.24	1.244
15	1.43	1.422
20	1.62	1.621
25	1.84	1.842
30	2.08	2.084
35	2.35	2.347

Table 2.2: Diffusion coefficient of methane in water and its regression

$$D_{mw} = 0.00042857 \cdot T^2 + 0.024829 \cdot T + 1.2443 \qquad [m^2/s] \tag{2.20}$$



Figure 2.6: Diffusion of methane in water v.s. temperature

There is no need to calculate the diffusion mol-flux of component air in gas phase and component water in water phase, since they can be computed via equation 2.21.

$$J_g^m + J_g^a + J_g^w = 0 \qquad [mole/(m^2/s)] J_w^m + J_w^a + J_w^w = 0 \qquad [mole/(m^2/s)]$$
(2.21)

### Specific Enthalpy and Specific Internal Energy

Both specific enthalpy and specific internal energy of each phase are required to be formulated for the calculation of the thermal energy balance equation 2.31 of the system. Equation 2.22 describes the specific enthalpy and specific internal energy relationship of each phase for changing volume.

$$h_{\alpha} = \mu_{\alpha} + \frac{p_{\alpha}}{\varrho_{mass,\alpha}} \qquad [J/kg] \tag{2.22}$$

Table (2.3) shows the notations in equation 2.22.

Abbreviation	Full name	Unit
$h_{lpha}$	specific enthalpy	J/kg
$\mu_{lpha}$	specific internal energy	J/kg
$p_{lpha}$	pressure	Pa
$\varrho_{lpha}$	mass density of phase $\alpha$	$kg/m^3$

 Table 2.3: Notations in equations 2.22

#### Heat Conductivity

Heat conductivity of the porous medium is calculated according to equation 2.23 (Class et al. [2002]), which is the modification of Somerton approach (Somerton et al. [1974]).

$$\lambda_{pm} = \lambda_{pm}^{Sw=0} + \sqrt{S_w} \cdot \lambda_{pm}^{Sw=1} - \lambda pm^{Sw=0} \qquad [Watt/({}^oK \cdot m)]$$
(2.23)

### **Saturation Constraint**

The sum of saturations of the phases is equal to 1.

$$S_g + S_w = 1 \tag{2.24}$$

### **Relative Permeability**

In this work Van Genuchten relative permeability saturation relationship is used (equations 2.25 and 2.26) ((van Genuchten [1980])).

$$k_{rw}(S_w) = \left(\frac{S_w - S_{wr}}{1 - S_{wr} - S_{nr}}\right)^{\frac{1}{2}} \cdot \left[1 - \left(1 - \left(\frac{S_w - S_{wr}}{1 - S_{wr} - S_{nr}}\right)^{\frac{1}{m}}\right)^m\right]^2$$
(2.25)

$$k_{rn}(S_w) = \left(1 - \left(\frac{S_w - S_{wr}}{1 - S_{wr} - S_{nr}}\right)\right)^{\frac{1}{3}} \cdot \left[1 - \left(\frac{S_w - S_{wr}}{1 - S_{wr} - S_{nr}}\right)^{\frac{1}{m}}\right]^{2m}$$
(2.26)

The figures 2.7 and 2.8 show the relative permeability saturation relationship for two different soil types which are used in this work.



Figure 2.7: Relative permeability saturation relationship of Van Genuchten equation for clayey-loam



Figure 2.8: Relative permeability saturation relationship of Van Genuchten equation for sand

#### **Capillary pressure**

In this work Van Genuchten capillary pressure saturation relationship is used (equation 2.27) (van Genuchten [1980]).

$$Pc(S_w) = \frac{1}{\alpha} \cdot \left[ \left( \frac{S_w - S_{wr}}{1 - S_{wr} - S_{nr}} \right)^{-\frac{1}{m}} - 1 \right]^{\frac{1}{n}}$$
 [Pa] (2.27)

Capillary pressure-saturation relationship of the clayey-loam is regulated to prevent too large capillary pressure around residual water saturation. The figures 2.9 and 2.10 show the capillary pressure saturation relationship for two different soil types which are used in this work.


Figure 2.9: Capillary pressure saturation relationship of Van Genuchten equation for clayey-loam



Figure 2.10: Capillary pressure saturation relationship of Van Genuchten equation for sand

# 2.2 Mathematical Model

In this work two-phase three-component multiphase multicomponent model is used. The model is based on 4 governing equations:

- 1 mass balance equation for each of the three components.
- 1 thermal energy balance equation

#### 2.2.1 Mass Balance

The mass conservation equations are derived for each component. Equations 2.28, 2.29, 2.30 describe the mass conservation for each component (Class et al. [2002]). The mass transport equation comprises of storage term, advective transport term, diffusive transport term and source/sink term.

#### Water Component:

$$\phi \frac{\partial(\varrho_{mol,w} x_w^w S_w + \varrho_{mol,g} x_g^w S_g)}{\partial t}$$
$$-div \left\{ \frac{k_{rw}}{\mu_w} \varrho_{mol,w} x_w^w \mathbf{K}(\mathbf{grad} P_w - \varrho_{mass,w} \mathbf{g}) \right\} - div \left\{ \frac{k_{rg}}{\mu_g} \varrho_{mol,g} x_g^w \mathbf{K}(\mathbf{grad} P_g - \varrho_{mass,g} \mathbf{g}) \right\}$$
$$-div (D_{pm_g}^w \varrho_{mol,g} \mathbf{grad} x_g^w) - div (D_{pm_w}^w \varrho_{mol,w} \mathbf{grad} x_w^w) - q^w = 0 \quad [mole/(m^3 \cdot s)]$$
$$(2.28)$$

#### Methane Component:

$$\phi \frac{\partial (\varrho_{mol,w} x_w^m S_w + \varrho_{mol,g} x_g^m S_g)}{\partial t}$$

$$-div\left\{\frac{k_{rw}}{\mu_w}\varrho_{mol,w}x_w^m\mathbf{K}(\mathbf{grad}P_w-\varrho_{mass,w}\mathbf{g})\right\}-div\left\{\frac{k_{rg}}{\mu_g}\varrho_{mol,g}x_g^m\mathbf{K}(\mathbf{grad}P_g-\varrho_{mass,g}\mathbf{g})\right\}$$
$$-div(D_{pm_g}^m\varrho_{mol,g}\mathbf{grad}x_g^m)-div(D_{pm_w}^m\varrho_{mol,w}\mathbf{grad}x_w^m)-q^m=0 \qquad [mole/(m^3\cdot s)]$$
(2.29)

#### Air Component:

$$\phi \frac{\partial(\varrho_{mol,w} x_w^a S_w + \varrho_{mol,g} x_g^a S_g)}{\partial t}$$
$$-div \left\{ \frac{k_{rw}}{\mu_w} \varrho_{mol,w} x_w^a \mathbf{K}(\mathbf{grad} P_w - \varrho_{mass,w} \mathbf{g}) \right\} - div \left\{ \frac{k_{rg}}{\mu_g} \varrho_{mol,g} x_g^a \mathbf{K}(\mathbf{grad} P_g - \varrho_{mass,g} \mathbf{g}) \right\}$$
$$-div (D_{pm_g}^a \varrho_{mol,g} \mathbf{grad} x_g^a) - div (D_{pm_w}^a \varrho_{mol,w} \mathbf{grad} x_w^a) - q^a = 0 \qquad [mole/(m^3 \cdot s)]$$
(2.30)

#### 2.2.2 Thermal Energy Balance

Although in this work almost isothermal calculations are carried out, the model is capable of simulating non-isothermal problems. Thermal energy balance eqaution 2.31 describes heat transport in the system. Since the mass that is transported carries its heat with itself, for each mass transport term there is a heat transport term. In addition to these terms, heat absorbtion by the soil and heat conductivity of the porous medium are considered in equation 2.31.

$$\phi \frac{\partial(\varrho_{mass,w} u_w S_w + \varrho_{mass,g} u_g S_g)}{\partial t} + (1 - \phi) \frac{\partial \varrho_s c_s T}{\partial t} - div(\lambda_{pm} \mathbf{grad}T)$$

$$-div \left\{ \frac{k_{rw}}{\mu_w} \varrho_{mass,w} h_w K(\mathbf{grad} P_w - \varrho_{mass,w} \mathbf{g}) \right\} - div \left\{ \frac{k_{rg}}{\mu_g} \varrho_{mass,g} h_g K(\mathbf{grad} P_g - \varrho_{mass,g} \mathbf{g}) \right\}$$

$$- div(D_{pm_g}^a \varrho_{mol,g} h_g^a M^a \mathbf{grad} x_g^a + D_{pm_g}^w \varrho_{mol,g} h_g^w M^w \mathbf{grad} x_g^w$$

$$+ D_{pm_g}^m \varrho_{mol,g} h_g^m M^m \mathbf{grad} x_g^m) - q^h = 0 \qquad [J/(m^3 \cdot s)] \quad (2.31)$$

Present Phase	Primary Variabales	Appearance	of Phase	Disappearance of Phase	
		water	gas	water	gas
w, g	$S_w, X_g^m, P_g, T$	-	-	$S_w < 0$	$S_g < 0$
W	$X_w^a, X_w^m, P_g, T$	-	$\overline{X_w^m} < X_w^m$	-	-
g	$X_g^w, X_g^a, P_g, T$	$P_g \cdot X_g^w > P_{sat}^w$	-	-	-

#### 2.2.3 Primary Variables and Phase Transition

 Table 2.4: Primary variables and phase appearance

In the system we have 3 mass conservation equations and 1 thermal energy balance equation. In addition to these 4 equations there exist 4 closure relations:

- $X_w^w + X_w^a + X_w^m = 1$
- $X_g^w + X_g^a + X_g^m = 1$
- $S_g + S_w = 1$
- $P_g = P_w + P_c$

However, there are 11 unknowns  $(X_w^w, X_w^a, X_w^m, X_g^w, X_g^a, X_g^m, S_g, S_w, P_g, P_w, T)$  in the system. Some of these unknowns disappear depending on the current available phase state. If water and gas phases exist at the same time, we need to solve the system for these 11 unknowns. The system with 11 unknowns can be solved if we have 11 equations. However, we have 8 equations. Additional 3 more equations are needed. These 3 extra equations are equation 2.6, equation 2.7, equation 2.5. Finally, the system of equations can be reduced to 4 main equations (3 mass conservation equations and 1 thermal energy balance equation) and the varibales can be reduced to 4 primary variables, if the other 8 equations are inserted into the 4 main equations.

