ANALYTICAL SOLUTIONS FOR THE SEQUESTRATION OF CARBON DIOXIDE IN SALINE AQUIFERS[*]

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Resumo

Procuramos soluções analíticas para o processo de injeção de um fluido supercrítico composto por uma mistura de dióxido de carbono e água, em um meio poroso com água. Após a injeção da mistura, uma complexa interação entre o transporte físico e a redistribuição das diversas componentes (i.e., água e CO_2) ocorre ao longo das duas fases. Esta redistribuição descreve-se usualmente em termos de equilíbrio termodinâmico local. Levamos em conta efeitos térmicos relacionados com a injeção de fluido frio e a dissolução de CO_2 em água.

Abstract

In this work we look for analytical solutions for the injection of a supercritical fluid mixture of carbon dioxide and water into porous rock filled with water. After injection of the water/CO_2 mixture a complex interaction between physical transport and the phase redistribution of the components, i.e., water and CO_2, occurs. This redistribution is usually described in terms of local thermodynamic equilibrium. We take into account the heat effects related to the cold fluid injection and to the dissolution of CO_2.

1. Introduction

Concern about global warming is generating interest in reducing the emissions of greenhouse gases such as CO_2. Injection of CO_2 in deep saline aquifers has been proposed as a large-scale mitigation strategy for attaining this goal. Examples of ongoing projects of CCS (Carbon Capture and Storage) in aquifers include the Sleipner Project in the North Sea (Utsira Formation) and the In-Salah Project in Algeria.

In this work we look for a certain type of analytical solutions (i.e., Riemann Solutions) for the injection of a supercritical fluid mixture of carbon dioxide and water into porous rock filled with water. Riemann solutions exhibit wave fronts found when studying piecewise initial value problems for material balance. A famous example widely used in Petroleum engineering is the solution given by Buckley and Leverett for pure gas or water injection in sandstones filled with oil, as initially described by their famous work (1942).

After injection of the water/CO_2 mixture a complex interaction between physical transport and the phase redistribution of the components, i.e., water and CO_2, occurs. This redistribution is usually described in terms of local thermodynamic equilibrium, which can be understood by the balancing effect of source/sink terms. There are no published complete analytical solutions for 1-D problems involving complex thermodynamics that include CO_2 and heat effects in the flow. In order to take into account the heat effects related to the cold fluid injection and related to the dissolution of CO_2, we must understand the fluid-phase equilibrium of the different components among the different phases that appear in the flow. A common sophisticated and effective approach for performing calculations for finding the thermodynamical properties of the flow, including mutual solubilities for carbon dioxide and water and their respective enthalpies, relies on the introduction of a "corrected pressure" term called the fugacity, which accounts for non ideal behavior. Nevertheless, by relying on simplified relations derived for ideal fluid mixtures we can perform a coherent qualitative analysis of the properties to be studied. Here we use this simplified approach, the *Quick Thermo Calculation*, described briefly in the Appendix.

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During the injection process, a supercritical fluid bank interacts with a region of cold water forming an intermediate region of multiphase flow composed of a CO_2-rich supercritical fluid phase and a H_2O-rich aqueous phase in thermodynamical equilibrium. This complex transport process can be described by the evolution of interfaces between and inside flow configurations, e.g., abrupt changes in the mixture concentrations, conveniently represented as shock waves, and by continuous changes of physical variables such as the temperature, represented as rarefaction fans. The mechanisms of CO_2 sequestration can be studied through the solution of Riemann problems associated to systems of balance laws governing the injection of water/CO_2 mixtures.

2. The Model

Our model captures the space-time evolution of the flow resulting from the co-injection of carbon dioxide and water into a thin linear horizontal porous core of constant porosity and permeability, initially filled with liquid water. We write a system of balance laws for the components of the flow, and for the conservation of energy, taking into account temperature effects. Due to high pressures and temperatures, the CO_2-H_2O mixture is found in supercritical state. We consider longitudinal heat conduction, but we disregard conduction with the porous rock. The pressure is assumed to be constant throughout the core; the fluids are considered incompressible. Gravity segregation does not have an important role in the transport process, as the cylindrical core is thin and horizontal. Variations of the physical properties of the fluids, e.g. viscosity and composition, can be important due to temperature changes; pressure changes are small along the core; therefore we assume it affects physical properties slightly. We assume ideal volume mixing rules. The 1D Darcy Law for multiphase flow relates the pressure gradient of each phase with its seepage speed

$$u_\alpha = -\frac{k k_{r\alpha}}{\mu_\alpha}\frac{\partial p_\alpha}{\partial x} \tag{2.1}$$

where k is the constant absolute permeability of the porous rock and $k_{r\alpha}$ is the relative permeability of phase α. One of the phases is supercritical, denoted by σ, and the other one is an aqueous phase, denoted by a. The partial permeabilities are functions of their respective saturations, s_σ and s_a. The symbols, μ_α and p_α stand for the viscosity and pressure of phase α.

