

# The effect of carbon dioxide in oil recovery from calcite reservoirs. Part I.\*

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# 1 Introduction

A large portion of the world's hydrocarbon reserves is in carbonate reservoirs. Such reservoirs may be fractured and the wetting properties are often oil-to-mixed wet. These two characteristics usually result in low hydrocarbon recovery rates. Indeed, the current production of oil occurs under increasingly difficult conditions; for example, oil recovered from deep deposits with high pressure and temperature conditions. Recovery methods for fractured reservoirs comprise [63] [64] supercritical gas injection, thermal methods [93] [106] [35] [104] and polymer [97] water injection. Our interest is in the injection of water with dissolved minerals into calcite reservoir. The application that we have in mind is in recovery from the presal formation [30], (Campos, Baumgartner et al. 2010), the deep "pre-salt discovery, which extends over 800 km off the Brazilian coast, from the state of Espírito Santo to Santa Catarina, below a thick salt layer that covers the sedimentary basins. The deposits consist of an aggregation of oil reservoirs that each contain of the order of ten billion barrels of oil in place. The reservoirs lie below a water depth of more than 2,000 m, a layer of sand sediment of 1,000 m and a layer of salt of 2,000 m. For example the oil in the Tupi basin has to be extracted from a depth of 5,000 to 7,000 m below sea surface. The high pressures ( $\sim 700$  bars) make these reservoirs excellent candidates for high pressure miscible gas injection, e.g.,  $\text{CO}_2$  injection or carbonated water injection.

Recently much research has been done on low salinity water injection [6] [9] [54] [59] [89] [90] [98] [114] [113] [115] [110] and there is an increased interest in the effect of dissolved minerals on oil recovery. For example, the presence of sulfate ions, which are naturally present in sea water can improve the oil recovery by 5-18% [36], but the effect of sulfate [100] depends on the chalk type and on the wettability of the rock [38]. There is a vast literature on low salinity injection in oil reservoirs and we refer the interested reader to the overview paper by Morrow and Buckley [69] [70] as a starting point.

There is also an increasing interest in the effect of injection of water minerals on the recovery efficiency [98]. Mixed-wet or weakly water-wet are often considered as optimum wetting conditions for oil recovery [50] [70]. The theory of wetting behavior is clearly explained in [48]. Contrary to sandstones, the majority of carbonate petroleum reservoirs are oil-wet [119]. The presence of asphaltenes [16] [17] [18] and their adsorption on kaolinite can render even a sandstone reservoir oil-wet [24]. The presence of a water film on the mineral surface may reduce the asphaltene adsorption [27], and induce more water-wet behavior. The presence of carboxylic acids [40] [41] [81] and amines in the oil determines the acid and base number [26]. Carboxylic acids and amines bind with other ions in the solution to form charged surface complexes, which determine the average charge on the oil. Brady and Krumhansl [13], [12]. point out that reservoirs with a

stable water film between the calcite and the oil are likely to have a favorable recovery.

In this paper our interest is in the effect of minerals on the carbon dioxide concentration. We leave the effect of surface complexes and relative permeability change for future work. The dissolution of carbon dioxide in the oleic phase depends on the mineral content and can in itself reduce the amount of oil left behind and thus increase the recovery of oil.

The calculation of the concentration of carbon dioxide requires the determination of the activity coefficients of all chemical species in the aqueous phase, which thus determine the ratio of carbon dioxide dissolved in the aqueous phase and the carbon dioxide in the oleic phase. To simplify the calculations we assume that no oil (decane) dissolves in the aqueous phase and vice versa. For the equilibrium calculations we use as an intermediate step that we consider the equilibrium between the liquid (aqueous or oleic phase) and the gas phase. We ignore the presence of decane and water in the gaseous phase. Carbon dioxide concentrations in the oleic phase and aqueous phase for the same pressure are also in equilibrium with each other. For the equilibrium in the aqueous phase with gaseous phase we can use a modified Henry's law, i.e., with corrections for non-ideal behavior. For the carbon dioxide equilibrium in the oleic phase and gaseous phase we need more sophisticated models as the carbon dioxide concentration can increase to 100%. We compute the decane-carbon dioxide equilibrium, using Racketts model for density calculations, Redlich Kwong EOS, the two suffix Margules rules [82] model for activity coefficients. Some experimental methods are described in [53]. The theory behind the calculations performed in ASPEN are summarized in chapter 8 of [82]. These experimental data can be used in ASPEN plus to obtain an optimal description of the phase behavior [117].

Part of the parameters that determine the activity coefficients for the aqueous solutions (i.e., relations between activities and concentrations) and the concentration-dependent partial molar volumes can be found in [23] [65] [79] [80] [95] [105]. An excellent data-base can be found in [37] and references cited therein (see also. Ananthaswamy and Atkinson [1]. Correct values are required if one extends geochemical behavior to other pressure and temperature regimes [10] [11]. An excellent overview of geochemistry can be found in [2] [56] and [103]. The general geochemical background is well explained in [4] [3] in combination with the accompanying software (PHREEQC) [76] [75] [92]. An overview of existing software for saturated and unsaturated transport problems in groundwater flow can be found in [108]. The solubility of carbon dioxide in electrolyte solutions can be found in [21] [87] [86] [85]. Extending Henry's law [91] requires the pressures to be replaced by fugacities [77] and the mole fractions to be corrected for the activity coefficient [22] [109].

Non-electrolyte solutions depend on the ionic strength as to their solubility [62]. The same coefficients can be used to determine the ionic strength dependence of the partial molar volume [46] [47] [68] [78]. Relevant coefficients can also be found in [75] [76]. Both Helgeson and Parkhurst also give the partial molar volume at infinite dilution; the found parameter values are often more or less equal but there can be a large discrepancy between parameters values found in the literature. Comparison of the parameter values allows the usage of specific data bases [43] [52].

Various aspects that are relevant to oil recovery must be studied with comprehensive modeling, i.e., with a model that describes two-phase flow and dissolution in phases combined with the geochemistry [34]. Noh et al. [73], use fractional flow theory in order to give a mathematical formalism of combined geochemical and multiphase flow. Holstadt [49] gives a general framework for multi-species, multiphase and non-isothermal flow, focusing on chemical reactions and transport. Evje et al. [32] propose a mathematical model for the weakening of chalk reservoirs due to chemical reactions. It consists of convection-diffusion transport coupled to dissolution/precipitation processes. Evje and Hiorth [31], include in their model the rock chemistry and its effect on the wetting state. More precisely they include the fact that the rock surface becomes more water-wet where dissolution of calcite takes place and incorporate it in the relative permeability and capillary pressure behavior. Relative permeabilities depend on the pore size distribution [20]. In another paper [33], Evje and Hiorth use an extended version of the Buckley-Leverett model that is coupled to a system of reaction-diffusion equations.