Table 2.4 shows the primary variables and the constrains that control the phase transition depending on the currently available phase state. In this work the appearnce of the gas phase is modified after Class et al. [2002], since mole fraction of methane in the water phase is described by the solubility function of methane not by the Henry coefficient of the methane. If there is only water phase, appearance of gas phase is controlled by  $\overline{X_w^m} < X_w^m$ , where  $\overline{X_w^m} = S_w^m (Pg, 1-X_g^a - X_g^w, T)$  is the mole fraction of methane in water phase assuming that gas phase is appeared. Furthermore,  $X_q^w$  can be calculated via equation 2.5 and  $X_a^a$  via equation 2.32.

$$X_{g}^{a} = \frac{X_{w}^{a}}{H_{w}^{a}(T) \cdot P_{q}} \qquad [-]$$
(2.32)

# 2.3 Numerical Simulator MUFTE–UG

The program MUFTE-UG is used to carry out numerical simulations. MUFTE-UG is developed in a joint-venture project of the Department of Hydromechanics and Modeling of Hydrosystems (part MUFTE), University of Stuttgart, and the Technical Simulation Group of the Interdiciplinary Center for Scientific Computing (part UG), University of Heidelberg. MUFTE-UG is a combination of MUFTE and UG. MUFTE stands for **MU**ltiphase **F**low, **T**ransport and **E**nergy model. MUFTE toolbox mainly contains the physical model concepts and discretization methods in porous and fractured porous media. Figure 2.11 shows an overview of the modeling system. UG stands for **U**nstructured **G**rid. UG toolbox provides data structures and fast solvers for the discretization of partial differential equations based on parallel, adaptive multigrid methods (Hinkelmann [2003]). MUFTE-UG incorporates several different type of spatial discretization methods (BOX, CVFE method) and time discretization schemes (explicit, implicit).



Figure 2.11: Numerical simulator MUFTE-UG

# 2.4 Discretization

#### 2.4.1 Discretization in Space

In this work for the discretization in space box method (subdomain collacation finite volume method) is used. There are two meshes in the box method. The primary mesh is the unstructured mesh which consists of elements e and nodes  $K_i$ . Then a secondary mesh is generated for the formation of a control volume around each node  $K_i$ . The control volume  $B_i$  is formed by connecting the gravity centers of each adjoining element and the mid points of the adjoining element facets (figure 2.4.1) (Helmig [1997]). Each control volume  $B_i$  has n subcontrol volumes  $b_i^n$ , where n is the number of adjoining elements around node  $K_i$  (equation 2.33).



Figure 2.12: Control volume in box method

$$B_i = \sum_{n=1}^n b_i^n \tag{2.33}$$

This method is called node centered finite volume method or box method because each node of the primary mesh can be uniquely assigned a box, even at the boundary. In practice, global stiffnes matrix is constructed according to the finite element formulation, i.e. all line integral within an element are computed by a loop over all elements. The integral over the segment of a straight line is approximated by the midpoint rule, i.e. the value at the midpoint of a straight lines segment is multiplied by the lenght of the corresponding box boundary. Local conservation is satisfied by construction boundary and volume integrals for each box (control volume)  $B_i$ . In the *Fully Upwind Box Method* mobility is constant within the element and it gets its value from the upstream node (equation 2.34). For more information about the Box Method see (Helmig [1997]).

$$\lambda_{\alpha,ij}^{n+1} \begin{cases} \lambda_{\alpha,i}^{n+1} if & (\psi_{\alpha j} - \psi_{\alpha i}) \ge 0\\ \\ \lambda_{\alpha,j}^{n+1} if & (\psi_{\alpha j} - \psi_{\alpha i}) \le 0 \end{cases}$$

$$where \qquad \psi_{\alpha i} = p_{w,i} + \delta_{\alpha,n} \cdot p_{c,i}^{n+1} - \varrho_{\alpha,i} \cdot g_i$$

$$(2.34)$$

#### 2.4.2 Discretization in Time

In this work for the time discretization first oder implicit finite difference scheme (backward Euler method) is used. Equation 2.35 shows backward Euler scheme. The unknowns on the new time level n+1 depend on each other and can not be solved in one step unlike explicit methods. Therefore, the computation effort of implicit methods are higher than explicit methods. There is no limit to the time step size considering the stability of the solution (Hinkelmann [2003]). However, time step should not be chosen too big considering the accuracy of the solution.

$$\frac{du}{dt} = f(u)$$

$$\frac{u^{n+1} - u^n}{\Delta t} = f(u^{n+1})$$
(2.35)

# **3** Solubility of Methane in Water

# 3.1 Significance

Since methane is lighter than air it propagates to the surface. If there is a water saturated layer within the domain, methane migration is strongly depended on the solubility of the methane in water phase. First methane should dissolve in the water phase. Then, the dissolved methane is transported via advection and diffusion. If there is a pressure drop, which might be caused by a well, methane degases. Both degassing and dissolving processes depends on the solubility of methane in water. Therefore, solubility of methane in water is important for the simulation of methane propagation.

## 3.2 Methods of Expressing Gas Solubilities

Since gas solubility is important for many scientific and engineering problems, it can be expressed in different ways:

• Mole Fraction Solubility,  $x_g$ :

$$x_g = \frac{n_g}{n_w} \quad [-]$$

,where  $x_g$  is the mole fraction solubility of gas in water phase,  $n_g$  number of moles of gas dissolved in water,  $n_w$  is the number of moles of water.

• Mass Per Cent Solubility, *mt*:

$$mt = 100 \times \frac{M_g}{M_g + M_w} \quad [\%]$$

, where  $M_g$  is dissolved mass of gas in water and  $M_w$  is mass of water.

• Molality, m:

$$Molality = \frac{\text{number of moles of solute}}{\text{mass of solvent}} \quad [mole/kg]$$

In this work solubility is expressed in the form of mole fraction.

# 3.3 Evaluation of the Aqueous Methane Solubility

The solubility of gases decreases with increasing temperature and decreasing pressure. The solubility of methane in water is very low, at standard conditions (273.15 [°K] and 1 [at]) mole fraction solubility of methane in water is 4.4537E-05 (A.Dean [1999]).

Experimental solubility values (table 3.1) should be carefully examined to decide, whether it is necessary to evaluate the aqueous methane solubility as a function of pressure and temperature.

- 1. Aqueous methane solubility for constant temperature and varying pressures:
  - T= 298.2 [°K], P= 25 [bar], mole fraction solubility =  $5.99 \cdot E 4$  [-]
  - T= 298.2 [°K], P= 50 [bar], mole fraction solubility =  $11.20 \cdot E 4$  [-]
- 2. Aqueous methane solubility for constant pressure and varying temperatures:
  - T= 273.15 [°K], P= 1.01 [bar], mole fraction solubility =  $4.45 \cdot E^{-5}$  [-]
  - T= 300.15 [°K], P= 1.01 [bar], mole fraction solubility =  $2.26 \cdot E^{-5}$  [-]

As it can be seen, both pressure and temperature changes have considerable effects on the solubility of methane in water. For a pressure increase of 25 [bar] at 298.2 [°K] solubility of methane in water doubles and for a temperature increase of 27 [°K] at 1.01 [bar] solubility of methane in water decreases by a factor of two. Therefore, the effect of temperature and pressure on the aqueous methane solubility should not be neglected.

There are experimental works which have been performed on the solubility of methane in pure water. However, only a few of them are performed under low temperatures  $(0 - 90 \ [^{o}C])$  and low pressures  $(1 - 52 \ [bar])$ , which is the interest in this work. In the literature there have been found two ways of calculating the solubility of methane in water:

- 1. Regression analysis based on the experimental results (Clever et al. [1987])
- 2. Balancing of the methane's chemical potentials in liquid and in gas phases (Duan et al. [1992])

#### 3.3.1 Regression Analysis

The idea in this evaluation is as follows: First, the necessary experimental results are assembled. Then, a regression function is chosen (equation 3.1). After that, multiple regression is done by using matlab program to find the unknown coefficients. This regression analysis is called as multiple regression ,because solubility is a function of two variables (pressure and temperature). Multiple regression solves for unknown coefficients  $A_0$ ,  $A_1$ ,  $A_2$  and  $B_0$ , by performing a least squares fit. After the first regression analysis 6 measurements are eliminated because they have more than 20 percent error compared to the first regression function. After eliminting these experimental data which have big deviation, 59 measurements are left. Then, a second multiple regression analysis has been performed for the remanining 59 measurements. Table 3.2 shows the result of the second regression analysis. Table 3.1 shows reduced experimental data which is between 0 - 90 [°C] and 1-52 [bar]. The accuracy of these measurements varies between 1-5 % (Clever et al. [1987]).