We write the equations for the conservation of total mass of carbon dioxide (appearing in the supercritical fluid phase, as well as dissolved in the liquid aqueous phase) and water (appearing in the aqueous phase and dissolved in the CO_2-rich supercritical fluid phase) as

$$\frac{\partial}{\partial t}\varphi(\rho_{\sigma c}s_\sigma + \rho_{ac}s_a) + \frac{\partial}{\partial x}(\rho_{\sigma c}u_\sigma + \rho_{ac}u_a) = 0 \tag{2.2}$$

$$\frac{\partial}{\partial t}\varphi(\rho_{\sigma w}s_\sigma + \rho_{aw}s_a) + \frac{\partial}{\partial x}(\rho_{\sigma w}u_\sigma + \rho_{aw}u_a) = 0 \tag{2.3}$$

where $\rho_{\alpha i}$ denotes the concentration of component i in phase α. The different components are carbon dioxide (c) and water (w); φ is the porosity of the porous media, assumed to be constant. We include an additional equation for the conservation of energy using the enthalpy (per unit volume) formulation

$$\frac{\partial}{\partial t}\varphi\left(\hat{H}_r + H_\sigma s_\sigma + H_a s_a\right) + \frac{\partial}{\partial x}(H_\sigma u_\sigma + H_a u_a) = 0 \tag{2.4}$$

The term $\hat{H}_r$ represents the temperature dependent rock enthalpy per unit volume divided by the porosity φ. The enthalpy of the supercritical fluid per unit volume is given approximately by $H_\sigma = \rho_{\sigma c}h_{\sigma C} + \rho_{\sigma w}h_W$. The terms $h_{\sigma C}$ and h_W are the temperature dependent specific enthalpies of pure supercritical CO_2 and of pure cooled water given by experimental values and interpolated by cubic splines (higher order splines suit better the numerical methods, as the ones given by Reinsch (1967)). We approximate the enthalpy of the aqueous phase by the enthalpy of pure liquid water $H_a \sim \rho_W h_W$ where ρ_W is the density of pure liquid water, taken as the constant 998 kg/m^3.

We can perform a practical modification of equations (2.2), (2.3) and (2.4), by performing a straightforward manipulation of expression (2.1) obtaining

$$u_\sigma = \frac{m_\sigma}{m_\sigma + m_a} u - k \frac{m_\sigma m_a}{m_\sigma + m_a} \frac{\partial p_c}{\partial x} \tag{2.5}$$

where p_c is the capillary pressure $p_c \overset{\text{def}}{=} p_\sigma - p_a$, and $m_\alpha = k_\alpha / \mu_\alpha$ is the mobility of phase α, u is the sum of the Darcy velocities. Observe that $u_a = u - u_\sigma$. Replacing Eq. (2.5) in the balance laws (2.2), (2.3) and (2.4) we obtain a diffusive term related to the capillary pressure: the effect of this term is to widen the evaporation front as well as other shock waves, while the convergence of the characteristic lines tries to sharpen this front. The balance of these effects yields the front width, whose magnitude is negligible compared to the cylinder length. Therefore we may disregard variations of capillary pressure along the core. We may write then

$$u_\alpha = u f_\alpha \tag{2.6}$$

where f_α is the well known Buckely-Leverett flux given by $f_\alpha = \frac{m_\alpha}{m_\sigma + m_a}$. In the following analysis we will use the notation $f \overset{\text{def}}{=} f_\sigma$.