Mathematical aspects of the model equations in terms of precipitation and dissolution waves provide important insights as to the effect of ions on the recovery of oil [14] [15] [45].

It is the purpose of the paper to provide the complete geochemical background for the modeling of carbonated water and carbon dioxide injection in a calcite reservoir. Section 2 describes a typical model for carbonated low salinity water injection in a calcite reservoir. It includes all equilibrium reactions and constants in the bulk, the formation of surface complexes and cation exchange modeling. Appendix A gives the definitions of activities and the equations for the activity coefficients. It also describes how to convert activities to molalities. Appendix 3 describes the partition of carbon dioxide between the oleic and aqueous phase, using Henry's law. Appendix C gives the data base and procedure to calculate partial molar volumes of the dissolved components in water. The expressions can be used to calculate the density of the solutions. Appendix D gives the Langmuir adsorption isotherms of the surface complexes. Appendix F gives a few basic programs to obtain the limiting expressions for the Debye-Hückel theory as a function of pressure to 1000 bars and temperatures to 200° C. Appendix E derives the charge

balance from mass balance considerations. It contains both an engineering example of this derivation and a general mathematical derivation.

## 2 Model description

We consider a calcite rock filled with an oleic phase that contains both oil and dissolved carbon dioxide as well as an aqueous phase with dissolved solutes like ions, minerals and carbon dioxide. The oil consists of an alkane (e.g., decane). We assume that all species are in chemical equilibrium in both phases. Carbon dioxide can be present both in the oleic phase and the aqueous phase. Calcium carbonate can occur both in the aqueous phase and in the solid phase. All other minerals and ionic species only occur in the aqueous phase. Dissolution of decane in the aqueous phase is disregarded. Initially, the pores of the rock are filled with the oleic phase and an aqueous phase with a range of pH values, sodium chloride concentrations and other minerals. The injected fluid has also a high carbon dioxide content, which is determined by the pH values and sodium chloride concentration. Our main interest is the oil recovery ensuing from these injection conditions. The flow is governed by Darcy's law and conservation laws for chemical species. For simplicity we consider one dimensional incompressible flow.

### 2.1 Gibbs phase rule

Before stating the governing equations, we apply Gibbs rule to determine the number of chemical degrees of freedom. Gibbs phase rule states (see, e.g., [66]) that the number of degrees of freedom is given by

$$N_f = N_s - N_r - N_c + 2 - p, \quad (1)$$

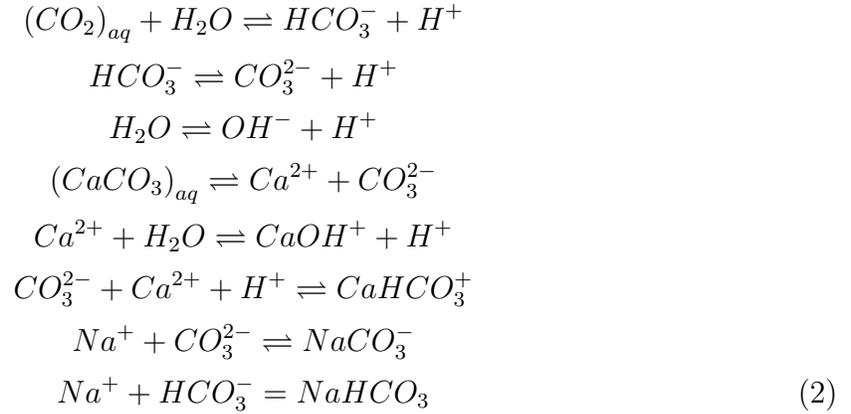
where  $N_s$  is the number of different chemical species,  $N_r$  is the number of possible equilibrium reactions (in the aqueous phase),  $N_c$  is the number of constraints, e.g., the charge balance. We call the charge balance a constraint as opposed to a mass balance equation, which involves accumulation, convection and diffusion terms; it can be stated as an algebraic equation satisfied everywhere. The number 2 represents the temperature and pressure and  $p$  the number of phases. Hence there are  $p$  equations of state (EOS).

As there is some judgment in enumerating the relevant aqueous species; we follow Appelo and Parkhurst [75] and [3] and use the geochemistry program PHREEQC to analyze phenomena in the aqueous phase. PHREEQC makes a choice to disregard certain components, of which the concentration is negligible when we add water,  $CaCO_3$  (*solid*) and  $NaCl$ . The programme tells us that there are fifteen different relevant chemical species, ( $N_s = 15$ ), twelve that occur only in the aqueous phase, one, i.e. carbon dioxide, that occurs both in the aqueous phase and one, alkane, that occurs only in the oleic phase. Calcium carbonate occurs both in the solid phase and in the aqueous phase. The

species that occur in the aqueous phase have fourteen concentrations denoted by  $c_{a,i}$  where  $i = CO_2, CO_3^{2-}, HCO_3^-, CaHCO_3^+, CaCO_3, NaCO_3^-, NaHCO_3, H_2O, H^+, OH^-, CaOH^+, Ca^{2+}, Cl^-, Na^+$ . The concentration of carbon dioxide in the oleic phase is denoted by  $c_{o,CO_2}$ . The concentration of alkane ( $A$ ) in the oleic phase is denoted by  $c_{o,A}$  in the oleic phase. The concentration of  $CaCO_3$  in the solid phase is denoted by  $c_{r,CaCO_3}$ , which is constant.

## 2.2 Equilibrium concentrations in the aqueous phase

We consider the following eight ( $N_r = 8$ ) equilibrium reactions in the aqueous phase [55], [75].



We dropped the subscript ( $aq$ ) on all compounds except for  $CaCO_3$  and  $CO_2$  as we assume that all other compounds only occur in the aqueous phase. All possible equilibrium reactions can be found by linear combinations of these eight equilibrium equations. The equilibrium constants are expressed in activities for which the reference state is an ideal solution with concentration of one molal. So the molal concentration is given by the activities divided by the activity coefficients (see Appendix A).

