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ORIGINAL PAPER

Two-phase, partially miscible flow and transport modeling in porous media; application to gas migration in a nuclear waste repository

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Abstract We derive a compositional compressible two-phase, liquid and gas, flow model for numerical simulations of hydrogen migration in deep geological repository for radioactive waste. This model includes capillary effects and the gas high diffusivity. Moreover, it is written in variables (total hydrogen mass density and liquid pressure) chosen in order to be consistent with gas appearance or disappearance. We discuss the well possedness of this model and give some computational evidences of its adequacy to simulate gas generation in a water-saturated repository.

Keywords Two-phase flow · Porous medium · Modeling · Underground nuclear waste management

1 Introduction

The simultaneous flow of immiscible fluids in porous media occurs in a wide variety of applications. The most concentrated research in the field of multiphase flows over the past four decades has focused on unsaturated groundwater flows and flows in underground petroleum reservoirs. Most recently, multiphase flows have generated serious interest among engineers concerned with deep geological repositories for radioactive waste. There is growing awareness that the effect of hydrogen gas generation, due to anaerobic corrosion of the steel engineered barriers (carbon steel overpack and stainless steel envelope) of radioactive waste packages, can affect all the functions allocated to the canisters, waste forms, buffers, backfill, and host rock. Host rock safety functions may be threaten by overpressurization leading to opening fractures of the host rock, inducing groundwater flow and transport of radionuclides.

The equations governing these flows are inherently nonlinear, and the geometries and material properties characterizing many problems in many applications can be quite irregular and contrasted. As a result, numerical simulation often offers the only viable approach to the mathematical modeling of multiphase flows. In nuclear waste management, the migration of gas through the near field environment and the host rock involves two components, water and pure hydrogen H_2, and two phases, “liquid” and “gas.” It is then not clear if conventional models, like, for instance, the black-oil model, used in petroleum or groundwater engineering are still valid for such a situation. Our ability to understand and predict underground gas migration is crucial to the design of reliable waste storages. This is a fairly new frontier in multiphase porous-media flows, and again, the inherent complexity of the physics leads to governing equations for which the only practical way to produce solutions may be numerical simulation. This exposition provides an overview of the types of standard models that are used in the field of compressible multiphase, multispecies flows in porous media and includes discussions of the problems coming from H_2 gas being one of the components. Finally, the paper also addresses one of the outstanding physical and mathematical problems in multiphase flow simulation:

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the appearance and disappearance of one of the phases, leading to the degeneracy of the equations satisfied by the saturation. It has been seen recently in a benchmark organized by the French agency in charge of nuclear waste management in France [15] that none of the usual codes used in that field where able to simulate adequately the appearance or/and disappearance of one of the phases. In order to overcome this difficulty, we will discuss a formulation based on new variables that does not degenerate. We will demonstrate, through two test cases, the ability of this new formulation to actually cope with the appearance or/and disappearance of one phase. The scope of the paper is limited to isothermal flows in rigid porous media and will not include the possible process of "pathway dilation" as described in [5].

2 Conceptual and mathematical model

Our goal is first to present a survey of the conventional models used for describing two-phase, two-component flow in porous media. Most of these models have been designed and widely used in petroleum engineering (see, for instance, [1–3, 7, 9, 11]). We consider herein a porous medium saturated with a fluid composed of two phases: *liquid* and *gas*. According to the application we have in mind, the fluid is a mixture of two components: water (mostly liquid) and hydrogen (H_2, mostly gas). Water is present in the gas phase through vaporization, and hydrogen is present in the liquid phase through dissolution. The fluids are compressible and the model is assumed to be isothermal. For simplicity, we assume first the porous medium to be rigid, meaning the porosity Φ is only a function of the space variable $\Phi = \Phi(\mathbf{x})$, and second, we neglect the pressure-induced dilation of gas pathways. Hydrogen being highly diffusive, we have described in detail how the diffusion could be taken in account in the models.

2.1 Petrographic and fluid properties

2.1.1 Fluid phases

The two phases will be denoted by indices l for liquid and g for gas. Associated to each phase in the porous media are the following quantities:

- Liquid and gas phase pressures: p_l and p_g
- Liquid and gas phase saturations: S_l and S_g
- Liquid and gas phase mass densities: ρ_l and ρ_g
- Liquid and gas phase viscosities: μ_l and μ_g
- Phase volumetric flow rates, $\mathbf{q}_l$ and $\mathbf{q}_g$

Then, the *Darcy–Muskat law* says:

$$\begin{aligned} \mathbf{q}_l &= -\mathbb{K}(\mathbf{x})\tfrac{kr_l(S_l)}{\mu_l}\left(\nabla p_l - \rho_l \mathbf{g}\right), \\ \mathbf{q}_g &= -\mathbb{K}(\mathbf{x})\tfrac{kr_g(S_g)}{\mu_g}\left(\nabla p_g - \rho_g \mathbf{g}\right), \end{aligned} \tag{1}$$

where $\mathbb{K}(\mathbf{x})$ is the absolute permeability tensor, kr_l and kr_g are the relative permeability functions, and $\mathbf{g}$ is the gravity acceleration.

The above phase mass densities and viscosities are all functions of phase pressures and of phase *composition*. Moreover, phase saturations satisfy

$$S_l + S_g = 1 \tag{2}$$

and the pressures are connected through a given experimental *capillary pressure law*:

$$p_c(S_g) = p_g - p_l. \tag{3}$$

From definition Eq. 3, we should notice that p_c is strictly increasing function of gas saturation, $p_c'(S_g) > 0$.

2.1.2 Fluid components

Water and pure hydrogen components will be denoted by indices w and h. Since the liquid phase could be composed of water and dissolved hydrogen, we need to introduce the water mass density in the liquid phase ρ_l^w and the hydrogen mass density in the liquid phase ρ_l^h. Similarly, we introduce the water and hydrogen mass densities in the gas phase: ρ_g^w and ρ_g^h. Note that the upper index is always the component index, and the lower one denotes the phase. We have, then,

$$\rho_l = \rho_l^w + \rho_l^h, \quad \rho_g = \rho_g^w + \rho_g^h. \tag{4}$$

Since the composition of each phase is generally unknown, we introduce *the mass fraction* of the component $i \in \{w, h\}$ in the phase $\alpha \in \{g, l\}$

$$\omega_\alpha^i = \frac{\rho_\alpha^i}{\rho_\alpha}; \quad \omega_\alpha^w + \omega_\alpha^h = 1, \ \alpha \in \{g, l\}. \tag{5}$$

2.2 Mass conservation equation

The conservation of the mass applies to each component i and reads, for any arbitrary control volume $\mathscr{R}$:

$$\frac{dm^i}{dt} + F^i = \mathscr{F}^i, \quad i \in \{w, h\}. \tag{6}$$

where

- m^i is the mass of the component i, in the control volume $\mathscr{R}$, at given instant t.
- F^i is the rate at which the component i is leaving (migrating from) the volume $\mathscr{R}$, at given instant t.
- $\mathscr{F}^i$ is the source term (the rate at which the i component is added to $\mathscr{R}$ by the source).

The mass of each component i is a sum over all phases g and l:

$$m^i = \int_{\mathscr{R}} \Phi \left(S_l \rho_l \omega_l^i + S_g \rho_g \omega_g^i \right) d\mathbf{x}, \quad i \in \{w, h\}.$$

In each phase, the migration of a component is due to the transport by the phase velocity and to the molecular diffusion:

$$F^i = \int_{\partial\mathscr{R}} \left(\rho_l \omega_l^i \mathbf{q}_l + \rho_g \omega_g^i \mathbf{q}_g + \mathbf{j}_l^i + \mathbf{j}_g^i \right) \cdot \mathbf{n}\, d\mathbf{x}; \quad i \in \{w, h\};$$

where $\mathbf{n}$ is the unit outer normal to $\partial\mathscr{R}$. The phase flow velocities, $\mathbf{q}_l$ and $\mathbf{q}_g$ are given by the Darcy–Muskat law Eq. 1, and the component i diffusive flux in phase α is denoted $\mathbf{j}_\alpha^i$, $i \in \{w, h\}$, $\alpha \in \{g, l\}$, and will be defined in the next paragraph, by Eq. 12. From Eq. 6, we get the differential equations:

$$\begin{aligned} \Phi \frac{\partial}{\partial t} & \left(S_l \rho_l \omega_l^w + S_g \rho_g \omega_g^w \right) \\ & + \operatorname{div} \left(\rho_l \omega_l^w \mathbf{q}_l + \rho_g \omega_g^w \mathbf{q}_g + \mathbf{j}_l^w + \mathbf{j}_g^w \right) = \mathscr{F}^w, \quad (7) \\ \Phi \frac{\partial}{\partial t} & \left(S_l \rho_l \omega_l^h + S_g \rho_g \omega_g^h \right) \\ & + \operatorname{div} \left(\rho_l \omega_l^h \mathbf{q}_l + \rho_g \omega_g^h \mathbf{q}_g + \mathbf{j}_l^h + \mathbf{j}_g^h \right) = \mathscr{F}^h. \quad (8) \end{aligned}$$

2.2.1 *Diffusion fluxes*

From M^w and M^h, the water and hydrogen molar masses, using definitions Eq. 5 we define the following water and hydrogen molar concentrations in each phase $\alpha \in \{g, l\}$:

$$c_\alpha^h = \frac{S_\alpha \rho_\alpha^h}{M^h} = \frac{S_\alpha \rho_\alpha \omega_\alpha^h}{M^h}, \quad c_\alpha^w = \frac{S_\alpha \rho_\alpha^w}{M^w} = \frac{S_\alpha \rho_\alpha \omega_\alpha^w}{M^w}. \quad (9)$$