3. Mathematical Classification of Wave-Patterns

Our main objective consists in understanding the wave pattern in the fluid transport, consisting of space-time variations of the different variables that characterize the flow. Different approaches may provide equivalent outcomes for the flow evolution. In fact, numerical simulations for systems of conservation laws may provide trustworthy results, even though they usually are computationally time-consuming, quality of the outcome may depend on the appropriate choice of the method to be used (e.g. Finite Volume Hyperbolic for systems of balance, as explained in detail by Leveque (2002)) and their use may compromise the understanding of the core mechanisms of the system of partial differential equations corresponding to the physical model, as well as the classification of the different possible outcomes depending on the inputs of the simulator. Fundamental improvements may be carried out for understanding the physical processes at the pore and reservoir scale through upscaling, as treated in many interesting examples; for instance see Salimi et. al. (2009). In a different approach, a deep analysis of the structure of the hyperbolic system of conservation laws corresponding to the quantities transported by the flow can provide a bifurcation diagram for the injection problem: inputs for the injection values belonging to the same *region* exhibit the same flow evolution pattern. This is the Wave-Curve Method, described in Azevedo et. al. (2009). A comprehensive study of this method can be found in Isaacson et. al. (1992). These *inputs* are the values of the *Riemann problem*, written as

$$U(x,0) = \begin{array}{ll} U_L & x < 0 \\ U_R & x > 0 \end{array} \tag{3.1}$$

where $U(x, 0)$ is the starting value of the vector of unknown variables: we want to predict its future $U(x, t)$. In this paper we will show the progress done for carrying out this classification for an example of two-phase mixed CO_2/water injection into a saline aquifer containing carbonated water saturated by CO_2. In the analysis that follows we show how this wave-pattern classification is carried out by studying the different possible types of waves that can appear in the flow, and by finding important bifurcation loci where the solutions may change type in state space.

3.1. Waves in the Two-Phase Configuration

As explained above we will concentrate our efforts in an injection problem where both the injected fluid and the fluid found initially in the reservoir are two-phase CO_2-H_2O mixtures (in particular carbon saturated water can be considered the limit case of a two-phase fluid where the vapor phase saturation tends to zero). In this case, we say that the fluids are in the *tp* configuration: a mixture of two phases in thermodynamical equilibrium, one of liquid water with dissolved CO_2, and the other one a CO_2-rich supercritical fluid phase with dissolved H_2O. We assume ideal mixture throughout the flow. We assume that the *tp* configuration is in local thermodynamical equilibrium, therefore satisfying Gibbs phase rule $f = c - p + 2$, where f represents Gibbs number of degrees of freedom, c and p are the number of chemical species and phases, respectively. In this case the pressure is fixed, $c = 2$, and $p = 2$, therefore we obtain $f = 1$. Therefore, the component distribution along the phases is given by the system temperature. In particular, the partial densities $\rho_{\alpha i}$, where $\alpha = \sigma, a$ and $i = c, w$, are functions of temperature. A concise method for finding these functions is briefly described in the Appendix. We conclude that the balance laws (2.2), (2.3) and (2.4) are governed in the *tp* configuration by s_σ, T, and u. We put $U = (V, u)$ where $V = (s_\sigma\ , \ T)$. Following this notation, and taking into account the modification (2.6), the balance laws (2.2), (2.3) and (2.4) can be written as a system of the form,

$$\frac{\partial}{\partial t} G(V) + \frac{\partial}{\partial x}\ uF(V) = 0 \tag{3.1.1}$$

Assuming that are G and F are differentiable functions, we may write Eq. (3.1.1) as

$$B\ \frac{\partial}{\partial t}\begin{pmatrix} S \\ T \\ u \end{pmatrix} + A\frac{\partial}{\partial x}\begin{pmatrix} S \\ T \\ u \end{pmatrix} = 0 \tag{3.1.2}$$

where the letter s stands for s_σ. B and A are the Jacobians of the accumulation term B and the flux term A.

We look for self-similar solutions of the Riemann problem for the system of PDE's (3.1.2), i.e., solutions that satisfy $U(x,t) = U(x/t)$. Therefore we want to analyze (3.1.2) under the change of variables $\varepsilon = x/t$. Applying the chain rule in (3.1.2) we obtain

$$(A - \varepsilon B)\frac{dU}{d\varepsilon} = 0 \tag{3.1.3}$$

We conclude that a special type of solutions of (3.1.2) can be found by looking for solutions of the generalized eigenvalue-eigenvector problem