Thermodynamic equilibrium between phases requires that the chemical potential of  $(CaCO_3)_r$  in the solid phase is equal to the chemical potential of  $(CaCO_3)_{aq}$  in the aqueous phase. This can be represented as

$$(CaCO_3)_r \rightleftharpoons (CaCO_3)_{aq}. \tag{3}$$

In the same way the chemical potential of carbon dioxide in the aqueous phase is equal to the chemical potential in the oleic phase. This can be represented as

$$(CO_2)_o \rightleftharpoons (CO_2)_{aq}. \tag{4}$$

As we consider a solid, an aqueous and an oleic phase, the number of phases is  $p = 3$ .

There is one ( $N_c = 1$ ) constraint, viz., the charge balance equation, which can be written as

$$\left( \begin{array}{l} 2m_{a,CO_3^{2-}} + m_{a,HCO_3^-} + m_{a,OH^-} + m_{a,NaCO_3^-} + m_{a,Cl^-} \\ = 2m_{a,Ca^{2+}} + m_{a,H^+} + m_{a,Ca(HCO_3)^+} + m_{a,Na^+} + m_{a,CaOH^+} \end{array} \right), \quad (5)$$

The molal concentrations can be converted to molar concentrations as explained in Eq. (91) in Appendix A. Such conversions couple each concentration to all others.

The charge balance equation can be derived from the mass balance equations (see Appendix E). We are therefore allowed to replace one balance equation by the charge balance equation. Note that the charge balance equation is an algebraic equation. Alternatively, we can combine the hydrogen and oxygen balance equations into a single equation, in such a way that the water concentration is eliminated, and use the charge balance equation (5) together with the combination of the hydrogen and oxygen balance equation to complete the system of equations. This replacement is considered to be helpful to enhance stability as the water concentration ( $\sim 55.5$  mole/liter) is much higher than the other concentrations, causing numerical problems in simulations.

### 3 Partition of carbon dioxide into the aqueous and oleic phases

By comparing the Henry coefficient of carbon dioxide between the oleic phase and the gas phase to the Henry coefficient between the aqueous and the gas phase it is possible to derive the equilibrium of carbon dioxide between an oleic phase and the aqueous phase.

Extended Henry's law, where the pressure is replaced by the fugacity and the concentration by the activity, describes the ratio between the activity of carbon dioxide in the gas phase and the activity in the liquid (o/w) phase. We obtain for the aqueous phase

$$H_{w-g}^H = a_{g,CO_2}/a_{w,CO_2} = f_{g,CO_2}/(x_{a,CO_2}\gamma_{a,CO_2}), \quad (6)$$

where  $x_{a,CO_2}$  is the mole fraction of carbon dioxide in the water phase,  $\gamma_{a,CO_2(aq)}$  the activity coefficient, and  $f_{CO_2(g)}$  is the fugacity of carbon dioxide in the gas phase. Henry coefficients as a function of temperature are tabulated in [91], [118]. The Henry's law reads  $P = kx$ , with  $P$  the pressure and  $x$  the mole fraction. They give for the inverse

Henry constant  $k_H$  [ $mole/atm$ ], where  $k_H = c_a/P$ ,

$$\ln k_H/k_H^0 = -\frac{\Delta H_w}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right),$$

where for carbon dioxide dissolution in water we have  $k_H^0 = 34$  [ $mole/m^3/atm$ ] at temperature  $T_0 = 298.15$  [ $K$ ] and  $\Delta H_w/R = 2400$  [ $K$ ] with  $R$  denoting the gas constant. The positive value arises as the inverse Henry theory gives the conversion of the dissolved phase to the gas phase and this reaction is endothermic. Conversion of  $k_H$  to  $H_{w-g}^H$  uses the equation  $H_{w-g}^H = (\rho_w/M_w)/k_H$  and

$$\ln H_{w-g}^H/H_{w-g}^{H,0} = \frac{\Delta H_w}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right), \quad (7)$$

and  $H_{w-g}^{H,0} = (\rho_w/M_w)$  [ $mole/m^3$ ] / 34 [ $atm/(mole/m^3) = atm$ ]. Indeed, the density of

water  $\rho_w$  is expressed in [ $kg/m^3$ ] and  $M_w$  is the molar weight expressed in [ $kg/mole$ ]. At low pressures the fugacity is equal to the pressure and this allows us to determine  $H_{w-g}^H$  at low pressures. However, at high pressure we use the same value of the Henry coefficient, but it is now given by Eq. (6). The calculation of activity coefficients of neutral molecules ( $CO_2$  (aq),  $SiO_2$  (aq),  $H_2S$ (aq)) is usually much simpler than the calculation of activity coefficients of ions [2], [87]. To obtain an approximate value of the activity coefficient  $\gamma_{a,CO_2}$  in electrolyte solutions we use the Setchénov coefficient

$k_S > 0$  [88] [87] [86] [85], with  $\gamma_{a,CO_2} = \exp(k_S\mu)$ , where  $\mu = \frac{1}{2} \sum_{i=1}^N c_j Z_j^2$  is the ionic

strength, with the consequence that the mole fraction of carbon dioxide decreases for increasing salt concentration (salting out effect). Here  $c_j$  denotes the molar concentration of component  $i$ . For single salt solutions, values can be found in [102]. Byrne et al. [21] use a more general equation, which takes into account the ionic species dependence

$$\log \gamma_{a,CO_2} = \sum_i k_{Si} \mu_i := \mu k_S, \quad (8)$$

where  $k_{Si}$  are the Setchénov coefficients contribution of a certain neutral species  $S$  due to ionic component  $i$  and  $\mu_i$  is the contribution of ions  $i$  to the ionic strength. This procedure is implemented in PHREEQC [75]. However, to add the individual values is cumbersome and we can approximate the values using that  $k_S = 0.1$  ([62]) ([101]), even if these values can vary, admitting that it is an approximation.