The regression function which is suggested by Clever et al. [1987]is:

$$ln(x_1) = A_0 + 100 \times \frac{A_1}{T} + A_2 \times ln(\frac{T}{100}) + B_0 \times ln(\frac{P}{10})$$
(3.1)

,where  $x_1$  is mole fraction solubility of methane, T is in  $[{}^{o}K]$  and P is in [bar].

	Temperature	Total Gas	Mole Fraction Solubility
Mesured By	(°K)	Pressure (bar)	(n_g/(n_g+n_w))
Culberson et al.	298.15	36.2	7.6941E-04
	298.2	23.5	4.9700E-04
	298.2	31.6	7.1700E-04
	298.2	45.4	1.0000E-03
"	310.9	22.8	4.4000E-04
	310.9	32.9	6.1900E-04
	310.9	45.8	8.3900E-04
	344.3	22.8	3.4000E-04
	344.3	32.2	4.7000E-04
	344.3	45.4	6.3200E-04
Amirijafari et al.	310.93	41.4	7.5900E-04
	344.26	41.4	6.0200E-04
Crovetto et al.	297.5	18.61	4.3510E-04
	333.7	13.27	2.1240E-04
Stoessell et al.	298.15	24.1	5.7300E-04
	298.15	37.9	8.5100E-04
	298.15	51.7	1.1210E-03
Yarym-Agaev et al.	298.2	25	5.9900E-04
	298.2	50	1.1200E-03
"	313.2	25	4.9000E-04
"	313.2	50	9.2900E-04
	338.2	25	4.0500E-04
	338.2	50	7.7100E-04
Cramer	285.8	30	8.7464E-04
	315.2	11	1.8966E-04
	334.15	11	1.7572E-04
"	363.55	11	1.6641E-04
John A.Dean(assembled)	273.15	1.01	4.4537E-05
	274.15	1.01	4.3221E-05
	275.15	1.01	4.1938E-05
	276.15	1.01	4.0712E-05
	277.15	1.01	3.9520E-05
	278.15	1.01	3.8361E-05
8. Bu	279.15	1.01	3.7259E-05
	280.15	1.01	3.6190E-05
	281.15	1.01	3.5178E-05
	282.15	1.01	3.4188E-05
	283.15	1.01	3.3243E-05
	284.15	1.01	3.2388E-05
	285.15	1.01	3.1555E-05
	286.15	1.01	3.0745E-05
	287.15	1.01	2.9980E-05
	288.15	1.01	2.9238E-05
"	289.15	1.01	2.8552E-05
	290.15	1.01	2.7877E-05
	291.15	1.01	2.7247E-05
	292.15	1.01	2.6651E-05
	293.15	1.01	2.6088E-05
	294.15	1.01	2.5537E-05
	295.15	1.01	2.4997E-05
"	296.15	1.01	2.4491E-05
"	297.15	1.01	2.3996E-05
	298.15	1.01	2.3523E-05
	299.15	1.01	2.3062E-05
	300.15	1.01	2.2623E-05
	301.15	1.01	2.2207E-05
	302.15	1.01	2.1802E-05
· ·	303.15	1.01	2.1420E-05
	308.15	1.01	1.9496E-05

 Table 3.1: Experimental solubility data in mole fraction

Coefficients of regression function	Coefficient values
$A_0$	-81.3439
$A_1$	112.5396
$A_2$	32.2372
$B_0$	0.9902

Table 3.2: Results of the multiple regression analysis

# 3.3.2 Balance of Methane's Chemical Potentials in Liquid and in Gas Phases

Chemical potential is defined as partial change in energy of a system as matter is transferred into or out of it. For a substance in a mixture, the chemical potential is defined as being the partial molar Gibbs energy. For two system in contact at equilibrium, the chemical potentials for each must be equal (Parker [1993]).

Chemical potential of methane in gas phase is (Duan et al. [1992]):

$$\mu_g^{CH4}(T, P_g, x) = \mu_{g(0)}^{CH4}(T) + R \cdot T \cdot \ln(x_g^{CH4}) \cdot P_g + R \cdot T \cdot \ln\phi^{CH4}(T, P_g, x) \quad (3.2)$$

Chemical potential of methane in liquid phase is (Duan et al. [1992]):

$$\mu_l^{CH4}(T, P_g, m) = \mu_{l(0)}^{CH4}(T, P_g) + R \cdot T \cdot \ln(m_l^{CH4}) + R \cdot T \cdot \ln\gamma^{CH4}(T, P_g, m) \quad (3.3)$$

At equilibrium equations 3.2 and 3.3 will result in equation 3.4 (Duan et al. [1992]).

$$ln\frac{x_g^{CH4} \times P_g}{m_l^{CH4}} = \frac{\mu_{l(0)}^{CH4}}{R \cdot T} - ln(\phi^{CH4}) + \sum_c 2\lambda_{CH4-c}m_c + \sum_a 2\lambda_{CH4-a}m_a + \sum_c \sum_a \zeta_{CH4-c-a}m_c m_a \quad (3.4)$$

Abbreviation	Full name	Unit
Т	temperature	$^{o}\mathrm{K}$
$P_{g}$	total gas phase pressure	bar
x	mole ratio	mole/mole
R	universal gas constant	$bar \cdot liter / (mole \cdot^{o} K)$
m	molality	mole/kg
$\gamma$	activity coef.	-
$\mu$	chemical potential	Joule/mole
$\mu_{(0)}$	chemical potential in standard state	Joule/mole
$\lambda$	interaction parameter	$N^2 \cdot s^2/(m^3 \cdot mole^2)$
$\zeta$	interaction parameter	$N^3 \cdot s^4/(m^4 \cdot mole^3)$
a	anion	-
с	cation	-

Table 3.3: Notations in equations 3.2, 3.3, 3.4

Table 3.3 shows the notations in equations 3.2, 3.3, 3.4.

If the equation 3.4 is simplified for pure water, the interaction parameters drop out, resulting in equation 3.5.

$$ln\frac{x_g^{CH4} \cdot P_g}{m_l^{CH4}} = \frac{\mu_{l(0)}^{CH4}}{R \cdot T} - ln(\phi^{CH4})$$
(3.5)

In equation 3.5  $\frac{\mu_{l(0)}^{CH4}}{RT}$  is dependent on pressure and temperature. Equation 3.6 is used for description of  $\frac{\mu_{l(0)}^{CH4}}{RT}$  (Pitzer et al. [1984]).

$$\frac{\mu_{l(0)}^{CH4}}{RT}(T,P) = c_1 + c_2T + c_3/T + c_4/T^2 + c_5/(680 - T) + c_6P + c_7Pln(T) + c_8P/T + c_9P/(680 - T) + c_10P^2/T \quad (3.6)$$

The constants in equation 3.6 can be get from Duan et al. [1992].

In equation 3.5  $ln(\phi^{CH4})$  can be calculated from equation of state for pure  $CH_4$  (Duan et al. [1992]):

$$Z = \frac{P_r \overline{V_r}}{T_r} = 1 + \frac{B}{\overline{V_r}} + \frac{C}{\overline{V_r}^2} + \frac{D}{\overline{V_r}^4} + \frac{E}{\overline{V_r}^5} + \frac{F}{\overline{V_r}^2} (\beta + \frac{\gamma}{\overline{V_r}^2} + exp(-\frac{\gamma}{\overline{V_r}^2}))$$

$$ln(\phi^{CH4}) = Z - 1 - ln(Z) + \frac{B}{\overline{V_r}} + \frac{C}{2\overline{V_r}^2} + \frac{D}{4\overline{V_r}^4} + \frac{E}{5\overline{V_r}^5} + G$$
(3.7)

Abbreviation	Full name	Definition	Unit
$P_r \ Tr \ \overline{V_r}$	reduced pressure reduced temperature reduced molar volume	$ \begin{array}{c} P/P_{c}(P_{c}=46.41[bar]) \\ T_{r}=T/T_{c}(T_{c}=190.6[^{o}K]) \\ \overline{V_{r}}=\overline{V}/\overline{V_{c}}(\overline{V_{c}}=0.34146)[dm^{3}/mol] \end{array} $	[-] [-] [-]

Table 3.4: Notations in equations 3.7, 3.8

The constants in equation 3.7 can be seen at Duan et al. [1992].

The evaluation of  $ln(\phi^{CH4})$  requires iteration of first equation in 3.7, which has 5 roots (5 different  $\overline{V_r}$  values). To get rid of iterations and to speed up the calculations equation 3.7 can be simplified by assuming the ideal gas law (equation 3.8), which is valid for low pressures. Equation 3.7 simplifies to equation 3.9:

$$P \cdot V = n \cdot R \cdot T$$

$$Z = \frac{P_r \overline{V_r}}{T_r} = 1$$
(3.8)

,where Z is the compressibility factor.

$$ln(\phi^{CH4}) = \frac{B}{\overline{V_r}} + \frac{C}{2\overline{V_r}^2} + \frac{D}{4\overline{V_r}^4} + \frac{E}{5\overline{V_r}^5} + G$$
(3.9)

Equation 3.5 can be reformed to get equation 3.10. Finally, the solubility of methane can be calculated by the combination of equations 3.6, 3.8, 3.9 and 3.10.

$$m_l^{CH4} = x_g^{CH4} \cdot P_g \cdot exp(\phi^{CH4}) \cdot exp(-\frac{\mu^{CH4}}{RT})$$
(3.10)



Figure 3.1: Surface plots of solubility functions of methane (regression analysis function (equation 3.1) and for chemical potential balance function (equation 3.10) from left to right respectively).