$$(A - \ l(U)B)r(U) = 0 \tag{3.1.4}$$

where

$$U = U(\varepsilon) \tag{3.1.5}$$

$$\frac{dU}{d\varepsilon} = r(U) \tag{3.1.6}$$

$$l\big(U(\varepsilon)\big) = \varepsilon \tag{3.1.7}$$

Solutions for the problem stated by (3.1.4), (3.1.5), (3.1.6) and (3.1.7) are called *rarefaction (fans) waves*. In the particular case we are studying, due to the absence of the unknown u in the system (3.1.1), the solution is given by two families of eigenvalues and eigenvectors

$$l_s = \frac{u}{\varphi}\frac{\partial f}{\partial s} \qquad , \qquad r_s = (1,0,0)^T \tag{3.1.8}$$

and

$$l_e = \frac{u}{\varphi}\frac{f - f_e}{s - s_e} \qquad , \qquad r_e = (r_e^1, r_e^2, r_e^3) = (g_1, g_2, ug_3) \tag{3.1.9}$$

where f_e and s_e are functions of temperature, and g_1, g_2 and g_3 are functions of s and T. We see immediately that the s-family (3.1.8) (s stands for saturation) corresponds to the Buckley-Leverett characteristic speed. Rarefaction fans for this family are straight lines, See (4.9b). Observe also that the eigenvalue l_e in (4.10a) has the form of a secant to the graph of the Buckley-Leverett fractional flow function.

Condition (3.1.7) implies that we can connect points in the (s, T, u)-space using rarefaction fans whenever the eigenvalue increases along the integral curve. Therefore we are interested in studying inflection locus for both families (3.1.8) and (3.1.9). This locus is a rarefaction fan "stopping" site. In our example, in order to find the rarefaction fans, we can restrict to looking for integral curves in the variables s and T.

The inflection locus for the Buckley-Leverett family (3.1.8) can be found by looking for zeros of $\partial^2 f/\partial s^2$. We denote this locus by I_s.

The coincidence locus of e-family (3.1.9) (e stands for *evaporation*), denoted by $C_{s,e}$ (i.e., where $l_e = l_s$) is contained in its inflection locus, denoted by I_e. The general theory for the bifurcation locus for this kind of multi-component multiphase transport problems was studied by Lambert et. al. (2009). It is easy to show that $\partial l_e/\partial s$=0, and r_e is parallel to r_s on the coincidence curve $C_{s,e}$. Moreover, we can show that $C_{s,e} \cup C_{e^*,e} = I_e$, where $C_{e^*,e}$ is given by the coincidence of l_e and l_{e^*}, where we have

$$l_{e^*} = \frac{u}{\varphi}\frac{f - f_{e^*}}{s - s_{e^*}} \tag{3.1.10}$$

where f_{e^*} and s_{e^*} are functions of temperature also.

In Fig. 1 we can see the inflection locus for both families. Above and below the coincidence curve C_e , the Buckley-Leverett characteristic speed is slower than the evaporation speed: when connecting the different waves for finding the solution to the Riemann problem, we should construct the wave-curve corresponding to the solution of the Riemann problem starting with a slow family, exhausting slow-wave pieces and continue with the process with a fast family. In Fig. 1 we also see the rarefaction fan curves together with the directions of increasing speed. We detail also the natural orientation of the vector field r_e.

Another kind of self-similar solutions are *shock waves* and *contact discontinuities*. Shock waves are discontinuities in the solution $U(x,t)$ that satisfy the *Rankine-Hugoniot* condition: even in the presence of a discontinuity an integral version of the system of conservation laws should be valid. The *RH* condition can be expressed for the system (3.1.1) as

$$v[G] = u^+F^+ - u^-F^- \tag{3.1.11}$$

where $[G] \stackrel{\text{def}}{=} G^+ - G^-$ is the difference between the limit values on the right and left of the shock curve, and v is the speed of the shock. For this type of systems, the *Rankine-Hugoniot Locus* of a given starting value $U^- = (V^-, u^-)$, i.e., the set of points of the form $U^+ = (V^+, u^+)$ that satisfy relation (3.1.11) together with the starting point, is found by looking for the values of V^+ that satisfy the *RH* condition. Surprisingly, v and u^+ can be found in terms of the remaining variables. In fact, Eq. (3.1.11) can be written as a system of the form:

$$\begin{bmatrix} [G_1] & -F_1^+ & F_1^- \\ [G_2] & -F_2^+ & F_2^- \\ [G_3] & -F_3^+ & F_3^- \end{bmatrix} \begin{bmatrix} v \\ u^+ \\ u^- \end{bmatrix} = 0 \tag{3.1.12}$$