In the same way we can also relate the equilibrium of carbon dioxide in the gas phase [116] [71] and oleic phase by (see chapter 8 of [82])

$$H_{o-g}^H = a_{g,CO_2}/a_{o,CO_2} = f_{g,CO_2}/(x_{o,CO_2}\gamma_{o,CO_2}). \quad (9)$$

We ignore the pressure dependence in the liquid phase of the Henry coefficient, i.e., and in this case the Krichevsky-Ilinskaya equation [82] becomes equivalent to Eq. (9). Indeed, we verified that the pressure correction can be disregarded. Using literature data of the carbon dioxide-decane equilibrium [72] For the activity coefficient we use the one parameter (A) twosuffix Margules equation [82]

$$\ln \gamma_{o,CO_2} = \frac{A}{RT} (1 - x_{o,CO_2})^2. \quad (10)$$

The word two-suffix indicates that the excess free energy is quadratic. The value of  $\dot{A}$  and the Henry coefficient are obtained by substituting experimental data into Eq. (9) and Eq. (10) and we obtain

$$\ln H_{o-g}^H/H_{o-g}^{H,0} = \frac{\Delta H_o}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right), \quad (11)$$

We obtain that  $H_{o-g}^{H,0} = \exp(16.31) [Pa]=119.54[atm]$  at temperature  $T_0 = 344.3 [K]$  and  $\Delta H_o/RT = 770.2$ . The coefficient  $A = 1870 [J/mol]$  at  $344.3 [K]$ . This can be compared with the value  $109.38 [atm]$  found in [112].

Therefore the ratio of the Henry coefficients give the ratio of the molalities

$$\frac{H_{w-g}^H}{H_{o-g}^H} = \frac{f_{g,CO_2}/(x_{a,CO_2}\gamma_{a,CO_2})}{f_{g,CO_2}/(x_{o,CO_2}\gamma_{o,CO_2})} = \frac{x_{o,CO_2}\gamma_{o,CO_2}}{x_{a,CO_2}\gamma_{a,CO_2}} \quad (12)$$

No salt dissolves in the oleic phase.

### 3.1 Density of mixtures

### 3.2 Water density

The volume of a solution is given in terms of the molar composition  $n_i$  by

$$V = \sum_{i=1}^N \bar{V}_i n_i, \quad (13)$$

where the partial molar volumes are defined by

$$\bar{V}_i = \left( \frac{\partial V}{\partial n_i} \right)_{n_{j \neq i}, T, P}. \quad (14)$$

This leads to the equation of state

$$\sum_{i=1}^N \bar{V}_i c_i = \sum_{i=1}^N \bar{V}_i \bar{\rho}_w x_i = 1, \quad (15)$$

where  $c_i$  is the concentration and  $\bar{\rho}_w$  is the molar density of water. It follows that the molar density of water is given by

$$\bar{\rho}_w = \frac{1}{\sum_{i=1}^N \bar{V}_i x_i} \quad (16)$$

PHREEQC gives the partial molar volumes at infinite dilution by

$$\bar{V}_{i,\text{inf}} = 41.84 \left( a_1/10 + \frac{100a_2}{2600 + P_b} + \frac{a_3}{T_K - 228} + \frac{10000a_4}{(2600 + P_b)(T_K - 228)} - WQ_{Born} \right), \quad (17)$$

where  $Q_{Born} = -\partial_P (1/\varepsilon_r) = 0.615\text{e-}06(\text{/bar})$ . The coefficient  $\varepsilon_r$  refers to the dielectric coefficient of the pure water phase. The reason to cast this equation in this form is that the coefficients  $a_1, a_2, a_3, a_4, W$  depend on the component  $i$  can be found in the literature. The constants are such that the term in brackets is in  $\text{cal/mol/bar}$ , with pressures  $P_b$  in bar and temperature  $T_K$  in Kelvin. The values of the constants  $a_1, a_2, a_3, a_4, W, \mathring{a}$  i1, i2, i3, i4 are  $a_1 = 8.615, a_2 = 0, a_3 = -12.21, a_4 = 0, W = 0, \mathring{a} = 1.667, i_1 = 0, i_2 = 264, i_3 = 0$  and  $i_4 = 1$  for the reaction  $\text{CO}_3^{2-} + \text{H}^+ \rightarrow \text{HCO}_3^-$ . Using the factor 41.84, leads to a volume  $\bar{V}_{i,\text{inf}}$  of  $\text{cm}^3/\text{mol}$ ., where we recall that the factor 4.184 converts calorie to Joule.

The volume in a salt mixture with ionic strength  $\mu$  is given by [10] [47] [52] [105] [92] [80] [79] [67] [68] is split in a ionic species dependent term  $\bar{V}_{i,\text{inf}}$  and a correction due to its presence in a solution of ionic strength  $\mu$

$$\bar{V}_i - \bar{V}_{i,\text{inf}} = \frac{\psi_i A_V \sqrt{\mu}}{\Lambda} + \frac{\psi_i A_\gamma \mathring{a} B_V \mu}{\Lambda^2} + \frac{\nu_i b_{V,i} \mu}{2}, \quad (18)$$

where alternatively to Eq. (18) we can also write

$$\bar{V}_i = \bar{V}_{i,\text{inf}} + \frac{1}{2} z_i^2 A_V \frac{\sqrt{\mu}}{1 + \mathring{a} B_\gamma \sqrt{\mu}} + \beta_i \mu^{i_4}, \quad (19)$$

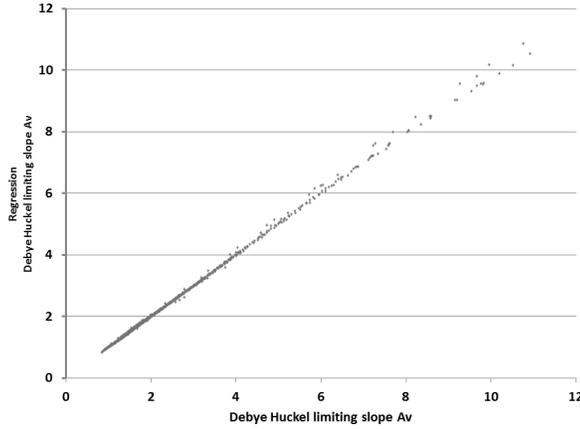


Figure 1: The Debye Huckel parameter  $(-1.63521E - 15T^3 + 1.66821E - 12T^2 - 0.00000000587862T + 0.0000000664581)P^3 + (9.26251E - 13T^3 - 9.12623E - 10T^2 + 0.000000341581T - 0.00004174)P^2 + (5.53046E - 11T^3 - 1.01197E - 7T^2 + 0.000023077T - 0.001447951)P + (-0.0000000716544T^3 + 0.0000929356T^2 - 0.027716004T + 2.530009631)$ . Comparison between observed and regression values.

where  $\beta_i = i_1 + i_2/(T_K - 228) + i_3(T_K - 228)$ . The various alternatives for  $i_1, i_2$  and  $i_3$  are useful because literature data are presented in various forms. The value  $\text{\AA}$  is set to zero for anions in some data sets. Note that some books use  $1/4z_i^2 A_V$ , but we stick to this formulation.