# 3.4 Comparison of Methane's Solubility Functions

There are now two possibilities to evaluate the solubility of methane. The first one is using equation 3.10, chemical balance of methane in liquid and gas phase. Equation 3.10 is valid for the temperature range of 0 - 250 [°C] and for the pressure range of 0 - 1600 [bar] with an accuracy of 7 % (Duan et al. [1992]). The second one is equation 3.1, the regression analysis of the solubility values. Both equations will be compared with each other and the experimental data (table 3.1) for the temperature range of 0 - 90 [°C] and pressure range of 1 - 52 [bar].

The general behavior of the functions can be seen in figure 3.1. They behave according to solubility rule of gases, the solubility increases with increasing pressure and decreases with increasing temperature. The correlation coefficient of the experimental data set (table 3.1) and equation 3.10 is 0.999. Like equation 3.10, equation 3.1 has the same correlation coefficient with the experimental data set. What can be get from correlation coefficient values is that both equations behave likely as a function of temperature and pressure. It is very hard to decide between



Figure 3.2: Absolute percentage error of chemical potential balance function and regression function at different temperatures

these two equations just looking at figure 3.1 and the correlation coefficient values.

Therefore an error analysis is performed for these two equations. The experimental data are taken as correct, since they have very low experimental error (1 - 5% (Clever et al. [1987])). Therefore, an absolute error of functions 3.10 and 3.1 can be calculated for each measurement. Figure 3.2 shows the absolute percentage error of both functions with respect to temperature on 59 discrete points, where the measurements are taken. Analogous to figure 3.2, figure 3.3 shows the absolute percentage error of both functions with respect to pressure on 59 discrete points.

Chemical potential balance function has a mean absolute error of 3.36 % and maximum error of 10.1 %. Whereas, regression function has a mean absolute error of 1.74 % and maximum error of 7.60 %. Regression analysis looks better than chemical potential balance function. However, when closely examined, it can be seen that regression function fits very good only for the data set of A.Dean [1999], which is taken at 1.01 [bar] (table 3.1). For the rest of the experimental data, none of the equations are overcoming to each other. In fact, there are only a few data which exceeds the 7 % error as it can be seen from figures 3.2 and 3.3.



Figure 3.3: Absolute percentage error of chemical potential balance function and regression function at different pressures



a) T = 283.15  $^o{\rm K}$ 



b) T = 298.16 
$$^{o}$$
K



c) T = 310.9  $^{o}$ K



d) T = 344.3  $^{o}$ K

Figure 3.4: Solubility v.s. pressure for constant temperatures



a)  $\mathbf{P}=1.01$  bar



b) P = 11bar



c)  $\mathbf{P}=25~\mathrm{bar}$ 



d) P = 50 bar

Figure 3.5: Solubility v.s. temperature for constant pressures

In Figures 3.4 and 3.5 the dashed-dotted lines represents the error range of chemical potential balance function ( $\mp 7$ %). According to Duan et al. [1992] solubility values calculated via chemical potential balance function (equation 3.4) have  $\mp 7$ % error. In this work equation 3.4 is simplified by assuming ideal gas law (equation 3.8), which is necessary to speed up the solubility calculation. If the figures 3.4 and 3.5 are closely examined, it can be seen that almost all experimental measurement are within  $\mp 7$ % range of the chemical potential balance function. Therefore, the error resulted by the ideal gas law simplification can be neglected. At low pressures the regression function and chemical potential balance functions are increasing (figure 3.4). If the figure 3.5d is closely examined, it can be seen that regression function is slightly increasing as temperatures increases beyond 340 [°K], which does not comply with the physical-chemistry solubility rules of gases, since solubility of gases should decrease with increasing temperatures. Therefore, the regression function can not be used for temperatures beyond 340 [°K].

As a result, the chemical potential function is chosen for the evaluation of solubility measurements. The reasons are stated as:

• Although the regression function gives less mean error than the potential balance function, this can not be considered as an advantage for the regression function, because the constants of the regression function are calculated according to least square error principle.

- Although the chemical potential balance function gives slightly more error than the regression function, it is based on the physical-chemistry solubility rules of gases.
- When a new experimental data is implemented in the future, the regression function of the old data set can not guarantee the same accuracy for the new data set.
- The regression function fails to realize the drop in solubility for temperatures higher than 340 [°K].

The interest of this work is the modelling of methane migration at constant low temperature (ex: 283 [°K]) and varying pressure within the range of 1 to 25 [bar]. Figure 3.4a shows the increase of the methane solubility at 283 [°K] as a function of pressure.

An example case:

- gas pressure = 10 bar, mole fraction solubility of methane =  $3.19 \cdot 10^{-4}$
- gas pressure = 20 bar, mole fraction solubility of methane =  $6.16 \cdot 10^{-4}$

As it is seen from the example calculation, pressure change of 10 bar can double the mole fraction solubility of methane in water. The chemical potential balance function which is implemented in MUFTE-UG program can estimate aqueous methane solubility with  $\mp\%7$  error.

# **4** Instability Phenomena

Under some conditions methane migration in the subsurface can show hydrodynamic unstable displacements called fingering. In this chapter the fingering phenomena, which is a result of the viscosity and density differences between the displacing fluid and displaced fluid, is described.

# 4.1 Fingering

The term "fingering" is used to describe the bypassing of a resident fluid by a displacing agent in a homogeneous, nonuniform medium. The actual bypassing region is a finger. This definition encompasses instabilities caused by both viscous forces (viscous fingers) and gravity forces (gravity fingers) but does not include bypassing by permeability heterogeneities (W.Lake [1989]). An example situation is analysed by W.Lake [1989], where the incompressible displacement of fluid 1 by fluid 2 in an inclined reservoir is considered (figure 4.1)



Figure 4.1: Schematic presentation of fingering

A perturbation length ( $\epsilon$ ) of the displacement front is mathematically analysed to determine wheter  $\epsilon(t)$  grows as a function of time. Mass conservation of fluid 1 in the region behind the displacing fluid front ( $x < x_f$  figure 4.1) and mass conservation of fluid 2 in the region after the displacing fluid front ( $x > x_f$  figure4.1) give rate of change of the perturbation ( $\dot{\epsilon} = d\epsilon/dt$ ) (equation 4.1). For the derivation of equation 4.1 see W.Lake [1989].

$$\frac{d\epsilon}{dt} = -\frac{K \cdot \lambda_1}{\phi \cdot \Delta S} \cdot \frac{\Delta P \cdot (1 - M^o) + L \cdot g \cdot \Delta \varrho \cdot \sin\alpha - L \cdot g \cdot \varrho_1 \cdot (1 - M^o) \cdot \sin\alpha}{[M^o \cdot L + (1 - M^o) \cdot x_f]^2} \cdot \epsilon$$

$$(4.1)$$

Table 4.1 shows the notations in equation (4.1). The perturbation grows if  $\dot{\epsilon} > 0$ , remains constant if  $\dot{\epsilon} = 0$ , and decays if  $\dot{\epsilon} < 0$ . If equation 4.1 is equated to 0, critical pressure drop ( $\Delta P_c$ ) can be calculated (equation 4.2). Equation 4.3 shows critical darcy velocity ( $u_c$ ) corresponding to  $\Delta P_c$  (W.Lake [1989]).

Abbreviation	Full name	Unit
$\epsilon$	perturbation length	[m]
K	intrinsic permeability	[m]
$\lambda_1$	mobility of fluid 1	[-]
$\phi$	porosity	[-]
$\Delta S$	saturation difference $(S_1 - S_2)$	[-]
$\Delta P$	pressure drop over distance (L)	[Pa]
$M^o$	mobility ratio $(\lambda_1/\lambda_2)$	[-]
L	width of the system (figure 4.1)	[m]
g	gravitational acceleration	$[kg \cdot m/s^2]$
$\Delta \varrho$	density difference $(\varrho_1 - \varrho_2)$	$[kg/m^3]$
$\alpha^{-}$	angle of the reservoir with the horizontal axis	[-]
$x_f$	distance to the boundary (figure $4.1$ )	[m]

Table 4.1: Notations in equations 4.1

$$-(\Delta P_c) = \frac{L \cdot \Delta \varrho \cdot g \cdot \sin\alpha}{1 - M^o} - L \cdot g \cdot \varrho_1 \cdot \sin\alpha \tag{4.2}$$

$$u_c \equiv -K \cdot \lambda_1 \cdot \left[\frac{-(\Delta P_c)}{L} + \varrho_1 \cdot g \cdot \sin\alpha\right] = \frac{K \cdot \lambda_1 \cdot \Delta \varrho \cdot g \cdot \sin\alpha}{M^o - 1}$$
(4.3)

Using the critical darcy velocity  $(u_c)$  the conditions for finger growth can be stated as following (W.Lake [1989]):

$$u_x \qquad \left\{ \begin{array}{ll} > u_c \qquad (unstable) \\ = u_c \qquad (neutral) \\ < u_c \qquad (stable) \end{array} \right.$$

, where  $u_x$  is darcy velocity. Condition for stability can be written as (W.Lake [1989]):

$$(M^o - 1) \cdot u_x < K \cdot \lambda_r \cdot \Delta \varrho \cdot g \cdot \sin\alpha \tag{4.4}$$

In equation (4.4) all the terms except  $(M^o-1)$  and  $\Delta \rho$  are positive. The sign of these two terms depend on the material properties of the fluids. Equations 4.5 and 4.6 describe mobility ratio and density difference respectively. Subscript 1 is for displacing fluid and subscript 2 is for displaced fluid. For horizontal flows  $(sin\alpha = 0)$  condition for stability is  $M^o < 1$  (equation 4.4). For flows with gravity effect, condition for stability is  $\Delta \rho > 0$  provided that mobility ratio is zero.

$$M^o = \frac{kr_1}{\mu_1} \cdot \frac{kr_2}{\mu_2} \tag{4.5}$$

$$\Delta \varrho = \varrho_1 - \varrho_2 \tag{4.6}$$

According to W.Lake [1989] stability possibilities can be divided into four cases:

Case	Viscous effect	Gravity effect	Condition
1	$M^{o} < 1$	$\begin{array}{l} \Delta \varrho \cdot g \cdot sin\alpha > 0 \\ \Delta \varrho \cdot g \cdot sin\alpha > 0 \\ \Delta \varrho \cdot g \cdot sin\alpha < 0 \\ \Delta \varrho \cdot g \cdot sin\alpha < 0 \end{array}$	stable
2	$M^{o} > 1$		conditionally stable
3	$M^{o} < 1$		conditionally stable
4	$M^{o} > 1$		unstable

 Table 4.2: Possible cases for a stable displacement

Case 1 (table 4.2) is unconditionally stable and case 4 (table 4.2) is unconditionally unstable (W.Lake [1989]).