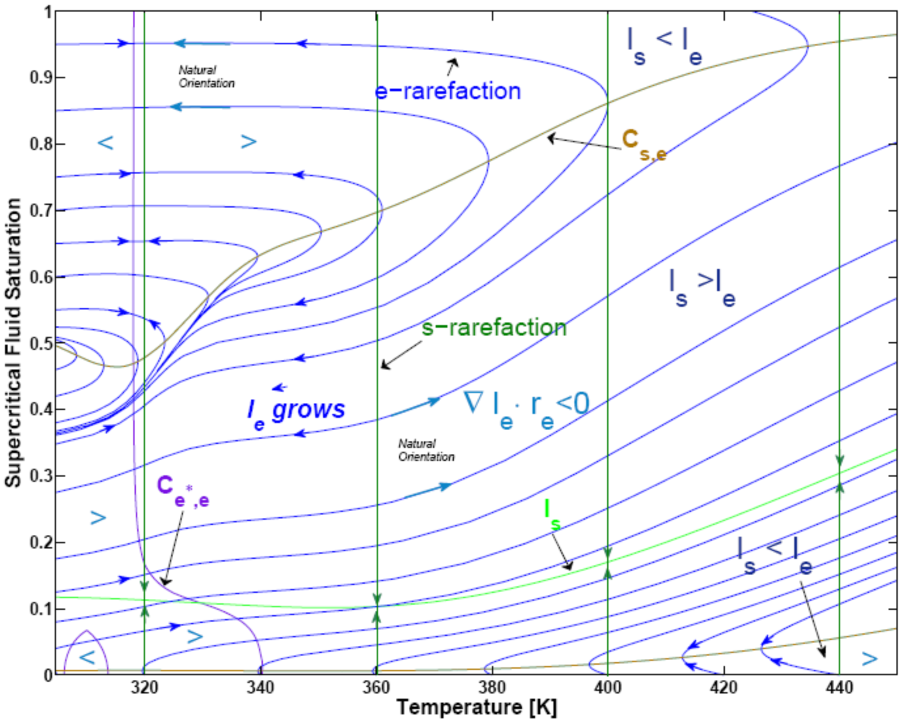

Figure 1. Rarefactions and inflection loci for the s and e families.

Under certain regularity assumptions, the *RH Locus* for systems of the type (3.1.1) is given by two curves, intersecting at the starting point U^- tangent to the rarefaction waves and possibly presenting auto-intersections. Each one of these two curves belongs to a different family (slow and fast). Each point U^+ in the *RH Locus* represents a shock wave between the states $U^-$and U^+ with speed $v = v(U^-, U^+)$.

Contact Discontinuities are abrupt changes in $U(x,t)$ that travel with characteristic speed. They are represented in the space of variables (s,T,u) by integral curves of the system (3.1.5), (3.1.6) where the eigenvalue l remains constant, i.e. where

$$\nabla l(U) \cdot r(U) = 0 \tag{3.1.13}$$

Moreover, these curves satisfy the *RH* Condition. In our case, inside of the *tp* configuration we don't observe this kind of waves.

In order to build the wave-curve we must carefully study the compatibility between the speed of the rarefaction fans, shocks waves and contact discontinuities (always starting with slow waves followed by fast waves) and determine the *admissibility* of the shock waves to be considered. A criterion for choosing physical shock waves comes from the *viscous* admissibility criterion (viscous or *diffusion* terms appear in the heat equation, viscous Burgers, Navier-Stokes, among others). Viscosity smoothes discontinuous initial data immediately. In the theory of hyperbolic conservation laws, e.g., of the type (3.1.1), in general this criterion reduces to the of study inequalities between the characteristic speeds of the system and the shock speed, inducing a classification of the different types of admissible shocks: Slow and Fast Lax, Transitional (as treated in Isaacson et. al. (1990)) and Super-compressive.

In Fig. 2 we show the initial value data for the injection problem. The *left* state $(x < 0)$ is a two-phase mixture of CO_2 and H_2O at the temperature of 360 [K]. The *right* state $(x > 0)$ is carbonated water saturated by CO_2 at 320 [K]. We show the *RH Locus* for different saturations at the temperature of 320 [K]. As explained above, in order to find a wave-curve linking the *left* and *right* states we need to build piece by piece a coherent sequence of waves satisfying the different admissibility criteria (this work is in current progress).