Then, the phase α molar concentrations, $\alpha \in \{g, l\}$, is:

$$c_\alpha = c_\alpha^h + c_\alpha^w = S_\alpha \rho_\alpha \left(\frac{\omega_\alpha^h}{M^h} + \frac{\omega_\alpha^w}{M^w} \right). \quad (10)$$

Usually, component i diffusive flux in phase α is assumed to depend on X_α^i, the component i molar fraction in phase $\alpha \in \{g, l\}$, defined from Eqs. 9 and 10:

$$\begin{aligned} X_\alpha^h &= \frac{c_\alpha^h}{c_\alpha} = \frac{\omega_\alpha^h}{\omega_\alpha^h + \left(M^h / M^w \right) \omega_\alpha^w}, \\ X_\alpha^w &= \frac{c_\alpha^w}{c_\alpha} = \frac{\omega_\alpha^w}{\omega_\alpha^w + \left(M^w / M^h \right) \omega_\alpha^h}; \quad \sum_{i=h,w} X_\alpha^i = 1, \quad (11) \end{aligned}$$

for $\alpha \in \{l, g\}$. Molar diffusive flux of component i in phase $\alpha \in \{g, l\}$ is given by

$$\mathbf{J}_\alpha^i = -c_\alpha D_\alpha^i \nabla X_\alpha^i; \quad \alpha \in \{g, l\}, \quad i \in \{w, h\}$$

and give molar diffusive flow rate of component i through the unit area. Coefficients D_α^h and D_α^w (unit L^2/T) are Darcy scale molecular diffusion coefficients of components in phase $\alpha \in \{g, l\}$. Mass flux of component i in phase α, in Eqs. 7 and 8 is then obtained by multiplying the above component molar diffusive fluxes, $\mathbf{J}_\alpha^i$, by the molar mass M_i of the component i, and by the rock porosity:

$$\mathbf{j}_\alpha^h = -\Phi M^h c_\alpha D_\alpha^h \nabla X_\alpha^h, \quad \mathbf{j}_\alpha^w = -\Phi M^w c_\alpha D_\alpha^w \nabla X_\alpha^w. \quad (12)$$

Remark 1 The number of unknowns in the system is eight: S_l, ρ_l^w, ρ_l^h, p_l, S_g, ρ_g^w, ρ_g^h, and p_g; but, up to now, we only have four equations, Eqs. 2, 3, 7, and 8, and therefore, four additional equations are needed to close the system.

Remark 2 Note that D_α^h and D_α^w are not exactly molecular diffusion coefficients in phase α, corresponding to molecule–molecule interactions in free space, but ΦD_α^i, $\alpha \in \{g, l\}$, and $i \in \{w, h\}$ are effective diffusion coefficients, obtained from the strict molecular diffusion coefficients by a kind of *averaging* through the whole porous medium (see Section 2.6 in [2], or [8] or [6]). Moreover, for simplicity, we have not included in diffusion of component i in phase α any dependency on phase saturations, and then, we did not consider possible nonlinear effects coming from coupling between advective–diffusive transport ("dusty gas" model) and molecular streaming effects (Knutsen diffusion) (see, for instance, [10]).

Remark 3 In a binary system, diffusive fluxes satisfy $\mathbf{j}_\alpha^h + \mathbf{j}_\alpha^w = 0$, for $\alpha \in \{g, l\}$, and therefore, we have

$$M^h D_\alpha^h = M^w D_\alpha^w, \quad \alpha \in \{g, l\}. \quad (13)$$

2.3 Phase equilibrium black-oil model

The additional equations needed to close the system of Eqs. 2, 3, 7, and 8 will come from the assumption that the two phases are in equilibrium; equilibrium meaning that at any time the quantity of hydrogen dissolved in the water is maximal for the given pressure, and similarly, the quantity of evaporated water is maximal for the given pressure. Composition of each phase is then uniquely determined by its phase pressure and saturation. In this flow situation, we say that water and gas phases are *saturated*. Nevertheless, it could happen that one of the phases disappears: either water can completely evaporate or hydrogen can be completely dissolved in the water. Then, in these situations, the composition of the remaining phase is not uniquely determined by its phase pressure, and the phase composition becomes an independent variable (instead of the saturation, which is now constant, 0 or 1). This flow situation corresponds to the so-called *unsaturated flow*. For unsaturated flow, the standard practice in petroleum reservoir engineering is to introduce the following quantities:

- Liquid and gas *formation volume factors*, $B_l = B_l(p_l)$, $B_g = B_g(p_g)$
- *Solution gas/liquid phase ratio* $R_s = R_s(p_l)$
- *Vapor water/gas phase ratio* $R_v = R_v(p_g)$

The explanation of formation volume factors and solution component/phase ratios, as used in the oil reservoir modelling, is as follows. Considering the volume $\Delta V_l^{\mathrm{res}}$ of liquid at reservoir conditions (reservoir temperature and pressure), when this volume of liquid is transported through the tubing to the surface, it separates at standard conditions to a volume of liquid $\Delta V_l^{\mathrm{std}}$ and a volume of gas $\Delta V_g^{\mathrm{std}}$ (coming out of the liquid, due to the pressure drop). At standard (i.e., stock tank) conditions, the liquid phase contains only an oil component (here only water component) and the gas phase contains only a gas component (here only hydrogen). Then, applying conservation of mass,

$$\Delta V_l^{\mathrm{res}} \rho_l = \Delta V_l^{\mathrm{std}} \rho_l^{\mathrm{std}} + \Delta V_g^{\mathrm{std}} \rho_g^{\mathrm{std}};$$

and denoting the solution gas/liquid ratio $R_s = \Delta V_g^{\mathrm{std}} / \Delta V_l^{\mathrm{std}}$, we may write:

$$\Delta V_l^{\mathrm{res}} \rho_l = \Delta V_l^{\mathrm{std}} \left(\rho_l^{\mathrm{std}} + R_s \rho_g^{\mathrm{std}} \right),$$

and the liquid phase mass density decomposition

$$\rho_l = \frac{\rho_l^{\mathrm{std}} + R_s \rho_g^{\mathrm{std}}}{B_l}, \tag{14}$$

where B_l is the liquid formation volume factor, $B_l = \Delta V_l^{\mathrm{res}} / \Delta V_l^{\mathrm{std}}$. Similarly, from $\Delta V_g^{\mathrm{res}} \rho_g$ and the gas formation volume factor $B_g = \Delta V_g^{\mathrm{res}} / \Delta V_g^{\mathrm{std}}$, we get the gas phase mass density decomposition

$$\rho_g = \frac{\rho_g^{\mathrm{std}} + R_v \rho_l^{\mathrm{std}}}{B_g}; \tag{15}$$

where the vapor water/gas phase ratio $R_v = \Delta V_l^{\mathrm{std}} / \Delta V_g^{\mathrm{std}}$. Now, in order to express the diffusion fluxes in terms of the new variables R_s, R_v, B_l, and B_g, we have to rewrite the molar concentrations defined in Eq. 9:

$$c_l^h = \frac{S_l R_s \rho_g^{\mathrm{std}}}{M^h B_l}, \quad c_l^w = \frac{S_l \rho_l^{\mathrm{std}}}{M^w B_l},$$
$$c_g^h = \frac{S_g \rho_g^{\mathrm{std}}}{M^h B_g}, \quad c_g^w = \frac{S_g R_v \rho_l^{\mathrm{std}}}{M^w B_g}. \tag{16}$$

These concentrations, defined in Eq. 16, may be slightly different from those previously defined in Eq. 9 if the gas at standard conditions is not composed only of hydrogen, and the liquid, also at standard conditions, is note made only of water. The phase molar concentrations, from Eq. 16, are then given by:

$$c_l = c_l^h + c_l^w = \frac{S_l}{B_l} \left(\frac{R_s \rho_g^{\mathrm{std}}}{M^h} + \frac{\rho_l^{\mathrm{std}}}{M^w} \right) = \frac{S_l}{B_l} \frac{\rho_g^{\mathrm{std}}}{M^h} (R_s + F),$$

$$c_g = c_g^h + c_g^w = \frac{S_g}{B_g} \left(\frac{\rho_g^{\mathrm{std}}}{M^h} + \frac{R_v \rho_l^{\mathrm{std}}}{M^w} \right) = \frac{S_g}{B_g} \frac{\rho_g^{\mathrm{std}}}{M^h} (1 + F R_v),$$

where F is given by:

$$F = \frac{M^h \rho_l^{\mathrm{std}}}{M^w \rho_g^{\mathrm{std}}}. \tag{17}$$

The component *molar fractions* in phase are now defined as:

$$X_l^h = \frac{c_l^h}{c_l} = \frac{R_s \rho_g^{\mathrm{std}}}{R_s \rho_g^{\mathrm{std}} + \left(M^h / M^w \right) \rho_l^{\mathrm{std}}} = \frac{R_s}{R_s + F},$$
$$X_l^w = \frac{c_l^w}{c_l} = \frac{\rho_l^{\mathrm{std}}}{\rho_l^{\mathrm{std}} + \left(M^w / M^h \right) R_s \rho_g^{\mathrm{std}}} = \frac{F}{R_s + F},$$
$$X_g^h = \frac{c_g^h}{c_g} = \frac{\rho_g^{\mathrm{std}}}{\rho_g^{\mathrm{std}} + \left(M^h / M^w \right) R_v \rho_l^{\mathrm{std}}} = \frac{1}{1 + F R_v},$$
$$X_g^w = \frac{c_g^w}{c_g} = \frac{R_v \rho_l^{\mathrm{std}}}{R_v \rho_l^{\mathrm{std}} + \left(M^w / M^h \right) \rho_g^{\mathrm{std}}} = \frac{F R_v}{1 + F R_v}. \tag{18}$$