Critical velocity condition for instability  $(u_x > u_c)$  does not say anything about how fingers propagate once they are formed. Homsy [1987] describes the finger propagation as: A finger forms, bifurcates into two branches, one of these dominates the other, and the dominant one then bifurcates again to repeat the process (figure 4.2).

Fingering in nature is triggered by small heterogenity differences. Whereas in mumerical simulations fingering is triggered by numerical errors or by localized artificial random permeability field (Garcia and Prues [2003]).

Methane migrates in the subsurface by displacing air. Then, in figure 4.1 fluid 1 is methane and fluid 2 is as air. Since both are in the same phase (gas), they have the same relative permeability.

Mobility ratio  $(M^o)$  is:

$$M^o \equiv \frac{kr_g}{\mu_{metahne}} \cdot \frac{\mu_{air}}{kr_g} = \frac{\mu_{air}}{\mu_{methane}}$$

at  $T = 288.15[^{o}K]$   $\mu_{air} = 1.785 \cdot 10^{-5}$   $[kg/(m^{2} \cdot s)];$   $\mu_{methane} = 1.069 \cdot 10^{-5}$   $[kg/(m^{2} \cdot s)]$ 

$$M^{o} = 1.67 (> 1)$$

Density difference  $(\Delta \varrho)$  is:

$$\Delta \varrho = \varrho_{methane} - \varrho_{air}$$

at  $T = 288.15[^{\circ}K], P_g = 1[at]: \rho_{methane} = 0.680 [kg/m^3]; \rho_{air} = 1.225 [kg/m^3]$ 

$$oldsymbol{\Delta}arrho=-0.545~~(<0)~~[\mathrm{kg/m^3}]$$

In this case both viscous forces and gravity forces are in favour of instability. According to table 4.2 methane migration in subsurface is a case 4 instability, provided that methane (at the bottom) is displacing air (at the top) and advective tarnsport is big enough since diffusive transport can damp fingering effect. Figure 4.2 shows case 4 instability for methane migration in the subsurface, where fingering is triggered by numerical errors.



Figure 4.2: Methane migration instability in the subsurface (fingering)

# **5** Discussion of the Results

## 5.1 Domain Description

Numerical Simulations will be carried out in a 2d-model-domain, which is 1 [km] long and 200 [m] deep. This domain consists of 4 horizontal layers. Out of these 4 layers, two layers are called aquitards with an intrinsic permability of  $K = 1.3 \cdot 10^{-15}$  [m<sup>2</sup>] and two layers are called aquifers with an intrinsic permeability of  $K = 1.3 \cdot 10^{-11}$  [m<sup>2</sup>]. The top surface of the domain is in contact with the atmosphere. The right and left sides of the domain are closed. There is constant methane flux  $(0.17 \ m^3/(m^2 \cdot a))$  into the system at the bottom of the domain. The system is described schematically in figure 5.1.



Figure 5.1: Schematical description of the model-domain

### 5.2 Discretization

The model-domain (figure 5.1) is discretized with 2000 squares. Each square has 10m long facet. Figure 5.2 shows the mesh of the discretized domain.



Figure 5.2: Discretization of the model-domain

## 5.3 Grid Convergence Test

Simulations with too coarse grids result in numerical diffusion. On the other hand simulations with very fine grids require too much time. Terefore, a grid convergence test is necessary to decide whether 10 [m] grid size is acceptable or not considering the amount of numerical diffusion. The test domain is a closed box (Neumann =0 boundary condition at each side), which is 100 [m] long and 10 [m] wide. The upper half of the domain is filled with methane and the lower half is filled with air (figure 5.3a). Initially mole fraction of methane in the gas phase  $(X_g^m)$  is 0.98 at the upper half of the domain and 0.01 at the lower half of the domain.  $X_a^m$  can never be 1.00 because there is always water vapour in the gas phase. The mole fraction of water vapour in the gas phase  $(X_g^w)$  is determined by equation 2.5  $(X_g^w = P_w^{sat}/P_g)$ , where  $P_w^{sat}$  (saturated vapour pressure of water) is only a function of temperature. Since the simulations are done under constant temperature (288.15  $[^{o}K]$ ),  $P_{w}^{sat}$  is contant in the domain. In the following calculations  $P_g$  is around 1 [at]. As a result  $(X_q^w = P_w^{sat}/P_g)$  is almost constant in the doamin (around 0.02). Therefore, water vapour in the gas phase is negligible. The system is behaves almost like a 1 phase (gas) 2 component (methane, air) system.

The system is filled with two different gases, where dense fluid (air,  $\rho_{air} = 1.225$   $[kg/m^3]$  at T = 283.15 [°K] and  $P_g = 1$  [at]) is at the bottom and less dense fluid (methane,  $\rho_{methane} = 0.680$   $[kg/m^3]$  at T = 283.15 [°K] and  $P_g = 1$  [at]) is at the top. Therefore, initially there is no driving force for advective transport. At steady state it is expected to have a system where both gases are fully mixed

as a result of diffusion, i.e. methane  $X_g^m \approx 0.5$ .  $X_g^m$  can not be exactly equal to 0.5 at steady state, because initially the subcontrol volumes just at the boundary are occupied either by methane or by air. In this case these subcontrol volumes are filled with methane initially, i.e. initially more than 50 % of the volume is filled with methane. The simulation is repeated 5 times for different grid sizes (10[m], 5 [m], 2.5 [m], 1.25 [m], 0.625 [m]). Figure 5.3b shows the mole fraction of methane in gas phase  $(X_g^m)$  at y = 30 [m] over time for different grid sizes. As figure 5.3b shows at steady state  $X_g^m$  is around 0.5 for all grid sizes. There is not too much difference between the grid with 10 [m] spacing and the grids with smaller spacings, i.e numerical diffusion for 10 [m] grid size is not too much. Therefore, 10 [m] grid size is acceptable for the rest of the calculations.



Figure 5.3: a) Initial condition: Upper half is filled with methane, lower half is filled with air b) Variation in mole fraction of methane in gas pahse  $(X_g^m)$  at y = 30 [m] with time for different grid sizes

# 5.4 Comparison of Advective and Diffusive Transport

In a system where both advective and diffusive transport exist, the peclet number helps to get an understanding of the importance of both processes. The peclet number  $(P_e)$  compares advective and diffusive transport (equation 5.1).

 $P_e$  is defined as :

$$P_e = \frac{v \cdot \Delta y}{D} \tag{5.1}$$

, where v is velocity,  $\Delta y$  is the grid size and D is the diffusion/dispersion coefficient.

 $P_e$  can be in one of the following ranges:

- If  $P_e \ll 1$ , diffusive transport is dominant to advective transport.
- If  $P_e \gg 1$ , advective transport is dominant to diffusive transport.
- If  $P_e \approx 1$ , none of them overcome to each other.

Approximation of  $P_e$  in the following unsaturated domain simulations:

The constant methane flux  $(0.17 \ [m^3/(m^2 \cdot a)])$ , results a small velocity in vertical direction, which can be calculated roughly as:

$$v = J$$
 where ,J is volume flux  $[m^3/(m^2 \cdot s)]$   
 $v = 0.17/(365 \cdot 24 \cdot 3600) [m/s]$  (5.2)  
 $v \approx 0.54 \cdot 10^{-8} [m/s]$ 

Velocity in the gas phase does not stay constant, because the velocity is a function of gas pressure and the pressure in the gas phase increases from the top boundary to the bottom boundary. In the unsaturated domain simulations velocity varies between  $10^{-7}$  [m/s] and  $10^{-8}$  [m/s]. The diffusion of the gas phase at T=288.15 [°K] and P=1 [bar] is  $2.23 \cdot 10^{-5}$  [ $m^2/s$ ] (figure 2.5). Grid size is 10 [m].

For this system  $P_e$ :

$$P_e \equiv \frac{10^{-7} \cdot 10}{2.23 \cdot 10^{-5}} = 4.48 \cdot 10^{-2} \ll 1$$

Since  $P_e$  is much less than 1, diffusive transport is dominant in the system.

# 5.5 Methane Migration in Homogeneous and Unsaturated Domain

Since the new 2-phase 3-component model includes many new functions, which have been described in chapter 2, it is necessary to test the model for simple case problems. First the model is tested for a homogeneous domain. Figure 5.4 describes the boundary conditions for the homogeneous and unsaturated domain. At the surface of the domain the dirichlet boundary condition for the methane component is:

- Case 1:  $X_g^m$  (mole fraction of methane in gas phase) at the surface = 0.00 [-]
- Case 2:  $X_g^m$  (mole fraction of methane in gas phase) at the surface = 0.25 [-]

The following 4 cases are simulated in an unsaturated homogeneous domain:

Cases	Adv.	Diff.	$\Delta \varrho$	$\Delta \mu$	B.C. at the surface
Case A	ves	no	no	no	case 1 and case 2 (figure 5.4)
Case B	no	yes	no	no	case1 and case2 (figure $5.4$ )
Case C	yes	no	yes	yes	case 1 (figure $5.4$ )
Case D	no	yes	yes	yes	case1 (figure 5.4)

 Table 5.1: Simulations in an unsaturated homgeneous domain

The notations in table 5.1 are described in table 5.2.