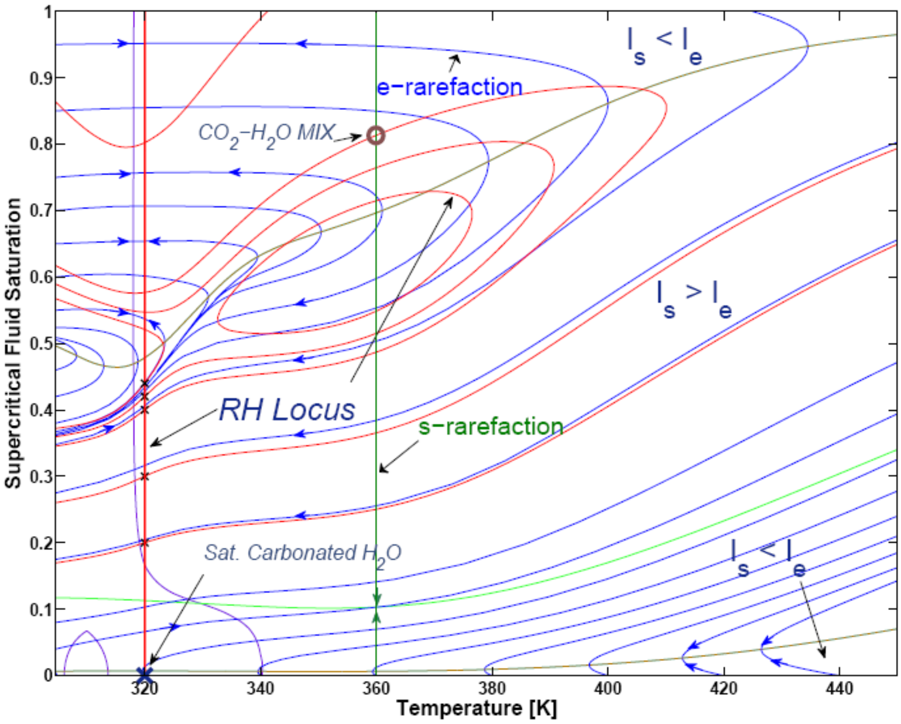

Figure 2. Example: Injection problem and *RH Locus*.

4. Appendix: Quick Thermo Calculations

In order to derive straightforward methods for calculating approximations for the thermodynamical equilibrium of the CO_2-H_2O system at supercritical conditions we can use basic thermodynamical principles such as Henry's Law, Raoult's Law, and Clausius-Clapeyron's Law. For calculating *P-V-T* values of the system, we choose the polar version of the Soave-Redlich-Kwong equation, proposed by Sandarusi et. al. (1986), which takes into account the binary interaction parameters between carbon dioxide and water, which is appropriate for supercritical conditions, even for two or more component mixtures. Assumptions such as ideal mixing rules (i.e., volume conservation principles) may be used as simplifying assumptions.

The method described below provides the base-data for studying the structure of analytical solutions of mixed CO_2-H_2O injection in porous media. Changes in the numerical values of high pressure phase equilibrium may affect quantitatively rather than qualitatively the Wave-Curve Method used in this paper for finding the dynamics of the compositional flow.

4.1. Brief Description of the Method

Raoult's Law is a relationship between the pure vapor pressure of water P_{gW} [Pa], and its partial vapor pressure P_{gw} in the gaseous phase

$$P_{gw} = x_w \, P_{gW} \tag{4.1.1}$$

where x_w denotes the molar fraction of water in the aqueous phase. In order to find the value of the pure vapor pressure we use the well known Clausius-Clapeyron's Law. Henry's Law is used for finding the concentration of a gas, (e.g. carbon dioxide), dissolved in the liquid in thermodynamical equilibrium, from its partial pressure in the gaseous phase

$$P_{gc} = y_c P_{res} = \frac{\rho_{ac}}{M_c} k_c^{T_{res}} \tag{4.1.2}$$

where the terms ρ_{ac} , M_c correspond to the concentration of carbon in the aqueous phase [kg/m^3], and the molar weight of carbon, respectively. Henry's coefficient of carbon dioxide at reservoir temperature $k_c^{T_{res}}$ $[m^3 Pa/mol]$, is temperature-dependent and has been corrected from its original value given at standard temperature 298.15 [K]. We assume ideal volume mixing rules for the aqueous phase