Alternatively Helgeson and Kirkham [46] write

$$\bar{V}_i = \bar{V}_{i,\text{inf}} + \frac{1}{2}\nu z_i^2 A_V \frac{\sqrt{\mu}}{1 + \text{\AA}B_\gamma\sqrt{\mu}} + \frac{1}{2} \frac{\nu z_i^2 A_\gamma \text{\AA} B_V \mu}{(1 + \text{\AA}B_\gamma\sqrt{\mu})^2} + \frac{\nu b_V \mu}{2}, \quad (20)$$

but it becomes nowhere clear what  $b_V$  is. Fortunately in another paper Helgeson and Kirkham write

$$\Lambda = 1 + \text{\AA}B_\gamma\sqrt{\mu} \quad (21)$$

$$\begin{aligned} \bar{V}_i = \bar{V}_{i,\text{inf}} + \frac{1}{2}z_i^2 A_V \frac{\sqrt{\mu}}{1 + \text{\AA}B_\gamma\sqrt{\mu}} - \frac{1}{2} \frac{z_i^2 A_V \sqrt{\mu}}{(\text{\AA}B_\gamma\sqrt{\mu})^3} \left( \Lambda - \frac{1}{\Lambda} - 2 \ln \Lambda \right) \\ + \frac{z_i^2 A_\gamma B_V}{\text{\AA}^3 B_\gamma^4 \mu} \left( \frac{\Lambda^2}{2} - 3\Lambda + \frac{1}{\Lambda} + 3 \ln \Lambda + \frac{3}{2} \right) + \frac{\nu B_V \mu}{4} \end{aligned} \quad (22)$$

where  $\nu$  is the number of moles of ions,

$$B_V = \ln(100)RT\partial_P B_\gamma \text{ and } b_V = \ln(100)RT\partial_P b_\gamma \quad (23)$$

The constant  $A_V$ , the Debye limiting slope, can be expressed as

$$A_V = -\ln(100)RT\partial_P A_\gamma = \ln(10)RTA_\gamma (3\partial_P \log \varepsilon - \kappa_0) \quad [(cm^3/mol)(mol/kg)^{0.5}], \quad (24)$$

where

$$B_\gamma = \left( \frac{8\pi N_A q_e^2 \rho_0}{1000 \varepsilon_r k_B T} \right)^{1/2} = \frac{50.29158649 \rho_0^{1/2}}{(\varepsilon_r T)^{1/2}} \quad (25)$$

where  $N_A$  is the Avogadro number ( $6.225 \times 10^{23}$ ) molecules per mole,  $q_e = 4.803 \times 10^{-10}$  esu (electrostatic unit of charge),  $\rho_0$  is the density of pure water water in  $[g/cm^3]$ ,  $\varepsilon_r$  is the relative dielectric coefficient,  $k_B = 1.38054 \times 10^{-16}$  erg/K is the Boltzmann constant,  $T$  is the temperature in  $K$ ,  $P$  is the pressure in atmosphere. and the compressibility  $\kappa_0 = (atm^{-1})$ . For the definition of  $B$  in Eq. (25) we need to express  $\text{\AA}$  in  $\text{\AA}$ ngstrom.

Moreover we can express the Debye-Hückel parameter for the activity coefficients as [95]

$$A_\gamma = \frac{(2\pi N_A)^{1/2} q_e^3 \sqrt{\rho^0}}{\sqrt{1000} (\varepsilon k_B T)^{3/2}} = \frac{1824829.238 \sqrt{\rho^0}}{(\varepsilon T)^{3/2}} \quad [(mol/kg)^{0.5}] \quad (26)$$

where  $\nu_i$  is the stoichiometric number of moles of ions in one mole of the  $i^{th}$  thermodynamic component of an electrolyte solution. Here  $\Lambda = 1 + \sum_k \nu_k B_\gamma \sqrt{\mu}$ . Furthermore  $\psi_k = Z_k^2/2$  where  $Z_k$  is the charge on the  $k^{th}$  ion.

Table 1: Coefficients in partial molar volume expression

$\bar{V}$	a1(i1)	a2(i2)	a3(i3)	a4(i4)	W	$\bar{a}$ /Ångstrom	$b_i$
Na (A)	1.403(0.162)	-2.285(47.67)	4.419(-3.09e-3)	-2.726(0.725)	-5.125E+5	4.08(1.91)	0.075
Ca	-0.3456 (1.60)	-7.252 (-57.1)	6.149 (-6.12e-3)	-2.479 (1.0)	1.239E+05	5.0(2.87)	0.165
Cl	4.465 (-0.331)	4.801 (20.16)	4.325 (0)	-2.847 (1)	1.75E+05	3.63	0.015
OH	0.126	7.38	1.8423	-2.7821	1.72E+05	3.5	
CO3	(2.8524)(-0.115)	-3.9844 (167)	6.4142 (-0.026)	-2.6143 (1)	3.3914E+05	5.4	0
HCO3 (S&H)	7.5621	1.1505	1.2346	-2.8266	1.2733E+05	5.4	0
CaOH <sup>+</sup>	2.7243	-1.1303	6.1958	-2.7322	0.4496E+05	6	
CaHCO <sub>3</sub> <sup>+</sup>	3.706	1.267	5.252	-2.831	0.308E+05	6	
NaCO <sub>3</sub> <sup>-</sup>	3.99 (2.7)	0(0)	15.3 (0.026)	-8.12 (1)	3.11E+05	5.4	
H <sup>+</sup>	0	0	0	0	0	9.0	
NaHCO <sub>3</sub>	0.51						
H2O	18.07 (cm <sup>3</sup> /mol)						
CO <sub>2</sub>	30.26 (cm <sup>3</sup> /mol)						
CaCO <sub>3</sub>	-14.60 (cm <sup>3</sup> /mol)						
CO <sub>2</sub>	15.2964	-10.0382	-55.4493	7.4092	-0.3107E+5		

The parameters to obtain the partial molar volume are obtained from the data base PHREEQC.DAT and Pitzer.DAT. For the reaction  $aA + bB = cC + dD$ , with  $\Delta v = cV_m(C) + dV_m(D) - aV_m(A) - bV_m(B)$ , where  $V_m(Q)$  denotes the partial molar volume of pure  $Q$  in  $cm^3/mol$ . To account for the pressure dependence of the equilibrium constants we write  $\log K = \log K_0 + \Delta V(P - 1) / (2.3RT)$ , where  $P$  is the pressure in atmosphere,  $R$  is the gas constant in  $[cm^3 atm/mole/K]$ ,  $T$  is the temperature in  $K$ .