Abbreviation	Meaning
Adv.	Advective transport is active
Diff.	Diffusive transport is active
$\Delta \varrho$	Density difference between air and methane
$\Delta \mu$	Viscosity difference between air and methane
B.C	Boundary condition

Table 5.2: Notations in table 5.1



Figure 5.4: Boundary conditions for the homogeneous and unsaturated domain

# 5.5.1 Case A: Purely advective transport without density and viscosity difference between the air and methane components

Since there is a constant methane source at the bottom of the domain (at -200 [m]), the system is flooded with the methane gas. The advancing front of the methane component propogates with the effective velocity (darcy velocity / effective porosity). At steady state mole fraction of methane in the gas phase  $(X_g^m)$  is 0.98 (can never be 1.0), since there is always water vapour in the gas phase, which has a mole fraction  $(X_g^w)$  of about 0.02. At steady state, case 1 and case 2 boundary conditions do not effect the vertical distribution of  $X_g^m$  except at the surface (figure 5.6). At the surface (at 0 [m]) under case 1 boundary condition  $X_g^m$  drops from 0.98 to 0.0. Whereas, under case 2 boundary condition  $X_g^m$  drops from 0.98 to 0.25.



**Figure 5.5:** Mole fraction of methane in the gas phase  $(X_g^m)$  at steady state for purely advective transport



**Figure 5.6:** Steady state variation of  $X_g^m$  in vertical crossection for purely advective transport

# 5.5.2 Case B: Purely diffusive transport without density and viscosity difference between the air and methane components

There is a constant methane source at the bottom of the domain (at -200 [m]). In the system there is only diffusive flux, which is equal to the constant methane flux (methane source flux). Diffusive methane flux in the gas phase can be described by equation 5.3. The diffusion coefficient of methane in the gas phase and density of the gas phase are constant. That means at steady state  $\operatorname{grad} X_g^m$  is constant. Figure 5.7 shows the mole fraction of methane in the gas phase  $(X_g^m)$  for case 1 boundary condition. Figure 5.8 shows the mole fraction of methane in the gas phase  $(X_g^m)$ for case 2 boundary condition. As figure 5.9 shows  $X_g^m$  has a constant gradient in vertical direction for both boundary conditions. Unlike the purely advective transport, in purely diffusive transport steady state  $X_g^m$  distribution in vertical direction is strongly effected by the dirichlet boundary condition at the surface.

$$J_g^m = D_g^m \cdot \varrho_{mol,g} \cdot \mathbf{grad} X_g^m \qquad [mole/(m^2 \cdot s)]$$
(5.3)



Figure 5.7: Mole fraction of methane in the gas phase at steady state for case 1



Figure 5.8: Mole fraction of methane in the gas phase at steady state for case 2


Figure 5.9: Vertical Cross-section: The effect of case 1 and case 2 boundary condition on the mole fraction of methane in the gas phase  $(X_g^m)$  at steady state

# 5.5.3 Case C: Purely advective transport with density and viscosity difference between the air and methane components

In this case real densities and viscosities of air and methane components are used. The simulation is carried out for case 1 boundary condition (figure 5.4). The temperature in the system is constant (283.15 [°K]). Air is more viscous and denser than water. Methane migrates in the subsurface upwards by displacing air. If less viscous and less dense fluid (methane) displaces more viscous and denser fluid, fingering, i.e. hydrodynamic unstable displacements, may appear.

According to W.Lake [1989] the stability of the system can be evaluated by comparing mobility and density of the two fluids (see section 4 for more details):

Case	Viscous effect	Gravity effect	Condition
$egin{array}{c} 1 \\ 2 \\ 3 \\ 4 \end{array}$	$M^{o} < 1$ $M^{o} > 1$ $M^{o} < 1$ $M^{o} > 1$	$\begin{array}{l} \Delta \varrho \cdot g \cdot \sin \alpha > 0\\ \Delta \varrho \cdot g \cdot \sin \alpha > 0\\ \Delta \varrho \cdot g \cdot \sin \alpha < 0\\ \Delta \rho \cdot g \cdot \sin \alpha < 0\end{array}$	stable conditionally stable conditionally stable unstable

Table 5.3: Possible cases for a stable displacement

Mobility ratio of methane and air  $(M^o)$  is:

$$M^o \equiv \frac{kr_g}{\mu_{metahne}} \cdot \frac{\mu_{air}}{kr_g} = \frac{\mu_{air}}{\mu_{methane}}$$

at 
$$T = 288.15[^{o}K]$$
  $\mu_{air} = 1.785 \cdot 10^{-5}$   $[kg/(m^{2} \cdot s)];$   $\mu_{methane} = 1.069 \cdot 10^{-5}$   $[kg/(m^{2} \cdot s)];$ 

$$M^o = 1.67 (> 1)$$

Density difference of methane and air  $(\Delta \rho)$  is:

$$\Delta \varrho = \varrho_{methane} - \varrho_{air}$$

at 
$$T = 288.15[{}^{o}K], P_{q} = 1[at]: \rho_{methane} = 0.680 [kg/m^{3}]; \rho_{air} = 1.225 [kg/m^{3}]$$

$$\Delta arrho = -0.545$$
 (< 0)  $[\mathrm{kg}/\mathrm{m^3}]$ 

In this case both viscous forces and gravity forces are in favour of instability. According to table 5.3 this condition is a case 4 instability, which is unconditionally unstable (W.Lake [1989]). Figure 5.10 shows fingering formation in homogeneous domain for purely advective transport. At t = 8.36 years there is a small fingering formation at the bottom of the domain (figure 5.10a). At t = 14.2 years fingering spreads to the upper part of the domain (figure 5.10b). At t = 20.05 years fingering is fully developed (figure 5.10c) and continues to flow unstable (figure 5.10d). The system never reaches steady state. Initial methane concentration is not a good guess, since methane which is initially in the system discharges to the surface under buoyancy forces ( $\rho_{methane} < \rho_{air}$ ) (see figures 5.10a and 5.10d).

Using the critical darcy velocity  $(u_c)$  the conditions for finger growth can be stated as following (W.Lake [1989]):

$$u_x \qquad \begin{cases} > u_c \qquad (unstable) \\ = u_c \qquad (neutral) \\ < u_c \qquad (stable) \end{cases}$$

where  $u_x$  is darcy velocity (see section 4 for  $(u_c)$ ). If the velocity in the system exceeds the critical velocity, the system is unstable. Since stability is related with the value of the velocity, advective transport is responsible for the instabilities in the flow. Therefore, for a systems where advective transport is dominant, the stability condition should be checked. In nature fingering is triggered by small permeability differences, whereas in this numerical simulation, it is triggred by numerical errors.



Figure 5.10: Fingering formation in homogeneous domain for purely advective transport

# 5.5.4 Case D: Purely diffusive transport with density and viscosity difference between the air and methane components

In this case real densities and viscosities of air and methane components are used. The simulation is carried out for case 1 boundary condition (figure 5.4). There is a constant methane flux at the bottom of the system. The flux in the system should be the same at each horizontal section considering mass conservation. Diffusive methane flux in the gas phase can be described by the equation 5.3. The interest in this simulation is whether mass density and viscosity will have an effect on the steady case mole fraction distribution of methane in the gas phase. As equation 5.3 shows diffusive flux does not include any mass density or viscosity terms. Therefore, it is expected to have the same  $X_g^m$  distribution in the steady case both for air having the material properties of methane and air having the material properties of itself. Figure 5.11 shows steady state distributon of  $X_g^m$  (mole fraction of methane in the gas phase) in homogeneoues domain for purely diffusive transport. Figure 5.12 shows steady state variation of  $X_q^m$  in vertical crossection for purely diffusive transport in homogeneous domain consdering density and viscosity effect. In figure 5.12 dashed dotted curve shows vertical variation of  $X_g^m$  for air having the material properties of methane and continious curve shows air having the material properties of itself. As it can be seen both curves overlap each other. That means mass density and viscosity does not have any effect on the steady case mole fraction distribution of methane in the gas phase for purely diffusive transport.



Figure 5.11: Steady state mole fraction distribution of methane in the gas phase  $(X_g^m)$  in homogeneous domain for purely diffusive transport



Figure 5.12: Steady state variation of  $X_g^m$  in vertical crossection for purely diffusive transport in homogeneous domain consdering density and viscosity effect

## 5.6 Methane Migration in Heterogeneous and Unsaturated Domain

Figure 5.13 shows boundary condition for heterogenous and unsaturated domain. The boundary condition is the same as case 1 boundary condition in homogenous domain except the methane source. Methane source has a value of  $0.17 \ [m^3/(m^2 \cdot a)]$  for case 1 boundary condition and  $0.0 \ [m^3/(m^2 \cdot a)]$  for case 2 boundary condition (figure 5.13). As already mentioned in subsection 5.1 there are aquifer and aquitard layers in the domain. The aquifers have an intrinsic permeability of  $K = 1.3 \cdot 10^{-11} \ [m^2]$  and the aquitards have an intrinsic premeability of  $K = 1.3 \cdot 10^{-11} \ [m^2]$ . The water saturation is initialized as residual water saturation, which has a value of 0.105 for aquifers and 0.132 for aquitards.

```
Methane -> Dirichlet, Xmg = 0.0 [-]
Water ----> Dirichlet, Sw = 0.232(Swrt) [-]
Air -----> Dirichlet, Pg = 1*10^5 [Pa]
Heat ----> Dirichlet, T = 288.15 [°K]
```



Figure 5.13: Boundary conditions for the heterogeneous and unsaturated domain with varying methane source

Cases	Adv.	Diff.	$\Delta \varrho$	$\Delta \mu$	B.C. at the bottom
Case E	yes	no	yes	yes	case 2 (figure $5.13$ )
Case F	no	yes	yes	yes	case 2 (figure $5.13$ )
Case G	yes	yes	yes	yes	case 1 and case 2 (figure $5.13$ )

The following 3 cases are simulated in an unsaturated heterogenous domain:

Table 5.4: Simulations in an unsaturated heterogeneous domain

The notations in table 5.4 are described in table 5.2.