$$\frac{\rho_{ac}}{\rho_{aC}} + \frac{\rho_{aw}}{\rho_W} = 1 \tag{4.1.3}$$

$$\rho_{ac} + \rho_{aw} = \rho_a \tag{4.1.4}$$

where ρ_{ac} and ρ_{aw} are the partial densities of CO_2 and H_2O respectively in the aqueous phase. The empirically introduced variable ρ_{aC} represents the density of *pure* dissolved carbon dioxide as present in a real aqueous mixture. The density of the aqueous phase ρ_a, can be found using the *MSRK Equations of State EOS*, proposed by Sandarusi, et. al. (1986), using the mixing assumption $x_c \ll 1$. Alternatively, we can find ρ_a by extrapolating experimental values found in the extense compilation of Gmelin (compiled from 1924 to 1998). This is done via orthogonal regressions. By simple physical proportions it is easy to verify that

$$x_c = \frac{M_W \rho_{ac}}{M_W \rho_{ac} + M_C \rho_{aw}} \tag{4.1.5}$$

where x_c is the molar fraction of carbon dioxide in the aqueous phase. The sum of the partial vapor pressures in the supercritical fluid phase (which is treated as a gaseous phase) $P_{\sigma c}$ and the aqueous phase $P_{\sigma w}$ are equal to the reservoir pressure P_{res}. At this point we stress the fact that we use as a poor approximation Henry's Law as well for a supercritical fluid phase, i.e., in various instances we imply we approximate $P_{\sigma i}$ with P_{gi} where the subindex i represents either carbon or water. Using equations (4.1.3), (4.1.4) and (4.1.5), after some calculations we obtain the non-linear system for the unknowns ρ_{ac} and ρ_{aC}

$$a\rho_{ac}^2 - b\rho_{ac} + c = 0 \tag{4.1.6}$$

$$\rho_{aC} = \rho_W \left(\frac{\rho_{ac}}{\rho_{ac} + \rho_W - \rho_a}\right) \tag{4.1.7}$$

where the coefficients of the quadratic equation (4.1.6) are given by

$$a = \frac{k_c^{res}}{M_C}\left(M_W \rho_{aC} - M_C \rho_W\right) \tag{4.1.8}$$

$$\mathrm{b} = \left(P_{gW} M_C \rho_W - k_c^{res} \rho_{aC} \rho_W + P_{res}\left(M_W \rho_{aC} - M_C \rho_W\right)\right) \tag{4.1.9}$$

$$\mathrm{c} = \left(P_{gW} - P_{res}\right) M_C \rho_{aC} \rho_W \tag{4.1.10}$$

We solve the system of nonlinear equations (4.1.6) and (4.1.7) using Matlab *fsolve* function, in the unknowns ρ_{ac} and ρ_{aC}. Using equation (4.1.5) we find x_c and x_w. From basic principles we proceed to calculate the remaining unknowns. From the mixing rule (4.1.4) we calculate ρ_{aw}. We use Henry's Law (4.1.2) to approximate $P_{\sigma w}$.

We calculate the concentrations of carbon dioxide and water in the supercritical fluid phase $\rho_{\sigma c}$ and $\rho_{\sigma w}$ in a three step procedure. First, from (4.1.2) we can find the molar fractions of carbon dioxide and water in the aqueous phase y_c and y_w. Second, from the *MSRK EOS* we can find the molar volume v_σ $[m^3/mol]$ of the supercritical fluid, and subsequently the phase density ρ_σ . Using basic physical relationships we can show that

$$\rho_{\sigma c} = \frac{\rho_{\sigma}}{1+\frac{M_W}{M_C}\left(\frac{y_W}{1-y_W}\right)} \tag{4.1.11}$$

Using Eq. (4.1.11) we proceed to find $\rho_{\sigma c}$ and using a mixing rule for the gaseous phase we find $\rho_{\sigma w}$. The pure supercritical carbon density $\rho_{\sigma C}$ can also be found using the *MSRK EOS* in order to find the corresponding molar volume $v_{\sigma C}$. The mutual solubilities of CO_2 and H_2O in the aqueous and supercritical fluid phase, x_c and y_w found by the means of the *Quick Method* for an overall pressure of $P = 10.09$ MPa., are compared in Fig. 3 with the experimental values given by King et. al. (1992) (taken at $P = 10.13$ MPa) and Bamberger et.al. (2000) (taken at the same pressure of the *QM*). Unfortunately, the error is big at high pressures.