Mass diffusive fluxes of components, defined in Eq. 12, depend on component *molar fractions* in phases; they have, then, to be rewritten. For instance, the mass diffusion flux of hydrogen in water takes now the form:

$$\mathbf{j}_l^h/\rho_g^{\mathrm{std}} = -\Phi \frac{M^h}{\rho_g^{\mathrm{std}}} \frac{S_l}{B_l} \frac{\rho_g^{\mathrm{std}}}{M^h} (R_s + F)\, D_l^h \nabla X_l^h$$

$$= -\Phi \frac{S_l}{B_l} \frac{F}{R_s + F} D_l^h \nabla R_s.$$

Other diffusion fluxes could be obtained by similar calculations, leading to the following formulas:

$$\boldsymbol{\phi}_l^h = \mathbf{j}_l^h/\rho_g^{\mathrm{std}} = -\Phi \frac{S_l}{B_l} \frac{F}{R_s + F} D_l^h \nabla R_s,$$

$$\boldsymbol{\phi}_l^w = \mathbf{j}_l^w/\rho_l^{\mathrm{std}} = \Phi \frac{S_l}{B_l} \frac{1}{R_s + F} D_l^w \nabla R_s, \tag{19}$$

$$\boldsymbol{\phi}_g^h = \mathbf{j}_g^h/\rho_g^{\mathrm{std}} = \Phi \frac{S_g}{B_g} \frac{F}{1 + F R_v} D_g^h \nabla R_v,$$

$$\boldsymbol{\phi}_g^w = \mathbf{j}_g^w/\rho_l^{\mathrm{std}} = -\Phi \frac{S_g}{B_g} \frac{1}{1 + F R_v} D_g^w \nabla R_v. \tag{20}$$

Remark 4 Let us recall, like in Remark 3, that the diffusion coefficients satisfy $M^h D_l^h = M^w D_l^w$ and $M^h D_g^h = M^w D_g^w$, and, like in Eq. 11, $\sum_{i=h,w} X_\alpha^i = 1$, for any phase $\alpha \in \{l, g\}$, in Eq. 18.

The Darcy fluxes Eq. 1 can now be rewritten in the following form:

$$\mathbf{q}_l = -\mathbb{K} \frac{kr_l}{\mu_l} \left(\nabla p_l - \frac{\rho_l^{\mathrm{std}} + R_s \rho_g^{\mathrm{std}}}{B_l} \mathbf{g} \right),$$

$$\mathbf{q}_g = -\mathbb{K} \frac{kr_g}{\mu_g} \left(\nabla p_g - \frac{\rho_g^{\mathrm{std}} + R_v \rho_l^{\mathrm{std}}}{B_g} \mathbf{g} \right),$$

and the component fluxes, normalized by standard densities, are:

$$\boldsymbol{\phi}^w = \frac{1}{B_l} \mathbf{q}_l + \frac{R_v}{B_g} \mathbf{q}_g + \boldsymbol{\phi}_l^w + \boldsymbol{\phi}_g^w,$$

$$\boldsymbol{\phi}^h = \frac{R_s}{B_l} \mathbf{q}_l + \frac{1}{B_g} \mathbf{q}_g + \boldsymbol{\phi}_l^h + \boldsymbol{\phi}_g^h. \tag{21}$$

Finally, we can write mass conservation Eqs. 7 and 8 in the following form:

$$\Phi \frac{\partial}{\partial t} \left(\frac{S_l}{B_l} + \frac{R_v S_g}{B_g} \right) + \operatorname{div}(\boldsymbol{\phi}^w) = \mathscr{F}^w/\rho_l^{\mathrm{std}}, \tag{22}$$

$$\Phi \frac{\partial}{\partial t} \left(\frac{S_l R_s}{B_l} + \frac{S_g}{B_g} \right) + \operatorname{div}\left(\boldsymbol{\phi}^h\right) = \mathscr{F}^h/\rho_g^{\mathrm{std}}. \tag{23}$$

These equations have to be completed by Eqs. 2 and 3. For instance, in Eqs. 22 and 23, we can take saturation and one of the pressures as independent variables, for example, S_g and p_l, and for the other terms the following functional dependencies:

$$B_l(p_l),\ B_g(p_g),\ R_s(p_l),\ R_v(p_g),$$

$$\mu_l(p_l),\ \mu_g(p_g),\ kr_w(S_g),\ kr_g(S_g).$$

According to their definition, F, ρ_g^{std}, ρ_l^{std}, and D_α^i ($\alpha \in \{l, g\}, i \in \{w, h\}$) are constants, and Φ and $\mathbb{K}$ depend only on space position.

2.3.1 Unsaturated flow

Equations 22 and 23, with saturation and pressure as unknowns, are valid if there is no missing phase (saturated flow); but if one of the phases is missing (unsaturated flow), equations and unknowns have to be adapted. There are two possible *unsaturated* cases, according to either the gas phase or the liquid phase disappearing:

1. Gas phase missing (Hydrogen totally dissolved in water): then, we have $S_g = 0$, $S_l = 1$. Generalized gas phase Darcy's velocity is equal to zero since $kr_g(0) = 0$. Independent variables are now p_l, the liquid phase pressure, and R_s, the solution gas/liquid phase Ratio; then, we must write $B_l = B_l(p_l, R_s)$ and $\mu_l = \mu_l(p_l, R_s)$, for $0 \le R_s \le \hat{R}_s(p_l)$, where $\hat{R}_s(p_l)$ is equilibrium solution gas/liquid phase ratio.
2. Liquid phase missing: then, $S_l = 0$ and $S_g = 1$. Generalized liquid phase Darcy's velocity is zero since $kr_w(S_g = 1) = 0$; independent variables are now p_g, the gas phase pressure, and R_v, the water vapor/gas phase ratio, become the new independent variables. However, pressure p_l can be kept as an independent variable since p_g could be expressed through the capillary pressure law Eq. 3. We must also write $B_g = B_g(p_g, R_v)$ and $\mu_g = \mu_g(p_g, R_v)$, for $0 \le R_v \le \hat{R}_v(p_g)$, where $\hat{R}_v(p_g)$ is the equilibrium water vapor/gas phase ratio.

These above conditions can be summarized as

$$S_g \ge 0, \quad \hat{R}_s(p_l) - R_s \ge 0, \quad (\hat{R}_s(p_l) - R_s) S_g = 0, \tag{24}$$

$$S_l \ge 0, \quad \hat{R}_v(p_g) - R_v \ge 0, \quad (\hat{R}_v(p_g) - R_v) S_l = 0. \tag{25}$$

Remark 5 In this last section, "Phase equilibrium black-oil model," we did not take in account a possible interplay between dissolution and capillary pressure.

2.4 Thermodynamical equilibrium Henry–Raoult model

Another way of closing the system of Eqs. 2, 3, 7, and 8 is to use phase thermodynamical properties for characterizing equilibrium. First, we use ideal gas law and Dalton law,

$$p_g = p_g^w + p_g^h, \tag{26}$$

where p_g^w and p_g^h are the vaporized water and hydrogen partial pressures in the gas phase, and

$$p_g^w = \frac{\rho_g^w}{M^w} RT, \quad p_g^h = \frac{\rho_g^h}{M^h} RT. \tag{27}$$

T is the temperature, R is universal gas constant, and M^w and M^h are the water and hydrogen molar masses.

Next, we apply *Henry's* and *Raoult's laws*, which say that, at equilibrium, the vapor pressure of a substance varies linearly with its mole fraction in solution. In *Henry's law*, the constant of proportionality is obtained by experiment, and in *Raoult's law*, the constant is the pressure of the component in its pure state. Here, we will assume, for simplicity, that the quantity of dissolved hydrogen in the liquid is small; then, these laws reduce to the linear *Henry's law*, which says that the amount of gas dissolved in a given volume of the liquid phase is directly proportional to the partial pressure of that same gas in the gas phase:

$$\rho_l^h = H(T) M^h p_g^h, \tag{28}$$

where $H(T)$ is the Henry's law constant, depending only on the temperature. For the liquid phase, we apply *Raoult's law*, which says that the *water vapor pressure* is equal to the vapor pressure of the pure solvent, at given temperature, multiplied by the mole fraction of the solvent. The water vapor partial pressure of the pure solvent depends only on the temperature and, therefore, is a constant, denoted here by $\hat{p}_g^w(T)$, so we have from definition Eq. 9

$$p_g^w = \hat{p}_g^w(T) X_l^w = \hat{p}_g^w(T) \frac{\rho_l^w}{\rho_l^w + \left(M^w/M^h\right) \rho_l^h}. \tag{29}$$

Further on, we can include in formula Eq. 29 the presence of capillary pressure, by using *Kelvin*'s equation (see [4]), which gives:

$$p_g^w = \hat{p}_g^w(T) \frac{\rho_l^w}{\rho_l^w + \left(M^w/M^h\right) \rho_l^h} e^{-M^w p_c/(RT\rho_l)}. \tag{30}$$

If now, to Eqs. 26–28 and 30 we add the relations

$$\rho_l^h + \rho_l^w = \rho_l, \quad \rho_g^h + \rho_g^w = \rho_g, \tag{31}$$

and the water compressibility, defined by

$$\rho_l^w = \frac{\rho_l^{\mathrm{std}}}{B_l(p_l)}, \tag{32}$$

then, we have eight equations: Eqs. 26, $27_{1,2}$, 28, 30, $31_{1,2}$, and 32 and 10 unknowns:

$$p_l, p_g, p_g^w, p_g^h, \rho_l^h, \rho_l^w, \rho_l, \rho_g^h, \rho_g^w, \rho_g.$$

We may, for instance, parametrize all these 10 unknowns by the two phase pressures p_l and p_g. For this, we should combine the Henry law Eq. 28, the Raoult–Kelvin law Eqs. 30 and 26 leading to the system of two equations for p_g^h and p_g^w:

$$p_g^w = \hat{p}_g^w(T) \frac{\rho_l^w}{\rho_l^w + (M^w H(T))\, p_g^h}$$
$$\times\, e^{-M^w(p_g - p_l)/(RT\left(\rho_l^w + M^h H(T) p_g^h\right)}$$
$$p_g = p_g^w + p_g^h.$$

It is easy to show that the above system of two equations has a unique solution $p_g^w, p_g^h > 0$ for any $p_g \geq \hat{p}_g^w(T)$, and solving this system, we obtain

$$p_g^w = f(p_g, p_l), \quad p_g^h = g(p_g, p_l).$$

By Eq. $27_{1,2}$, we can then write ρ_g^h, ρ_g^w, and ρ_g as functions of p_l and p_g, and by Eqs. 28 and 32, we can finally express ρ_l^h, ρ_l^w, and ρ_l as functions of the phase pressures.