#### 5.6.1 Case E: Purely Advective Transport in Heterogeneous and Unsaturated Domain

This simulation is carried out under case 2 (figure 5.13) boundary conditions. Like purely advective transport in homogenous case (section 5.5.3) the heterogenous case shows instabilities. The condition of instability can be checked by comparing the mobility ratio and the density difference of the two fluids. The mobility ratio  $(M^o)$ and the density difference of methane and air  $(\Delta \rho)$  are exactly same as for homogenous case. Since  $M^o = 1.67$  (> 1) and  $\Delta \rho = -0.545$  (< 0)  $[kg/m^3]$ , it is again case 4 unconditionally unstable situation (table 5.3).

Figure 5.14 shows fingering formation in heterogenous domain for purely advective transport. At t = 5.6 years fingering is formed in the lowest layer (aquifer2). Then, methane accumulates at the bottom of the aquitard 2 and methane concentration is increasing in aquifer 2, because the velocity in aquitard 2 is less than the velocity in aquifer2 (aquitards are  $E^4$  times less permeable than aquifers). At t = 77.1 years methane passes through aquitard 2 and fingering formation starts to develop in aquifer 1. At t = 175.3 years fingering effect can be seen in both of the aquifers. Less permeable layers (aquitards) result in concentration increase (methane) in the hole domain. Unlike the purely advective transport in homogenous case (section 5.5.3) purely advective transport in heterogenous case can reach steady state condition, since increasing methane concentration in the hole domain reduces the density forces which are in favour of fingering. At t = 361.5 years steady case is reached, where mole fraction of methane in the gas phase  $(X_g^m)$  has a values of 0.98 in the hole domain.  $X_g^m$  can never be 1.0, since there is always water vapour in the system.



Figure 5.14: Fingering formation in heterogeneous domain for purely advective transport

#### 5.6.2 Case F: Purely Diffusive Transport in Heterogeneous and Unsaturated Domain

In this simulation there is only diffusive transport and the simulation is carried out under case 2 (figure 5.13) boundary conditions. The interest in this example is to see the effect of the permeability on the steady state mole fraction distribution of methane in the gas phase  $(X_g^m)$  in heterogenous domain for purely diffusive transport. The diffusion flux of methane can be calculated according to equation 5.3. As equation 5.3 shows there is no permeability term in the diffusive flux equation. Therefore, it is expected to have the same  $X_g^m$  distribution at steady state for the homogenous and heterogenous domains. Figure 5.15 shows steady state distribution of  $X_q^m$  in heterogenous domain for purely diffusive transport. Figure 5.16 compares the variation of  $X_g^m$  in vertical crossection for purely diffusive transport in homogenous and heterogenous domains. The two curves (figure 5.16) are not exactly the same, because diffusion coefficients are a function of saturation (see equations 2.17) and 2.18) and saturations in the gas phase are different for aquifers and aquitards. As figure 5.16 shows both curves are very close to each other. Therefore, it can be stated that permeability does not have a considerable effect on the steady state mole fraction distribution of methane in the gas phase.



Figure 5.15: Steady state mole fraction distribution of methane in the gas phase  $(X_g^m)$  in heterogeneous domain for purely diffusive transport



**Figure 5.16:** Steady state variation of  $X_g^m$  in vertical crossection for purely diffusive transport in homogenous and heterogenous domains

#### 5.6.3 Case G: Verification of the Excess Pressures in Heterogeneous and Unsaturated Domain

After analysing and interpreting the advective and diffusive transport in the heterogeneous domain with the 2-phase 3-component model, it is necessary to verify the field measurements for the real domain (figure 5.1). In the field two pressure measurements were taken. The first pressure measurement gave an excess pressure of 500 [Pa] against the aerostatic pressure in the middle of the aquifer 1 and the second measurement gave an excess pressure of 1000 [Pa] against the aerostatic pressure in the middle of the aquifer 2. The intrinsic permeabilities of the aquifer 1 and the aquifer 2 are well known as  $1.3251 \cdot 10^{-11} m^2$ . Knowing these two (excess pressures and intrinsic permeabilities of the aquifers) a calibration analysis was performed for 1-phase (gas phase) model to find out the intrinsic permeabilities of aquitard1, aquitard 2 and the methane source at the bottom of the domain (see Ochs et al. [2003]). The calibration analysis gave the intrinsic permeabilities of the aquitards as  $6.6251 \cdot 10^{-15}$  $[m^2]$  and the methane source as  $0.17 [m^3/(m^2 \cdot a)]$ .

The calibration results of the 1-phase model, the intrinsic permeability of the aquitards and the methane source, are put as an input to the 2-phase 3-component model . If it is shown that the 2-phase 3-component model gives the same excess pressures around 500 [Pa] and 1000 [Pa] as the 1-phase model, it can be stated that the 2-phase 3-component system behaves for this particular problem almost the same as 1-phase model.

To obtain the excess pressures at measurement points (-75 [m] and -175 [m]) it is necessary to calculate the pressure distribution in the vertical cross-section for two cases. First case is aerostatisch pressure distribution  $(Q = 0.0 \quad m^3/(m^2 \cdot a))$  and the second case is pressure distribution with constant flux  $(Q = 0.17 \quad m^3/(m^2 \cdot a))$ . The boundary and initial conditions are described in figure 5.13.

Total pressure in the system can be calculated as:

$$P_{total} = P_{atm} + P_{stat} + P_{excess} \qquad [Pa] \tag{5.4}$$

Total pressure  $(P_{total})$  is the sum of atmospheric pressure  $(P_{atm})$ , aerostatic pressure  $(P_{stat})$  and the excess pressure  $(P_{excess})$ . Excess pressure is a result of the mass flux, which is caused by the methane source, in the gas phase. The mass balance of the gas phase can be described by the simplification of the mass transport equations 2.28, 2.29, 2.30 for the steady unsaturated case:

$$- div \left\{ \frac{k_{rg}}{\mu_g} \varrho_{mol,g} x_g^w \mathbf{K}(\mathbf{grad} p_g - \varrho_{mass,g} \mathbf{g}) \right\} - div (D_{pm_g}^w \varrho_{mol,g} \mathbf{grad} x_g^w) = 0$$
  
$$- div \left\{ \frac{k_{rg}}{\mu_g} \varrho_{mol,g} x_g^m \mathbf{K}(\mathbf{grad} p_g - \varrho_{mass,g} \mathbf{g}) \right\} - div (D_{pm_g}^m \varrho_{mol,g} \mathbf{grad} x_g^m) - q^m = 0$$
  
$$- div \left\{ \frac{k_{rg}}{\mu_g} \varrho_{mol,g} x_g^a \mathbf{K}(\mathbf{grad} p_g - \varrho_{mass,g} \mathbf{g}) \right\} - div (D_{pm_g}^a \varrho_{mol,g} \mathbf{grad} x_g^a) = 0$$
  
$$[mole/(m^3 \cdot s)] \quad (5.5)$$

The pressure of gas phase can be calculated as a result of the solution of the equation system (equation 5.5) with a given boundary condition (figure 5.13). Since the pressure gradient of the gas phase only appears in the advective term of the equation system 5.5, the advective term is decisive in the evaluation of the gas pressure. If the advective mass flux of each component is summed up, the advective mass flux of the gas phase can be obtained as:

$$J_{gas} = \left\{ \frac{k_{rg}}{\mu_g} \varrho_{mass,g} \mathbf{K} (\mathbf{grad} p_g - \varrho_{mass,g} \mathbf{g}) \right\} \qquad [kg/(m^2 \cdot s)]$$
(5.6)

As equation 5.6 shows the advective mass flux of the gas phase depends on the relative permeability of the gas phase  $(k_{rg})$ , the dynamic viscosity of the gas phase  $(\mu_g)$ , the intrinsic permeability of the layer (K) and mass density of the gas phase  $(\varrho_{mass,g})$ . The mass flux should be the same at each horizontal cross-section to satisfy the continuity of the mass transport, since the system is closed at the right and left boundaries. The relative permeability of the gas phase  $(k_{rg})$  is 1, because the system is totally unsaturated. That means pressure distribution in the system is effected mainly by the the dynamic viscosity of the gas phase  $(\mu_g)$ , the intrinsic permeability of the layer (K) and the mass density of the gas phase  $(\rho_{mass,g})$ . Except the intrinsic permeability (K),  $\mu_g$  and  $\rho_{mass,g}$  depends on the mole fraction of the components in the gas phase  $(X_g^{\alpha})$ , which is eventually determined by the diffusive flux.