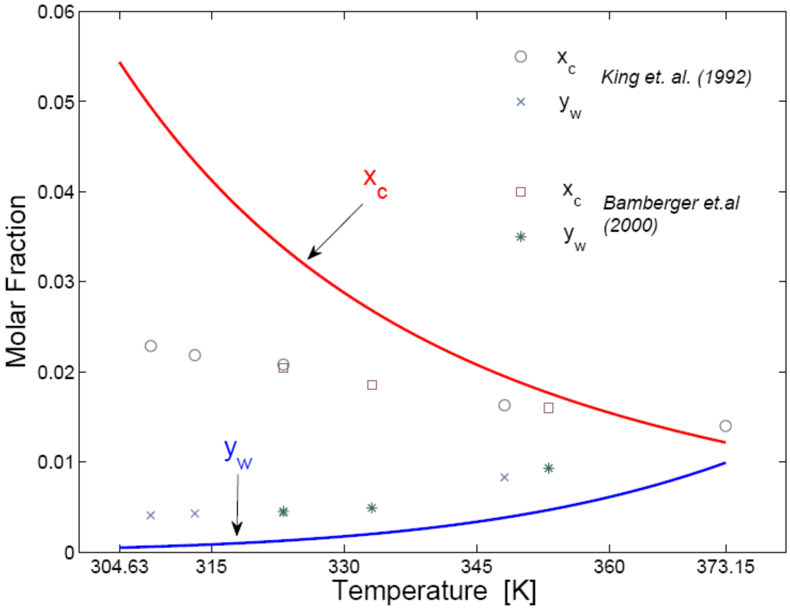

Figure 3. Comparison of the Quick Method with experimental values.

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6. References

AZEVEDO, A., DE SOUZA, A., FURTADO, F., MARCHESIN, D. PLOHR, B. *The Solution by the Wave Curve Method of Three-Phase Flow in Virgin Reservoirs*, Transport in Porous Media, Published Online June 2009.

BUCKLEY S.E., LEVERETT M.C., *Mechanism of Fluid Displacement in Sands.* Petroleum Transactions, AIME, Vol.146, pg.107-116, 1942. SPE

Gmelin Institute for Inorganic Chemistry of the Max-Planck-Society for the Advancement of Science, Founded by L.Gmelin. *Handbook of Inorganic and Organometallic Chemistry*, Springer-Verlag 8th Edition.

ISAACSON, E., MARCHESIN, D., PLOHR, B. *Transitional Waves for Conservation Laws*, Siam J. Math. Anal. Vol. 21, No.4, pp. 837-866, July 1990.

ISAACSON, E., MARCHESIN, D., PLOHR, B., TEMPLE, J.B. *Multiphase flow models with singular Riemann problems,* Mat. Apl. Comput. 11 (2) 147-166 (1992).

KING M.B., MUBARAK A., KIM J.D. AND BOTT T.R. *The mutual solubilities of water with supercritical and liquid carbon dioxide,* J. Supercrit. Fluids 5, pp. 296-302 (1992).

LAMBERT, W. MARCHESIN, D., *The Riemann problem for compositional flows in porous media with mass transfer between phases*, Journal of Hyperbolic Differential Equations, Vol 6, No.4 p. 725-751, (2009).

LEVEQUE, R.J. *Finite Volume Methods for Hyperbolic Problems* Cambridge Texts in Applied Mathematics, (2002).

BAMBERGER, A., SIEDER, G., MAURER, G., *High-pressure (vapor liquid) equilibrium in binary mixtures of (carbon dioxide or acetic acid) at temperatures from 313 to 353 K.* J. Supercritical Fluids, 17, (2000), pp. 97-100.

REINSCH, C., *Smoothing by Spline Functions,* Numerische Mathematik 10, pp. 177-183, (1967).

SALIMI, H., BRUINING, H., *Upscaling in Vertically Fractured Oil Reservoirs Using Homogenization.* Transport in Porous Media, Published online 22 Oct. 2009

SANDARUSI J.A. YESAVAGE V.F., *Compilation of parameters for a polar fluid Soave-Redlich-Kwong equation of state*. *Ind. Eng. Chem. Process Des. Dev.,* 25 (4) (1986), pp. 957-963.