Remark 6 The gas phase will appear only if there is a sufficient quantity of dissolved hydrogen in the liquid phase, and this quantity is exactly the dissolved gas quantity, at equilibrium, given by Henry's law. However, when the dissolved gas (hydrogen) quantity is smaller than the quantity of hydrogen at equilibrium, then the Henry law does not apply, and S_g is then equal to zero and could not be taken as unknown. In this situation, instead of saturation, we may take ρ_l^h as an independent variable. We notice that the Henry–Raoult model based on thermodynamical equilibrium leads to similar concepts as the ones developed for establishing the black oil model for reservoir modeling.

Remark 7 In the Henry–Raoult model, if there is no vaporized water, $p_g = p_h^g$, the criteria for nonsaturated flow is simple and reads

$$\frac{\rho_l^h}{M^h H(T)} < p_g = p_l + p_c(0), \tag{33}$$

if there is a threshold pressure, i.e., $p_c(0) \neq 0$. The same criterion can be used also if there is vaporized water, as long as the pressure in porous medium is much larger than vaporized water pressure.

Remark 8 In Henry–Raoult model, above, we were assuming, for simplicity, no complete evaporation of the water.

2.4.1 Comparison of equilibrium models

We will now consider in more detail a special case, where we may, from the Henry–Raoult model, get back the black oil model. In both models, we will then use diffusive fluxes developed in Section 2.3. For simplicity, we will neglect in Eq. 29 the influence of capillary pressure and solved gas on water vapor partial pressure, leading to $p_g^w = \hat{p}_g^w(T)$ being a constant. Then, we have from Eqs. 28, 32, and 31

$$\begin{aligned}\rho_l &= \rho_l^h + \rho_l^w = H(T)M^h p_g^h + \frac{\rho_l^{\text{std}}}{B_l(p_l)} \\ &= \frac{\rho_l^{\text{std}} + B_l(p_l)H(T)M^h\left(p_g - \hat{p}_g^w(T)\right)}{B_l(p_l)},\end{aligned} \tag{34}$$

and also, from Eq. 27,

$$\rho_g = \rho_g^h + \rho_g^w = \frac{M^h}{RT}\left(p_g - \hat{p}_g^w(T)\right) + \frac{M^w}{RT}\hat{p}_g^w(T). \tag{35}$$

Therefore, Eqs. 34 and 35 can be written in a form similar to Eqs. 14–15 by defining the gas formation volume factor B_g, solution gas/liquid phase ratio R_s and vapor water/gas phase ratio R_v, from the above thermodynamical relations:

$$R_s = B_l(p_l)\frac{H(T)M^h}{\rho_g^{\text{std}}}\left(p_g - \hat{p}_g^w(T)\right) \tag{36}$$

$$B_g = \frac{RT\rho_g^{\text{std}}}{M^h\left(p_g - \hat{p}_g^w(T)\right)}, \quad R_v = \frac{1}{F}\frac{\hat{p}_g^w(T)}{p_g - \hat{p}_g^w(T)}, \tag{37}$$

where F is given by Eq. 17.

Compared to the black oil model, Section 2.3, here, it is clear from Eq. 36 that the solution gas/liquid phase ratio R_s depends on p_l and p_g and not only on p_l.

Remark 9 For the case without any water vapor, the corresponding thermodynamical model is obtained simply by taking $\hat{p}_g^w(T) = 0$ in Eqs. 36 and 37 and $R_v = 0$ in Eqs. 22 and 23. In the same way, if we neglect dissolved hydrogen, the corresponding thermodynamical model is obtained simply by taking $H(T) = 0$ in Eqs. 36 and 37 and $R_s = 0$ in Eqs. 22 and 23.

2.4.2 Model assuming water incompressibility and no water vaporization

In the Henry–Raoult model, we assume now that the water is incompressible and the water vapor quantity is neglectful, i.e., the gas phase contains only hydrogen, then (see Remark 7), $p_g^h \equiv p_g$ and $p_g^w = \hat{p}_g^w(T) = 0$ in Eq. 37, leading to $R_v \equiv 0$. Formulas Eqs. 36 and 37 could be rewritten as

$$B_l \equiv 1, \quad R_s = C_h p_g, \quad \frac{1}{B_g} = C_v p_g, \tag{38}$$

where we have denoted

$$C_h = \frac{H(T)M^h}{\rho_g^{\text{std}}}, \quad C_v = \frac{M^h}{RT\rho_g^{\text{std}}}, \tag{39}$$

and Eqs. 14–15 become:

$$\rho_l(R_s) = \rho_l^{\text{std}} + R_s\rho_g^{\text{std}}, \quad \rho_g(p_g) = C_v\rho_g^{\text{std}}p_g. \tag{40}$$

Similarly to constant F defined by Eq. 17, we use the density ratio

$$G = \frac{\rho_l^{\text{std}}}{\rho_g^{\text{std}}}, \tag{41}$$

and Eqs. 22 and 23 reduce to

$$\Phi\frac{\partial S_l}{\partial t} + \operatorname{div}\left(\mathbf{q}_l - \frac{1}{G}\mathbf{J}\right) = \mathscr{F}^w/\rho_l^{\text{std}}, \tag{42}$$

$$\begin{aligned}&\Phi\frac{\partial}{\partial t}\left(S_lR_s + C_vp_gS_g\right) \\ &\quad + \operatorname{div}\left(R_s\mathbf{q}_l + C_vp_g\mathbf{q}_g + \mathbf{J}\right) = \mathscr{F}^h/\rho_g^{\text{std}},\end{aligned} \tag{43}$$

$$\mathbf{q}_l = -\mathbb{K}\frac{kr_l}{\mu_l}\left(\nabla p_l - \left(\rho_l^{\text{std}} + R_s\rho_g^{\text{std}}\right)\mathbf{g}\right),$$

$$\mathbf{q}_g = -\mathbb{K}\frac{kr_g}{\mu_g}\left(\nabla p_g - C_v\rho_g^{\text{std}}p_g\mathbf{g}\right), \tag{44}$$

$$\mathbf{J} = -\frac{\Phi S_l F}{R_s + F}D_l^h\nabla R_s, \tag{45}$$

where we have denoted $\boldsymbol{\phi}_l^h = \mathbf{J}$ and used Remark 3 to get $FD_l^h = GD_l^w$, from which it follows $\boldsymbol{\phi}_l^w = -\mathbf{J}/G$.

Here, there is only hydrogen in phase gas, $p_g^h = p_g$ and Henry's law assumes thermodynamical equilibrium in which quantity of dissolved hydrogen is proportional to gas phase pressure. In saturated case (where two phases are present), Henry's law reads $R_s = C_hp_g$, and we can then work with variables p_g and S_l in Eqs. 42–45.

When the gas phase disappears, the gas pressure drops to the liquid pressure augmented by entry pressure, $p_g = p_l + p_c(0)$, the liquid can contain any quantity of dissolved hydrogen ρ_g^h between zero and $C_h \rho_g^{\text{std}}(p_l + p_c(0)) = H(T) M^h (p_l + p_c(0))$, from Henry's law (see Eq. 28 and definition Eq. 39).

Then, when the gas phase is absent (one of the unsaturated cases), $S_g = 0$, we will replace saturation, as we did in the black oil model for the same unsaturated case in Section 2.3.1, by a new variable R_s (see definitions Eqs. 28, 36, 39), such that

$$R_s \rho_g^{\text{std}} = \rho_l^h$$

is the mass density of dissolved hydrogen in the liquid phase.

Assuming that, at standard conditions, the gas phase contains only hydrogen (hydrogen component mass≈gas phase mass) and the liquid phase contains only water, with water incompressibility and no vaporized water, we see that, in definition Eq. 36, $R_s = \rho_l^h / \rho_g^{\text{std}} \simeq \Delta V_g^{\text{std}} / \Delta V_l^{\text{std}}$, which is exactly the definition given in the black oil model in Section 2.3.