Figure 5.17 shows steady case mole fraction of methane in the gas phase for  $Q = 0.0 \quad [m^3/(m^2 \cdot a)]$  and for  $Q = 0.17 \quad [m^3/(m^2 \cdot a)]$ . The dashed dotted line shows that all the initial methane fraction  $(X_g^m = 0.3)$  is discharged to the atmosphere as a result of the diffusive transport and density driven advective transport. At steady state the gas phase is mainly composed of air. The continious line shows that at steady state mole fraction of methane in the gas phase  $(X_g^m)$  is increasing from 0 [-] at the bottom.

Figure 5.18 shows the excess pressures at measurement points. In the middle of aquifer1 (at -75 [m]) the aerostatic case  $(Q = 0.0 \ [m^3/(m^2 \cdot a)])$  has a gas pressure of 100887 [Pa] and the aerodynamic case  $(Q = 0.17 \ [m^3/(m^2 \cdot a)])$  has a gas pressure of 101517 [Pa]. Therefore at -75 [m] there is an excess pressure of 630 [Pa] (101517 [Pa] - 100887 [Pa]). In the middle of aquifer2 (at -175 [m]) the aerostatic case has a gas pressure of 102083 [Pa] and the aerodynamic case has a gas pressure of 102083 [Pa] and the aerodynamic case has a gas pressure of 102083 [Pa]. Therefore at -175 [m] there is an excess pressure of 1205 [Pa](103288 [Pa] - 102083 [Pa]).



Figure 5.17: Steady case methane mole fraction for the heterogeneous and unsaturated case with varying methane source

By using the calibration results of the 1-phase model, the intrinsic permeability of the aquitards and the methane source, in the 2-phase 3-component model, the measured pressure difference in the field could be verified, which means that the 2-phase 3-component system behaves for this particular problem almost the same as 1-phase system.



Figure 5.18: Excess pressures at measurement points( at -75 [m] and at -175 [m])

## 5.7 Methane Migration in Partially Saturated Heterogeneous Domain

Figure 5.19 shows the boundary conditions for partially saturated heterogeneous domain. There is a 30 [m] thick saturated water body in aquifer1. Two sides of the domain are closed (Neumann = 0.0). Field measurements show that the water level in the aquifer 1 is constant over time. In order to keep the water level constant, the relative permeability of the water phase  $(k_{rw})$  is set to 0.0 (water phase is immobile), otherwise water moves downwards as a result of gravity forces. In the immobile water body water saturation is set to  $1 - 2 \cdot S_{gr}$ , where  $S_{gr} = 0.01$ . There is little space for the gas phase  $(S_g = 0.02)$  in the water body, which allows the gas phase to be mobile.





Figure 5.19: Boundary condition for the heterogeneous and partially saturated domain with varying methane source

Two simulations are carried out in partially saturated heterogeneous domain. In the first simulation methane source at the bottom of the domain is set to 0.17  $[m^3/(m^2 \cdot a)]$ , whereas in the second simulation methane source at the bottom of the domain is set to 0.0  $[m^3/(m^2 \cdot a)]$ .

Figure 5.20 shows gas phase pressure in vertical crossection for partially saturated heterogeneous domain with varying methane source. For the case where there is a constant methane flux at the bottom of the system, pressure is high below the water layer since methane source increases pressure and gas phase in the water body is not so mobile. For the case where there is no methane flux at the bottom of the system, there is excess pressure below the suspended water body at t = 8425 years. This is an effect of the initial pressure distribution, since initially gas phase pressure is set to water pressure within the water body considering the fact that  $pc \approx 0$  [bar]. However, gas phase is mobile in the water and at steady state gas phase pressure should become aerostatic pressure. At steady state pressure difference between these two cases are 930 [Pa] (101814 - 100884 [Pa]) at y = -75 [m] and 14671 [Pa] (118027 - 103356 [Pa]) at y = -175 [m].

Figure 5.21 shows methane propagation in partially saturated homogeneous domain for Q = 0.17  $[m^3/(m^2 \cdot a)]$ . At t = 18 days methane concentration did not change at all, i.e. almost initial condition. At t = 41.2 years the difference below the water body and above the water body can be clearly seen (figure 5.21b). Above the water body methane discharges very fast to the atmosphere as a result of diffusion, whereas below the water body methane concentration increases. At t = 172.2 years methane concentration below the water body further increases ( $X_g^m \approx 0.8$ ). In the immobile water body methane has little space to move ( $S_g = 0.02$ ), i.e. methane can pass through water layer. Figures 5.21c, d show that methane concentration in the gas phase between -50 [m] and -70 [m] increases too. At t = 527.4 years steady state is reached (figure 5.21d).

Figure 5.22 shows methane propagation in partially saturated homogeneous domain for  $Q = 0.00 \quad [m^3/(m^2 \cdot a)]$ . Initially methane has a mole fraction of 0.3 in the gas phase throughout the domain. At t = 2.5 years methane concentration above the water body starts to decrease (figure 5.22a). The decrease in the methane concentration is a result of strong diffusive transport. The drop in methane concentration stops just above the immobile water body, i.e. water retards the vertical methane migration (5.22b). After 29.1 years methane concentration above the water body drops to almost 0 ( $X_g^m \approx 0$ ). If figures 5.22c and d are compared, it can be seen that methane is passing through the suspended water body. However, this process is very slow. Methane can pass the suspended water body either in water phase (by only diffusion) or in gas phase, since there is little space ( $S_g = 0.02 > S_{gr} = 0.01$ ). A similar case without water body is analyzed, where at steady state  $X_g^m$  drops to 0 as a result of diffusion for a dirichlet boundary condition of  $X_g^m = 0$  at the top (figure 5.17). Steady state is not reached yet but it might take thousands of years to have a methane concentration of 0 below the water body, since in 8425 years methane concentration decreased very little. Therefore, it can be assumed that at steady state there is no methane at all in the hole domain.

In these two simulations water phase is set to immobile for the sake of keeping the water level constant. Otherwise water would move downwards. Setting relative permeability of the water phase zero (between -70 [m] and -100 [m]) prevents advective transport within the water body, this creates errors in the results.



Figure 5.20: Pressure distribution in vertical crossection for partially saturated heterogeneous domain with varying methane source



Figure 5.21: Methane propogation in partially staurated homogeneous domain with methane source of  $Q = 0.17 \quad [m^3/(m^2 \cdot a)]$  at - 200 [m]



Figure 5.22: Methane propogation in partially saturated homogeneous domain without methane source

# 6 Conclusion and Recommendations for Further Study

#### 6.1 Summary

In regions with abandoned coal mines considerable amount of methane migrates to the surface. This methane can cause restricted use of land and is a potential risk for the residents. This fact resulted in the installation of extraction wells in many mining areas to be able to control the methane migration to the surface. If the amount and concentration of the extracted methane-air mixture is high enough, it can be utilized as an energy source. For the development of mine gas repositories no reliable tests exist to evaluate the productiveness or the optimal operation of the extraction wells. Due to usual complex geology and physical behavior of mine gas repositories numerical simulations can help to get better understanding of these systems and to identify the important processes influencing the productiveness.

In this work the model of Kobayashi [2004], a 2-phase (water,gas) 3-component (methane, air, water) model, was extended by introducing the mixture viscosity of the gas phase as a function of temperature, the effect of tortuosity on the diffusion of the components, the diffusion of methane in the water phase as a function of temperature and the solubility of methane in the water phase as a function of temperature and pressure.

The comparison of the advective and diffusive transports showed that diffusive transport was dominant for the test cases ( $P_e \ll 1$ ). Several cases were successfully tested in the unsaturated homogeneous domain. In purely advective transport fingering effect was observed, if less viscous and less dense fluid (methane) displaces more viscous and more dense fluid (air), flow may show instabilities called fingering. In purely diffusive transport density and viscosity differences between air and methane did not effect the transport process.

Subsequent to the homegenous case, the methane migration in a heterogeneous and unsaturated domain was tested. For purely advective transport the heterogeneous case showed instabilities too. However, the low velocities reduced the fingering effect in the low permeable aquitards. Unlike the homogeneous case, the heterogeneous case could reach the steady state, because with time the density effect got smaller. For the heterogenous case pressure distribution correleted very well with previous 1-phase simulations and measurements.

Finally, methane migration in partially saturated heterogeneous domain was tested. Within the water body relative permeability of the water phase was set to zero for the sake of keeping the water level constant over time, which prevented advective transport in the saturated water body. It was observed that for a constant methane source pressure in the gas phase is increasing below the water body. This results in higher pressure differences in partially saturated heterogeneous domain than in unsaturated heterogeneous domain.

### 6.2 Recommendations for Further Study

In this work most of the simulations were carried out to test the consistency of the new model in the undisturbed subsurface (without wells). The effect of the solubility of methane in water phase could not be seen since there was no considerable pressure gradient in these examples. However, in reality there are active wells in the domains, which creates high pressure gradients. Therefore, more simulations are necessary to investigate the effect of aqueous methane solubility.

The diffusion coefficients of the components were described by using binary diffusion coefficients. However, there are three components in both gas and water phases. Therefore, new approaches have to be tested because diffusion seams to be very important for three component systems.

If there are active gas wells in a domain, high velocities can develop, which may result in instabilities (fingering) in the gas flow. Therefore, fingering phenomena can occur in a domain where active wells are installed. Furthermore, the sizes and spacings of the fingers are effected by the grid sizes and boundary conditions (Garcia and Prues [2003]). Therefore, more simulations with varying grid sizes and boundary conditions are necessary to analyze the finger sizes and spacings.

In this work absorption and desorption processes were neglected. Absorption of methane to coal seams and desorption of methane from the coal seams effect the methane source. These processes need to be formulated and implemented into the MUFTE-UG program.

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