Unfortunately the data base of PHREEQC in their data base (e.g., phreeqc.dat) are incorrect as to the calculation of molar volumes. Using data from the papers in Helgeson [47] [46] [52] [95] [105] leads to results that agree within 10% with the calculations using PHREEQC. Hence we assume that we can use the results of PHREEQC to substitute in Eq. (44) to obtain the molar aqueous phase density as the main contribution is from water and the presence of the other ions constitute a correction on this.

### 3.3 Density of oleic phase

The density in the oleic phase is obtained from experimental data of carbon dioxide decane mixtures. We used the data set at  $71,11^\circ C$ , because at that temperature many measurements were obtained and reported in the literature [72]. Near the critical point we used a critical pressure of  $12800 [kPa]$  as opposed to the value  $12740 [kPa]$  chosen by [72] and a value of the critical density  $\rho_c$  of  $568 [kg/m^3]$  instead of the value in of  $590.5 [kg/m^3]$  used in [72]. We note that the authors also modified their measured critical pressure  $P_c$  to  $12740 [kPa]$ , as their measured value  $12760 [kPa]$  was considered not reliable. Using these values we obtain a smooth behavior near the critical point when we use

$$A = \frac{\rho - \rho_c}{(P_c - P)^{0.325}},$$

where  $A$  has a value 20.44 near the critical point. If we denote  $\rho - \rho_c$  by  $y$  and  $(P_c - P)^{0.325}$  by  $x$  and use polynomial regression we obtain

$$y = 6.8416 \times 10^{-5}x^6 - 3.8214 \times 10^{-3}x^5 + 0.082894x^4 - 0.85533x^3 + 3.1352x^2 + 17.120x$$

We used the data set of [72], as it shows less scatter than other data sources and it reports both the compositions and the densities and moreover gives data for a relevant temperature value, i.e.,  $t=71.11^\circ C$ . Unfortunately the dataset of [72] do not show any results for pressures below 63.85 bar. The data presented by other authors are not of sufficient quality. Instead we used the Krichevsky-Ilinskaya equation, which is also quoted in [82] and reads

$$\ln \frac{f}{x_2} = \ln H_{og}^H + \frac{A}{RT} x_1^2 + \frac{v_2^\infty}{RT} (P - P_1^s),$$

where  $P_1^s$  is the vapor pressure of decane, which is much less than the ambient pressures  $P$  and can thus be disregarded. Polling uses for the activity coefficient  $\gamma_{o,CO_2} = A(x_2^2 - 1)/RT$ . The index "2" indicates carbon dioxide and the index "1" indicates decane. The mole fractions are indicated by  $x_i$ . The pressure term is not included in Eq. (9) and is indeed small. The activity coefficient uses the two suffix (having quadratic terms) Margules equation  $\gamma_{o,CO_2} = Ax_1^2/RT$ , where  $A$  is a parameter. The fugacity is obtained from the equation

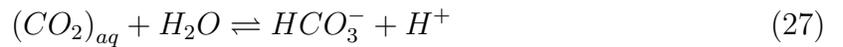
$$\Delta G = RT \ln \frac{f}{p_{ref}} = \int_{p_{ref}}^P V dp,$$

where it is easily verified that for an ideal gas ( $V = RT/P$ ), the fugacity  $f$  is equal to the pressure  $P$ . Also at low pressures the fugacity is equal to the pressure;  $p_{ref}$  is a reference pressure for which this is satisfied. We obtain  $V = ZRT/P$ , where we obtain the compressibility factor  $Z(P, T)$  from the Span-Wagner equation of state [99] and use the integration routine "qtrap" in Numerical Recipes [84], which uses the extended trapezoidal rule. If the integration with twice the number of points gives a difference less than  $\varepsilon = 0.00001$ , the required accuracy is reached. We obtain  $H_{og}^H$  and  $A$ , by minimizing the variance of 18 data points between 63.8 and 117 bar. The standard deviation  $s = 0.026$  being the square root of the variance is for the logarithm of the Henry coefficient ( $\ln H_{og}^H = 16.044$ ). Using this procedure we get a smooth transition between the measured high pressure data and the interpolated low pressure data.

## 4 Ionic Carbon Dioxide-Oil-Water (ICDOW) model

In this section we present a model that focuses on the effects of carbon dioxide without brine. We study the transport of chemical reactions that occur in this process. Also, knowing that the injection of water saturated with carbon dioxide at high pressure and medium temperature improves the efficiency of oil recovery, we will quantify these improvements. For simplicity we consider one dimensional incompressible flow that is governed by balance laws for chemical species and Darcy's law.

We consider the following three ( $N_r = 3$ ) equilibrium reactions in the aqueous phase.





All possible equilibrium reactions can be found by linear combinations of these three equilibrium equations. The equilibrium constants are defined in Eqs. (?? - ??).

The relevant equilibrium constants are given by

$$K_a = \frac{a_{a,HCO_3} a_{a,H}}{a_{a,CO_2} a_{a,H_2O}},$$

$$\log_{10}(K_a) = -356.309 - 0.06092T + 21834.37/T + 126.8339 \log(T)/\log(10) - 1684915/T^2,$$

$$K_b = \frac{a_{a,CO_3} a_{a,H}}{a_{a,HCO_3}},$$

$$\log_{10}(K_b) = -107.8871 - 0.03252849T + 5151.79/T + 38.92561 \log(T)/\log(10) - 563713.9/T^2$$

$$K_w = \frac{a_{a,OH} a_{a,H}}{a_{a,H_2O}},$$

$$\log_{10}(K_w) = 293.29227 + 0.1360833T - 10576.913/T - 123.73158 \frac{\log(T)}{\log(10)} - 6.996455 * 10^{-5} * (T^2).$$

The equilibrium constants are expressed in activities for which the reference state is an ideal solution with concentration of one molal. So the molal concentration is given by the activities divided by the activity coefficients (see Appendix A).