The physical meaning of R_s then stays the same either in Henry–Raoult or in black oil models even in the unsaturated case. Moreover, from mass conservation law, it follows that the dissolved hydrogen mass density $R_s \rho_g^{\text{std}}$ is continuous when the gas phase vanishes, and this can be expressed as a unilateral condition:

$$0 \le S_g \le 1, \quad 0 \le R_s \le C_h p_g, \quad S_g (C_h p_g - R_s) = 0.$$

In *unsaturated region*, where $S_l = 1$ (that is, $S_g = 0$), we replace variable S_l by R_s, and Eqs. 42–45 degenerate to:

$$\operatorname{div}\left(\mathbf{q}_l - \frac{1}{G}\mathbf{J}\right) = \mathscr{F}^w / \rho_l^{\text{std}}; \tag{46}$$

$$\Phi \frac{\partial R_s}{\partial t} + \operatorname{div}\left(R_s \mathbf{q}_l + \mathbf{J}\right) = \mathscr{F}^h / \rho_g^{\text{std}}; \tag{47}$$

$$\mathbf{q}_l = -\mathbb{K}\lambda_l(1)\left(\nabla p_l - \left(\rho_l^{\text{std}} + R_s \rho_g^{\text{std}}\right)\mathbf{g}\right); \tag{48}$$

$$\mathbf{J} = -\frac{\Phi F}{R_s + F} D_l^h \nabla R_s. \tag{49}$$

2.5 Saturated/unsaturated state, general formulation

Finally, in the saturated region, we used p_l and S_g as variables in Eqs. 42–45, but in the unsaturated region, we should use other variables, p_l and R_s, in Eqs. 46–49. In order to avoid the change of variables and equations in different regions as above, we prefer to introduce a new variable

$$X = (1 - S_g) R_s + C_v p_g S_g; \tag{50}$$

in view to make Eq. 43 parabolic in X.

This new variable X is well defined both in saturated and unsaturated regions. Moreover, from Eqs. 38 and 28, $R_s = \rho_l^h / \rho_g^{\text{std}}$; from Eq. 40 $C_v p_g = \rho_g / \rho_g^{\text{std}}$, and since $\rho_g = \rho_g^h$, this new variable X is a "normalized total hydrogen mass density": $X = (S_l \rho_l^h + S_g \rho_g^h)/\rho_g^{\text{std}}$. It is easy then to see that parabolicity is possible only if we take liquid pressure p_l as another independent variable. Knowing that, in the saturated case, $S_g > 0$, $R_s = C_h p_g$ from Henry's law, we may write X defined in Eq. 50 as:

$$X = \begin{cases} \left(C_h\left(1 - S_g\right) + C_v S_g\right)\left(p_l + p_c\left(S_g\right)\right) & \text{if } S_g > 0 \\ R_s & \text{if } S_g = 0. \end{cases} \tag{51}$$

Since, for capillary pressure, defined as a function of gas saturation, we have $p_c'(S_g) > 0$, and since usually, like for hydrogen, in Eq. 39 $\omega = C_v / C_h > 1$, we get the following bounds:

$$\begin{aligned} a\left(S_g\right) &= C_h\left(1 - S_g\right) + C_v S_g \in \left[C_h, C_v\right], \\ a'\left(S_g\right) &= C_v - C_h = C_\Delta > 0. \end{aligned} \tag{52}$$

Then, for any $S_g > 0$ from Eq. 51:

$$\frac{\partial X}{\partial S_g} = C_\Delta\left(p_l + p_c\left(S_g\right)\right) + a\left(S_g\right) p_c'\left(S_g\right) > 0,$$

and therefore, for each $p_l > 0$, we can find inverse function $S_g = S_g(p_l, X)$, which satisfies

$$\frac{\partial S_g}{\partial X} > 0 \quad \text{for } S_g > 0.$$

After taking derivatives with respect to p_l and X of Eq. 51, we obtain:

$$\begin{aligned} \frac{\partial S_g}{\partial p_l} &= -\frac{a\left(S_g\right)^2 \chi\left(p_l, X\right)}{C_\Delta X + a\left(S_g\right)^2 p_c'\left(S_g\right)}, \\ \frac{\partial S_g}{\partial X} &= \frac{a\left(S_g\right) \chi\left(p_l, X\right)}{C_\Delta X + a\left(S_g\right)^2 p_c'\left(S_g\right)}, \end{aligned} \tag{53}$$

where $\chi(p_l, X)$ is a characteristic function of the set $\{X > C_h(p_l + p_c(0))\}$. In Eq. 53, we remark from Eq. 52 and definition Eq. 3 that $\partial S_g / \partial p_l \le 0$.

Let us note that property

$$p_c'(S_g = 0) = +\infty, \tag{54}$$

of van Genuchten p_c functions, leads to continuity of the two above partial derivatives since we have

$$\lim_{S_g \to 0} \frac{\partial S_g}{\partial p_l} = \lim_{S_g \to 0} \frac{\partial S_g}{\partial X} = 0.$$

We now introduce auxiliary function $N(p_l, X)$, defined as

$$N(p_l, X) = \frac{C_\Delta X}{C_\Delta X + a\left(S_g\right)^2 p_c'\left(S_g\right)} \chi(p_l, X) \in [0, 1),$$

which verifies

$$\chi(p_l, X) + p_c'\left(S_g\right) \frac{\partial S_g}{\partial p_l} = N(p_l, X),$$

$$p_c'\left(S_g\right) \frac{\partial S_g}{\partial X} = \frac{1 - N(p_l, X)}{a\left(S_g\right)} \chi(p_l, X). \quad (55)$$

Note that function $N(p_l, X)$ is continuous under condition Eq. 54.

Darcy's fluxes in Eq. 44 and diffusive flux Eq. 45 now take the form, with $p_g = p_l + p_c(S)$,

$$\mathbf{q}_l = -\mathbb{K}\lambda_l\left(S_g\right)\left(\nabla p_l - \left(\rho_l^{\mathrm{std}} + R_s(p_l, X)\rho_g^{\mathrm{std}}\right)\mathbf{g}\right) \quad (56)$$

$$\mathbf{q}_g = -\mathbb{K}\lambda_g\left(S_g\right), \left(\nabla p_l + \nabla p_c\left(S_g\right) - C_v \rho_g^{\mathrm{std}} p_g(p_l, X)\mathbf{g}\right), \quad (57)$$

$$\mathbf{J} = -\frac{\Phi\left(1 - S_g\right) F}{R_s(p_l, X) + F} D_l^h \nabla R_s(p_l, X); \quad (58)$$

where S_g is a function of p_l and X and where R_s, defined as in Eq. 38, can now be expressed in both saturated and unsaturated regions as a function of new variables p_l and X:

$$R_s(p_l, X) = \min(C_h p_g(p_l, X), X),$$

$$p_g(p_l, X) = p_l + p_c(S_g(p_l, X)).$$

After expanding the capillary pressure gradient in Eq. 57 and the gradient of R_s in Eq. 58, we may write:

$$\mathbf{q}_g = -\mathbb{K}\lambda_g(S_g)\left(\left[1 + p_c'\left(S_g\right)\frac{\partial S_g}{\partial p_l}\right]\nabla p_l + p_c'\left(S_g\right)\frac{\partial S_g}{\partial X}\nabla X - C_v \rho_g^{\mathrm{std}} p_g(p_l, X)\mathbf{g}\right),$$

$$\mathbf{J} = -\frac{\Phi(1 - S_g(p_l, X))F}{R_s(p_l, X) + F} D_l^h C_h \chi\left(1 + p_c'(S_g)\frac{\partial S_g}{\partial p_l}\right)\nabla p_l - \frac{\Phi\left(1 - S_g(p_l, X)\right) F}{R_s(p_l, X) + F} D_l^h C_h p_c'\left(S_g\right)\frac{\partial S_g}{\partial X}\nabla X - \frac{\Phi F}{X + F} D_l^h (1 - \chi)\nabla X.$$

From Eq. 21 water component flux $\boldsymbol{\phi}^w$ and hydrogen component flux $\boldsymbol{\phi}^h$, with the assumptions of incompressible water and absence of water vapor, reduce to

$$\boldsymbol{\phi}^w = \mathbf{q}_l + \boldsymbol{\phi}_l^w = -\left(\tilde{A}_{1,1}\nabla p_l + \tilde{A}_{1,2}\nabla X + \tilde{B}_1\right), \quad (59)$$

$$\boldsymbol{\phi}^h = R_s \mathbf{q}_l + C_v p_g \mathbf{q}_g + \boldsymbol{\phi}_l^h = -\left(A_{2,1}\nabla p_l + A_{2,2}\nabla X + B_2\right), \quad (60)$$

where the coefficients $A_{ij}(p_l, X)$ and $B_i(p_l, X)$ are given by the following formulas (note that, from Eq. 45, $\boldsymbol{\phi}_l^h = \mathbf{J}$ and $\boldsymbol{\phi}_l^w = -\mathbf{J}/G$):

$$\tilde{A}_{11}(p_l, X) = \mathbb{K}\lambda_l(S_g) - \frac{\Phi(1 - S_g)F}{(R_s + F)G} D_l^h C_h N, \quad (61)$$

$$\tilde{A}_{1,2}(p_l, X) = -\frac{\Phi(1 - S_g)F}{(R_s + F)G}\frac{1 - N}{a(S_g)} D_l^h C_h, \quad (62)$$

$$A_{2,1}(p_l, X) = \mathbb{K}\lambda_l(S_g)R_s + \mathbb{K}\lambda_g(S_g)C_v p_g N + \frac{\Phi(1 - S_g)F}{R_s + F} D_l^h C_h N, \quad (63)$$

$$A_{2,2}(p_l, X) = \mathbb{K}\lambda_g(S_g)\frac{1 - N}{a(S_g)} C_v p_g + \frac{\Phi(1 - S_g)F}{R_s + F}\frac{1 - N}{a(S_g)} D_l^h C_h, \quad (64)$$

$$\tilde{B}_1(p_l, X) = -\mathbb{K}\lambda_l(S_g)\left[\rho_l^{\mathrm{std}} + R_s\rho_g^{\mathrm{std}}\right]\mathbf{g}, \quad (65)$$

$$B_2(p_l, X) = -\mathbb{K}\lambda_l(S_g)R_s\left[\rho_l^{\mathrm{std}} + R_s\rho_g^{\mathrm{std}}\right]\mathbf{g} - \mathbb{K}\lambda_g(S_g)C_v^2\rho_g^{\mathrm{std}} p_g^2\mathbf{g}; \quad (66)$$

where we have used Eq. 55 and $\lambda_g(S_g)(1 - \chi) = 0$.

Equations 42–45 become:

$$-\Phi\frac{\partial S_g}{\partial p_l}\frac{\partial p_l}{\partial t} - \operatorname{div}\left(\tilde{A}_{1,1}\nabla p_l + \tilde{A}_{1,2}\nabla X + \tilde{B}_1\right) - \Phi\frac{\partial S_g}{\partial X}\frac{\partial X}{\partial t} = \mathscr{F}^w/\rho_l^{\mathrm{std}} \quad (67)$$

$$\Phi\frac{\partial X}{\partial t} - \operatorname{div}\left(A_{2,1}\nabla p_l + A_{2,2}\nabla X + B_2\right) = \mathscr{F}^h/\rho_g^{\mathrm{std}}. \quad (68)$$

The gain in this form is that Eq. 68 is a parabolic equation for X since

$$A_{2,2}(p_l, X)\boldsymbol{\xi}\cdot\boldsymbol{\xi} = \mathbb{K}\boldsymbol{\xi}\cdot\boldsymbol{\xi}\lambda_g(S_g)\frac{1 - N}{a(S_g)}C_v p_g + \frac{\Phi(1 - S_g)F}{R_s + F}\frac{1 - N}{a(S_g)}D_l^h C_h|\boldsymbol{\xi}|^2$$

is strictly positive in the whole domain if the diffusion and capillary pressure are not neglected.

If we eliminate diffusive terms from Eq. 67 (the “pressure equation”), by forming an equation for total flow $\boldsymbol{\phi}_{\mathrm{tot}}$, defined in Eq. 69, that is summing Eqs. 68 and 67, we obtain

$$\begin{aligned}\boldsymbol{\phi}_{\mathrm{tot}} &= G\boldsymbol{\phi}^w + \boldsymbol{\phi}^h = (G+R_s)\mathbf{q}_l + C_v p_g \mathbf{q}_g \\ &= -(A_{1,1}\nabla p_l + A_{1,2}\nabla X + B_1),\end{aligned} \tag{69}$$

where G is the density ratio defined in Eq. 41, and coefficients $A_{1,1}$, $A_{1,2}$, and B_1 are given by:

$$\begin{aligned}A_{1,1}(p_l, X) &= G\tilde{A}_{1,1} + A_{2,1} = \mathbb{K}\lambda_l\big(S_g\big)(G+R_s) \\ &\qquad + \mathbb{K}\lambda_g\big(S_g\big)C_v p_g N,\end{aligned} \tag{70}$$

$$\begin{aligned}A_{1,2}(p_l, X) &= G\tilde{A}_{1,2} + A_{2,2} \\ &= \mathbb{K}\lambda_g\big(S_g\big)\frac{1-N}{a\big(S_g\big)}C_v p_g,\end{aligned} \tag{71}$$

$$\begin{aligned}B_1(p_l, X) &= G\tilde{B}_1 + B_2 \\ &= -\mathbb{K}\lambda_l\big(S_g\big)(G+R_s) \times \Big[\rho_l^{\mathrm{std}} + R_s\rho_g^{\mathrm{std}}\Big]\mathbf{g} \\ &\quad - \mathbb{K}\lambda_g\big(S_g\big)C_v^2\rho_g^{\mathrm{std}}p_g^2\mathbf{g}.\end{aligned} \tag{72}$$

Now, the “pressure equation” Eq. 67 is transformed to:

$$\begin{aligned}&-G\Phi\frac{\partial S_g}{\partial p_l}\frac{\partial p_l}{\partial t} - \operatorname{div}\big(A_{1,1}\nabla p_l + A_{1,2}\nabla X + B_1\big) \\ &\quad + \Phi\left(1 - G\frac{\partial S_g}{\partial X}\right)\frac{\partial X}{\partial t} = G\mathscr{F}^w/\rho_l^{\mathrm{std}} + \mathscr{F}^h/\rho_g^{\mathrm{std}}.\end{aligned} \tag{73}$$

With this last formulation, we see that the pressure equation Eq. 73 is parabolic/elliptic equation in p_l since

$$\begin{aligned}A_{11}(p_l, X)\boldsymbol{\xi}\cdot\boldsymbol{\xi} &= \mathbb{K}\boldsymbol{\xi}\cdot\boldsymbol{\xi}\lambda_l\big(S_g\big)(G+R_s) \\ &\quad + \mathbb{K}\boldsymbol{\xi}\cdot\boldsymbol{\xi}\lambda_g\big(S_g\big)C_v p_g N,\end{aligned}$$

is strictly positive, independently of presence of diffusion or capillary forces, and the coefficient in front of $\partial p_l/\partial t$ is positive since, as we remarked in Eq. 53, $\partial S_g/\partial p_l \le 0$.

Finally, the transport of water and hydrogen is described by differential Eqs. 73 and 68, which are rewritten here, using Eqs. 60 and 69, in the form

$$\begin{aligned}&\Phi\frac{\partial}{\partial t}\big(X - GS_g(p_l, X)\big) + \operatorname{div}\big(\boldsymbol{\phi}_{\mathrm{tot}}\big) \\ &\quad = G\mathscr{F}^w/\rho_l^{\mathrm{std}} + \mathscr{F}^h/\rho_g^{\mathrm{std}},\end{aligned} \tag{74}$$

$$\Phi\frac{\partial X}{\partial t} + \operatorname{div}\Big(\boldsymbol{\phi}^h\Big) = \mathscr{F}^h/\rho_g^{\mathrm{std}}, \tag{75}$$

where the fluxes are given by Eqs. 60 and 69, while the coefficients are given by formulas Eqs. 61–66 and Eqs. 70–72.

2.5.1 Boundary conditions

Equations 74 and 75, given in porous domain Ω, must be complemented by initial and boundary conditions. Following [3], we assume that the boundary $\partial\Omega$ is divided in several disjoint parts: impervious, inflow, and outflow boundaries. We present now a set of standard boundary conditions on each of these boundary parts.

- On impervious boundary Γ_{imp}, we take Neumann conditions:

$$\boldsymbol{\phi}_{\mathrm{tot}}\cdot\boldsymbol{\nu} = 0 \quad\text{and}\quad \boldsymbol{\phi}^h\cdot\boldsymbol{\nu} = 0. \tag{76}$$

- On inflow boundary when pure water is injected, we impose, for hydrogen component, $X = 0$ and, for liquid pressure, either $p_l = p_{l,\mathrm{in}}$ or $\boldsymbol{\phi}_{\mathrm{tot}}\cdot\boldsymbol{\nu} = Q_d$.
- On inflow boundary, when pure gas is injected, we have $\boldsymbol{\phi}^w\cdot\boldsymbol{\nu} = 0$ and we can impose, for the pressure, total injection rate, which is then equal to gas injection rate:

$$\boldsymbol{\phi}_{\mathrm{tot}}\cdot\boldsymbol{\nu} = Q_d^h = \boldsymbol{\phi}^h\cdot\boldsymbol{\nu}. \tag{77}$$

- On the outflow boundary, when liquid is displaced by gas, we have the possibility to impose for gas phase $X = 0$ and for liquid pressure $p_l = p_{l,\mathrm{out}}$, only before gas reaches this outflow boundary (breakthrough time). Alternatively, with the same Dirichlet condition for liquid pressure, for gas saturation, we can set either Neumann condition $\nabla S_g\cdot\boldsymbol{\nu} = 0$, or Dirichlet condition $S_g = 0$.

2.6 Model without capillary pressure, diffusion, or gravity

When capillary pressure is neglected, we have only one pressure $p_g = p_l = p$, then definition Eq. 51 of variable X simplifies to:

$$X = \begin{cases}\big(C_h\big(1 - S_g\big) + C_v S_g\big)p & \text{if } S_g > 0 \\ R_s & \text{if } S_g = 0,\end{cases} \tag{78}$$

and partial derivatives Eq. 53 can be calculated explicitly,

$$\frac{\partial S_g}{\partial p} = -\frac{X}{C_\Delta p^2}\chi(p, X), \qquad \frac{\partial S_g}{\partial X} = \frac{1}{C_\Delta p}\chi(p, X),$$

where $\chi(p, X)$ is the characteristic function of saturated region, as before.