There is one ( $N_c = 1$ ) constraint, viz., the charge balance equation, which can be written as

$$\left( 2m_{a,CO_3^{2-}} + m_{a,HCO_3^-} + m_{a,OH^-} = m_{a,H^+} \right), \quad (30)$$

The molal concentrations can be converted to molar concentrations as explained in Eq. (91) in Appendix A. Such conversions couple each concentration to all others. The number of degrees of freedom (as we disregard surface complexes) is given by

$$N_f = N_s - N_r - N_c + (T, P) - p, \quad (31)$$

There are now six species ( $N_s = 6$ ), viz.  $CO_3^{2-}$ ,  $CO_2$ ,  $OH^-$ ,  $H_2O$ ,  $HCO_3^-$ ,  $H^+$ . There are three equilibrium reactions ( $N_r = 3$ ). There is one constraint, i.e., the charge balance (Eq (30)), i.e.,  $N_c = 1$ . For a given temperature and pressure and considering one phase, i.e.  $p = 1$ , we have  $N_f = 6 - 3 - 1 - 1 = 1$ , thus one degree of freedom for which we

choose  $H^+$ . To obtain the composition one first uses the equilibrium relations Eq. (27), Eq. (28), Eq. (29) and the charge balance equation Eq. (30). Another relationship to be used is the equation of state, which gives the density  $\rho_w$  of the solution as a function of the concentrations. The equation of state is derived using the partial molar volumes. The data base Appelo gives the partial molar volumes of many compounds, and if not the claims to use the method of Millero, which also requires input parameters. Unfortunately these parameters are not explicitly stated in his program.

There are three total balance equations, viz., the total carbon, the total hydrogen and the total oxygen balance. We are using the output by Appelo to obtain the concentrations of  $CO_2$ ,  $HCO_3^-$ ,  $CO_3^{2-}$ ,  $OH^-$ ,  $H_2O$  as a function of the  $H^+$  concentration, using regression on the output data of a compositional simulation. The simulations of the programme by Appelo and Parkhurst satisfy the charge balance. It can also be shown that the charge balance is a consequence of the mass balance equations, provided that initial and boundary conditions satisfy the charge balance. Therefore we only need two out of the three balance equations, which we take to be the total carbon and the (oxygen - 2 \* hydrogen). The latter equation eliminates the water from the equation, which would otherwise be the dominating term.

The total moles [*mol*] of carbon per kilogram of water can be expressed in terms of molalities  $m_{a,j}$  as follows

$$m_{a,C(4)} \left[ \frac{mol}{kg \text{ water}} \right] = m_{a,CO_2} + m_{a,CO_3} + m_{a,HCO_3}. \quad (32)$$

In the same way the total moles of hydrogen is given by

$$m_{a,H(1)} = m_{a,HCO_3} + m_{a,H} + m_{a,OH} + 2m_{a,H_2O}. \quad (33)$$

The total moles of oxygen is given by

$$m_{a,O(-2)} = 2m_{a,CO_2} + 3m_{a,CO_3} + 3m_{a,HCO_3} + m_{a,OH} + m_{a,H_2O}. \quad (34)$$

Taking the difference between Eq. (33) minus twice Eq. (34) leads to

$$m_{a,O-H} = m_{a,H} - 4m_{a,CO_2} - 6m_{a,CO_3} - 5m_{a,HCO_3} - m_{a,OH}, \quad (35)$$

an equation from which the water has been eliminated using  $m_{a,O-H} = m_{a,H(1)} - 2m_{a,O(-2)}$

The total molar concentration in the aqueous phase is given by

$$m_{a,tot} = m_{a,CO_2} + m_{a,CO_3} + m_{a,HCO_3} + m_{a,H} + m_{a,OH} + m_{a,H_2O} \quad (36)$$

and we find the aqueous phase mole fractions  $x_i$  as

$$\begin{aligned}
x_{a,C(4)} &= \frac{m_{a,C(4)}}{m_{a,tot}} \\
x_{a,C_{a,H}(1)} &= \frac{m_{a,H(1)}}{m_{a,tot}} \\
x_{a,O(-2)} &= \frac{m_{a,O(-2)}}{m_{a,tot}} \\
x_{a,O-H} &= \frac{m_{a,O-H}}{m_{a,tot}}
\end{aligned} \tag{37}$$

The total molar concentration in the oleic phase is given by

$$\rho_{o,tot} = \rho_{o,CO_2} + \rho_{o,C_{10}H_{22}}, \tag{38}$$

The mole fraction of  $CO_2$  and decane ( $C_{10}H_{22}$ ) is given by

$$\begin{aligned}
x_{o,CO_2} &= \frac{\rho_{o,CO_2}}{\rho_{o,tot}} \\
x_{o,C_{10}H_{22}} &= \frac{\rho_{o,C_{10}H_{22}}}{\rho_{o,tot}}
\end{aligned} \tag{39}$$

All of them will be functions only of  $x_{a,H^+}$ .

## 4.1 Two-phase simple model equations

When we describe the equations in two phase, we include the saturation and add an equation that describes in addition one component oil flow. Moreover we denote the product of the molar density  $\rho_w$  and the mole fractions  $x_{a,i}$  by  $\rho_{a,i}$  and obtain the product of the oil molar density  $\rho_o$  and the mole fractions  $x_{o,i}$  by  $\rho_{o,i}$ . Note that  $\rho_{a,i}$  and  $\rho_{o,i}$  are only dependent of the single degree of freedom of choice, for instance the  $H^+$ .