When we neglect capillary pressure, and also diffusive and gravity fluxes, the system of Eqs. 74 and 75 reduces to the following two equations:

$$\Phi \frac{\partial}{\partial t}\left(X - GS_g(p, X)\right) + \operatorname{div}\left(\boldsymbol{\phi}_{\mathrm{tot}}\right) = G\mathscr{F}^w/\rho_l^{\mathrm{std}} + \mathscr{F}^h/\rho_g^{\mathrm{std}} \tag{79}$$

$$\Phi \frac{\partial X}{\partial t} + \operatorname{div}\Big(f^h(p, X)\boldsymbol{\phi}_{\mathrm{tot}}\Big) = \mathscr{F}^h/\rho_g^{\mathrm{std}}, \tag{80}$$

where

$$\boldsymbol{\phi}_{\mathrm{tot}} = -\Lambda_{\mathrm{tot}}(p, X)\mathbb{K}\nabla p, \quad \boldsymbol{\phi}^h = f^h(p, X)\boldsymbol{\phi}_{\mathrm{tot}}. \tag{81}$$

Total mobility $\Lambda_{\mathrm{tot}}(p, X)$ and hydrogen fractional flow functions $f^h(p, X)$ are defined by:

$$\Lambda_{\mathrm{tot}}(p, X) = \lambda_l(S_g)\big(G + R_s(p, X)\big) + \lambda_g(S_g)C_v p,$$

$$\Lambda^h(p, X) = \lambda_l(S_g)R_s(p, X) + \lambda_g(S_g)C_v p,$$

$$f^h(p, X) = \frac{\Lambda^h(p, X)}{\Lambda_{\mathrm{tot}}(p, X)}.$$

The system of Eqs. 79–81 is very close to immiscible two-phase system (see, for instance, [3]); the only difference in hydrogen transport Eq. 80 is the presence of $R_s(p, X)$ in fractional flow function $f^h(p, X)$, and if we write pressure Eq. 79 in the form

$$G\chi\Phi \frac{X}{C_\Delta p^2}\frac{\partial p}{\partial t} + \operatorname{div}\left(\boldsymbol{\phi}_{\mathrm{tot}}\right) + \Phi\left(1 - \frac{G\chi}{C_\Delta p}\right)\frac{\partial X}{\partial t} = G\mathscr{F}^w/\rho_l^{\mathrm{std}} + \mathscr{F}^h/\rho_g^{\mathrm{std}}, \tag{82}$$

then we see that the presence of dissolved gas introduces an additional "source" term in total flow Eq. 79, namely, $\Phi(1 - G\chi/(C_\Delta p))\partial X/\partial t$.

Remark 10 Considering the boundary conditions defined in the previous section, on the boundary part where there is hydrogen outflow, to impose a Dirichlet condition on X will lead to a boundary layer.

3 Numerical simulations

This section presents two test cases and their simulations using the new formulation given by system Eqs. 74 and 75. Both test cases are not built to correspond with particular real situations but rather to illustrate the gas appearance phenomenon. Assuming horizontal two-dimensional problems, gravity effects are neglected in both cases. The first test case is a one-dimensional-like situation where hydrogen is injected through an inflow boundary, and the second test case is a two-dimensional situation where hydrogen is injected via a volume source term.

3.1 Setting test cases

3.1.1 Physical data

In the two test cases, we consider the same isotropic porous medium with a uniform absolute permeability tensor $\mathbb{K} = k$, where k is scalar and a uniform porosity Φ. The capillary pressure function, p_c, is given by the van Genuchten model (see [12]) and relative permeability functions, kr_l and kr_g, are given by the van Genuchten–Mualem model (see [12] and [13]). According to these models, we have:

$$p_c = P_r\left(S_{le}^{-1/m} - 1\right)^{1/n}, \; kr_l = \sqrt{S_{le}}\left(1 - \left(1 - S_{le}^{1/m}\right)\right)^2$$

$$\text{and } kr_g = \sqrt{1 - S_{le}}\left(1 - S_{le}^{1/m}\right)^{2m}$$

$$\text{with} \quad S_{le} = \frac{S_l - S_{lr}}{1 - S_{lr} - S_{gr}} \quad \text{and} \quad m = 1 - \frac{1}{n}$$

where parameters P_r, n, S_{lr}, and S_{gr} depend on the porous medium. Values of parameters describing the considered porous medium and fluid characteristics are given in Table 1. Fluid temperature is fixed to $T = 303$ K.

3.1.2 Test case 1

In the first test case, we consider the domain $\Omega^1 = [0m\,; 200m] \times [-10m\,; 10m]$ with an impervious boundary $\Gamma^1_{\mathrm{imp}} = [0m\,;\, 200m] \times \{-10m, 10m\}$, an inflow boundary $\Gamma^1_{\mathrm{in}} = \{0m\} \times [-10m\,; 10m]$, and an outflow

Table 1 Values of porous medium parameters and fluid characteristics

Porous medium parameters		Fluid characteristics	
Parameter	Value	Parameter	Value
k	$5\ 10^{-20}$ m^2	D_l^h	$3\ 10^{-9}$ m^2/s
Φ	0.15 (–)	μ_l	$1\ 10^{-3}$ Pa.s
P_r	$2\ 10^6$ Pa	μ_g	$9\ 10^{-6}$ Pa.s
n	1.49 (–)	$H(T{=}303\text{ K})$	$7.65\ 10^{-6}$ mol Pa^{-1} m^{-3}
S_{lr}	0.4 (–)	M_l	10^{-2} kg/mol
S_{gr}	0 (–)	M_g	$2\ 10^{-3}$ kg/mol
		ρ_l^{std}	10^3 kg/m^3
		ρ_g^{std}	$8\ 10^{-2}$ kg/m^3

boundary $\Gamma^1_{\text{out}} = \{200m\} \times [-10m\,;\,10m]$. The following boundary conditions are imposed:

- $\phi_{\text{tot}} \cdot \nu = \phi^h \cdot \nu = 0$ on the impervious boundary Γ^1_{imp}
- $\phi_{\text{tot}} \cdot \nu = \phi^h \cdot \nu = Q^h_d$ on the inflow boundary Γ^1_{in}
- $X = 0$ and $p_l = p^1_{l,\text{out}}$ on the outflow boundary Γ^1_{out}

where Q^h_d and $p^1_{l,\text{out}}$ are constant scalars. Source terms are fixed to zero ($\mathscr{F}^h = \mathscr{F}^w = 0$). Initial conditions are $X(t=0) = 0$ and $p_l(t=0) = p^1_{l,\text{out}}$ on Ω^1. The boundary parameters are fixed to $Q^h_d = 1.5\ 10^{-5}$ m/years and $p^1_{l,\text{out}} = 10^6$ Pa.

3.1.3 Test case 2

In the second test case, we consider the domain $\Omega^2 = [0m\ ;\ 200m] \times [-100m\ ;\ 100m]$ with an outflow boundary $\Gamma^2_{\text{out}} = \partial\Omega^2$ and where $B^2_h = [90m\ ;\ 110m] \times [-10m\ ;\ 10m]$ is the support of hydrogen source term. On the outflow boundary Γ^2_{out}, we impose $X = 0$ and $p_l = p^2_{l,\text{out}}$. Source terms are defined by $\mathscr{F}^h = F^2_h \chi_{B^2_h}$ and $\mathscr{F}^w = 0$. Initial conditions are $X(t=0) = 0$ and $p_l(t=0) = p^2_{l,\text{out}}$ on Ω^2. Here, $p^2_{l,\text{out}}$ and F^2_h are constant scalars fixed to $p^2_{l,\text{out}} = 10^6$ Pa and $F^2_h = 8\ 10^{-13}$ kg/m^3/s $\approx 2.5\ 10^{-5}$ kg/m^3/year.

3.2 Numerical results

System Eqs. 74 and 75 is a coupled nonlinear partial differential equation system. Numerical simulations use an implicit scheme for time discretization, a finite-volume scheme (using multipoint flux approximation) for space discretization and a Newton–Raphson-like method to solve nonlinearities. All computations are performed with the Cast3m software (see [16]).

In both cases we present, at several times, spatial evolutions of the liquid pressure, the total hydrogen molar density, and the gas saturation along the line $\mathscr{L}_{\text{cut}} = [0m\ ;\ 200m] \times \{0m\}$. Computations are performed since the time $t = 0$ up to the stationary state.

3.2.1 Results and comments

Results of test case 1 are plotted on Figs. 1, 2, and 3. The total hydrogen molar density $\frac{\rho^{\text{std}}_g}{M^h} X$ (Fig. 1), the

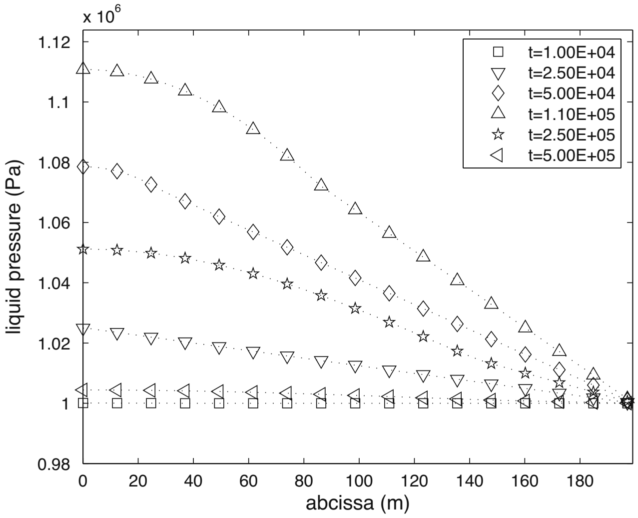

Fig. 2 Test case 1: spatial evolution along the line $\mathscr{L}_{\text{cut}}$ of the liquid pressure p_l at several times t (in years)

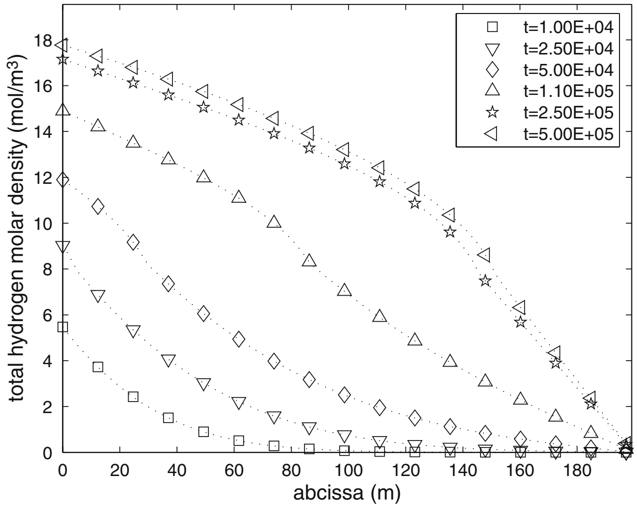

Fig. 1 Test case 1: spatial evolution along the line $\mathscr{L}_{\text{cut}}$ of the total hydrogen molar density $\frac{\rho^{\text{std}}_g}{M^h} X$ at several times t (in years)

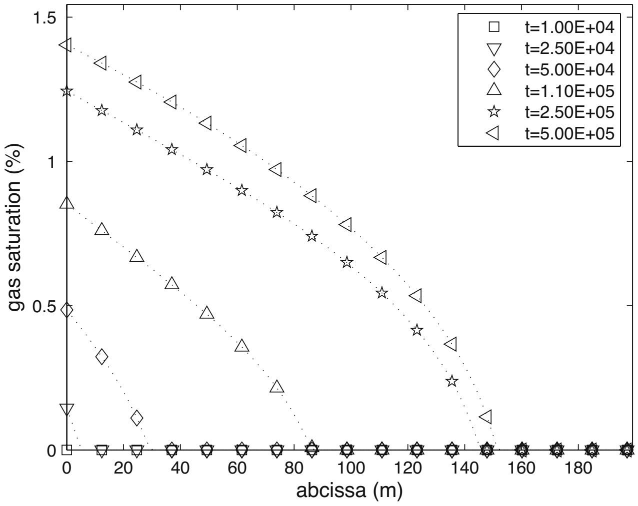

Fig. 3 Test case 1: spatial evolution along the line $\mathscr{L}_{\text{cut}}$ of the gas saturation S_g at several times t (in years)

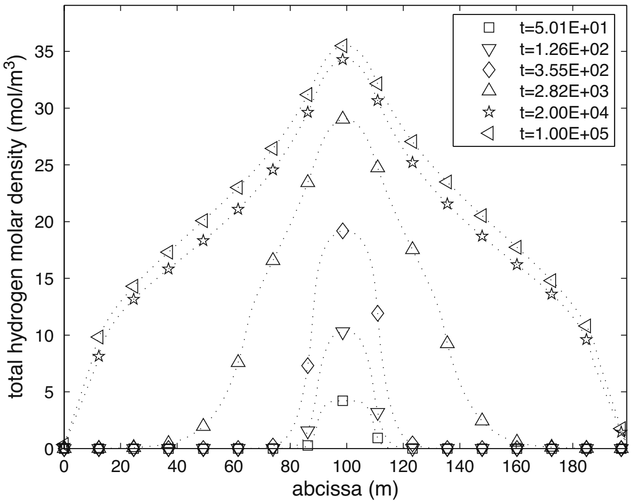

Fig. 4 Test case 2: spatial evolution along the line $\mathscr{L}_{\text{cut}}$ of the total hydrogen molar density $\frac{\rho_g^{\text{std}}}{M^h}X$ at several times t (in years)

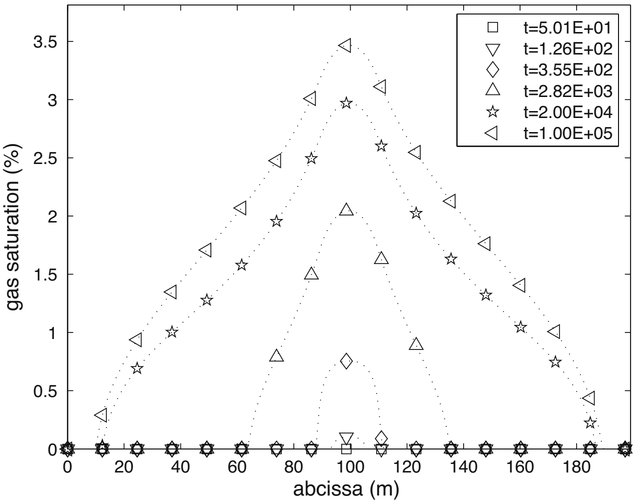

Fig. 6 Test case 2: spatial evolution along the line $\mathscr{L}_{\text{cut}}$ of the gas saturation S_g at several times t (in years)

liquid pressure p_l (Fig. 2), and the gas saturation S_g (Fig. 3) are plotted at times $t = 1\ 10^4$, $2.5\ 10^4$, $5\ 10^4$, $1.1\ 10^5$, $2.5\ 10^5$, and $5\ 10^5$ years. Results of test case 2 are plotted on Figs. 4, 5, and 6. The total hydrogen molar density $\frac{\rho_g^{\text{std}}}{M^h}X$ (Fig. 4), the liquid pressure p_l (Fig. 5), and the gas saturation S_g (Fig. 6) are plotted at times $t = 50.1$, 125, 355, 2820, $2\ 10^4$, and 10^5 years.

In both cases, we can identify three characteristic times: at $t = T_1$, the gas phase appears; at $t = T_2$, the maximum liquid pressure is reached; at $t = T_3$, the system is close to the stationary state. For test case 1, we have

$$T_1 \approx 2\ 10^4 \ \textit{years},\ T_2 \approx 1.1\ 10^5 \textit{years} \text{ and } T_3 \approx 5\ 10^5 \textit{years};$$

for test case 2, we have

$$T_1 \approx 90 \ \textit{years},\ \ T_2 \approx 355;\ \textit{years} \text{ and } T_3 \approx 10^5 \ \textit{years}.$$

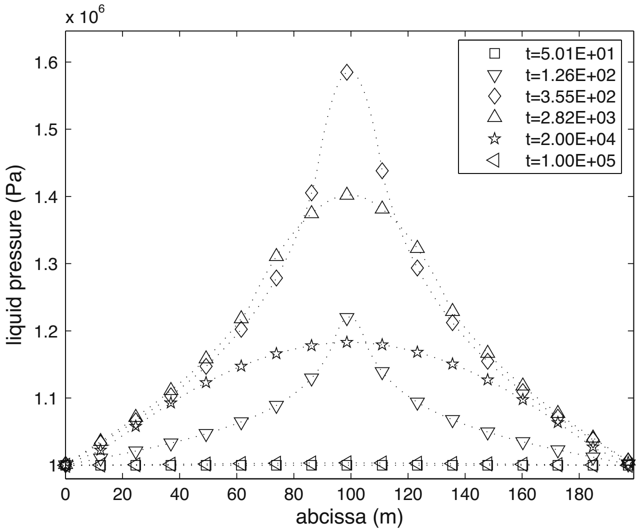

Fig. 5 Test case 2: spatial evolution along the line $\mathscr{L}_{\text{cut}}$ of the liquid pressure p_l at several times t (in years)

Global behaviors of both cases are similar and can be summarized as follows:

- For $0 \leq t < T_1$: only total hydrogen density increases, while liquid pressure and gas saturation stay constant; during this stage, $X < C_h p_l$, and the entire domain is saturated in water ($S_g = 0$).
- From $t = T_1$, $X \geq C_h p_l$ in a part of the domain, meaning that gas phase exists ($S_g > 0$) in this part.
- For $T_1 \leq t \leq T_2$: while gas phase appears, liquid pressure increases and a nonzero pressure gradient appears that corresponds to a fluid displacement according to the Darcy–Muskat law. Total hydrogen density and gas saturation increase, and the saturated area grows.
- For $T_2 \leq t$: while total hydrogen density and gas saturation continue to increase, liquid pressure and pressure gradient decrease. When $t \to \infty$, the system reaches a stationary state where saturated and unsaturated areas coexist and liquid pressure gradient is null.

4 Concluding remarks

From balance equations, constitutive relations, and equations of state, assuming thermodynamical equilibrium, we have derived a model for describing underground gas migration in water saturated or unsaturated porous media, including diffusion of components in phases and capillary effects. In Section 2.5, we have introduced a new set of variables leading to a model describing both saturated and unsaturated state by a single pair of variables X and p_l (see Eq. 51). A major advantage of this choice of primary variables, compared to standard models using either a mixed formulation of one pressure and one saturation, or a two-pressure formulation method, is to be able to handle phase transitions on the wet end when the system becomes unsaturated. In order to avoid collapse of the formulation, at a single-phase condition (as explained, for instance, in [14]), usual models use either variable substitution (or variable switching), depending on the phase conditions of a given point, when gas saturation is near the residual or unity (see Section 2.3.1 and Remark 6 in Section 2.4), or add a residual gas saturation in water-saturated material. However, it is clear that applying an artificial residual gas saturation has no physical ground and that the switching procedure being done over a Newton's iteration will complicate significantly the model numerical implementation and may even cause a convergence problem. In the last part of this paper, numerical simulations on simplified situations inspired by the "Couplex-gas" benchmark [15] show evidence of developed model ability: – to describe gas (hydrogen) generation and migration – and to treat the difficult problem, as it appeared in the results of "Couplex-gas" [15], of correctly simulating evolution of the unsaturated region, in a deep geological repository, created by gas generation. A forthcoming paper will be devoted to the use of this model for solving the "Couplex-gas" benchmark [15] and other three-dimensional situations of gas migration in water-saturated or unsaturated porous media, including the design of numerical test cases synthesizing the main challenges appearing in gas generation and migration.

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