For the total carbon we have

$$\begin{aligned}
&\partial_t (\varphi S_w \rho_{a,C(4)}) + \partial_t (\varphi S_o \rho_{o,CO_2}) + \partial_x (u f_w \rho_{a,C(4)}) + \partial_x (u f_o \rho_{o,CO_2}) = \\
&\partial_x \varphi D_w S_w \partial_x \rho_{a,C(4)} + \partial_x \varphi D_w S_o \partial_x \rho_{o,CO_2} + \partial_x D_c \rho_{a,C(4)} \cdot \partial_x S_w + \partial_x D_c \rho_{o,CO_2} \cdot \partial_x S_o
\end{aligned} \tag{40}$$

For the total hydrogen we have

$$\partial_t (\varphi S_w \rho_{a,H(1)}) + \partial_x (u f_w \rho_{a,H(1)}) = \partial_x \varphi D_w S_w \partial_x \rho_{a,H(1)} + \partial_x D_c \rho_{a,H(1)} \cdot \partial_x S_w \tag{41}$$

For the total oxygen we have

$$\begin{aligned} & \partial_t (\varphi S_w \rho_{a,O(2)}) + 2\partial_t (\varphi S_o \rho_{o,CO_2}) + \partial_x (u f_w \rho_{a,O(2)}) + \partial_x (u f_o \rho_{o,CO_2}) = \\ & \partial_x \varphi D_w S_w \partial_x \rho_{a,O(2)} + \partial_x D_c \rho_{a,O(2)} \partial_x S_w + 2\partial_x \varphi D_o S_o \partial_x \rho_{a,O(2)} + 2\partial_x D_c \rho_{o,CO_2} \partial_x S_o \end{aligned} \quad (42)$$

For the total organic carbon we have

$$\partial_t (\varphi S_o \rho_{o,C(-4)}) + \partial_x (u f_o \rho_{o,C(-4)}) = \partial_x \varphi D_o S_o \partial_x \rho_{o,C(-4)} + \partial_x D_c \rho_{o,C(-4)} \partial_x S_o \quad (43)$$

Here  $\rho_{w,j}$  and  $\rho_{o,j}$  are the mole fractions times the molar density  $\rho_w$  in the water and  $\rho_o$  oleic phase respectively. The molar density of water is given by

$$\rho_w = \frac{1}{\sum_{i=1}^6 x_i \bar{V}_i}, \quad (44)$$

where  $x_i$  is the mole fraction in the solution of component  $i$ , and  $\bar{V}_i$  is the molar volume of component  $i$ .

$$\bar{V}_{i,\text{inf}} = 41.84 \left( a_1/10 + \frac{100a_2}{2600 + P_b} + \frac{a_3}{T_K - 228} + \frac{10000a_4}{(2600 + P_b)(T_K - 228)} - W Q_{Born} \right), \quad (45)$$

where  $Q_{Born} = -\partial_P (1/\varepsilon_r) = 0.615e-06$  (/bar). The constants are such that the term in brackets is in  $cal/mol/bar$ , with pressures  $P_b$  in bar and temperature  $T_K$  in Kelvin. Using the factor 41.84, leads to a volume  $\bar{V}_{i,\text{inf}}$  of  $cm^3/mol.$ , where we recall that the factor 4.184 converts calorie to Joule. The molar density of the aqueous phase is obtained from symbolic regression (EUREQA)

$$\begin{aligned} \rho_w &= 7.80736561756858 \times 10^{-6} \exp(\sinh(10.0623537260726 + x)) - 29426.3880030756 \\ &\quad - 29481.5059857005 \tanh(1.25155492484017 + x), \\ \rho_o &= 7.25664915670081 \times 10^{-7} \exp(\sinh(10.2710874945997 + x)) \\ &\quad - 353329.945742431 - 4.50333572865423 \times 10^{-5} x - 353385.063109827 \tanh(x), \end{aligned}$$

where  $x = \ln(H^+)$ . For the molar density of the oleic phase we obtain

$$\begin{aligned} \rho_o &= 5.08860409653381 + 0.0012873299795674x + 43541853141.7085/ \\ &\quad (1 + \exp(-3.20371179817114x)), \end{aligned}$$

where again  $x = \ln(H^+)$

The regression expression of the molar concentration of decane is

$$\begin{aligned} \rho_{o,C(-4)} = \rho_o x_{C(-4)} = & 2.52613380627472 \operatorname{erf} c(951.675792766272 \\ & + 132.737013788747x) \operatorname{erf} c(10076103.4203491 \exp(2.5883061564501x \\ & + 1073.23321331289 (2.5883061564501)^x)), \end{aligned}$$

The parameters to obtain the partial molar volume are displayed in the data base PHREEQC.DAT and Pitzer.DAT. For the reaction  $aA + bB = cC + dD$ , with  $\Delta v = cV_m(C) + dV_m(D) - aV_m(A) - bV_m(B)$ , where  $V_m(Q)$  denotes the partial molar volume of pure  $Q$  in  $\text{cm}^3/\text{mol}$ . To account for the pressure dependence of the equilibrium constants we write  $\log k = \log k_0 + \Delta V(P - 1) / (2.3RT)$ , where  $P$  is the pressure in atmosphere,  $R$  is the gas constant in  $[\text{cm}^3 \text{atm}/\text{mole}/\text{K}]$ ,  $T$  is the temperature in  $K$ .

$$\bar{V}_i = \bar{V}_{i,\text{inf}} + \frac{1}{2} z_i^2 A_V \frac{\sqrt{\mu}}{1 + \mathring{a}B_\gamma \sqrt{\mu}} + \beta_i \mu^{i_4}, \quad (46)$$

where  $A_V = 1.927$ ,  $\mathring{a}B_\gamma = 0.3281$  and  $\beta_i = i_1 + i_2 / (T_K - 228) + i_3 (T_K - 228)$ . The value  $\mathring{a}$  is set to zero for anions in some data sets. Note that some books use  $1/4 z_i^2 A_V$ , but we stick to this formulation. Note that the additional contribution of the ionic strength for neutral molecules in this model  $\bar{V}_i - \bar{V}_{i,\text{inf}}$  is zero.

Unfortunately the data base of PHREEQC in their data base (e.g., phreeqc.dat) are incorrect as to the calculation of molar volumes. Using data from the papers in Helgeson leads to results that agree within 10% with the calculations using PHREEQC. Hence we assume that we can use the results of PHREEQC to substitute in Eq. (44) to obtain the molar aqueous phase density as the main contribution is from water and the presence of the other ions constitute a correction on this.

## 4.2 Numerical calculation of terms

The activity coefficients can be given by the Davies equation, which does not depend on any other properties of the ion than its charge

$$\ln \gamma_j(\mu) = -\frac{A_\gamma |z_j|^2 \sqrt{\mu}}{1 + B_\gamma \sqrt{\mu}} + 0.3\mu, \quad (47)$$

where at ambient temperatures  $A_\gamma = 1.1708$  and  $B_\gamma = 0.3281$ . The derivative towards the ionic strength is given by

$$\partial_\mu \ln \gamma_j(\mu) = \frac{-A_\gamma |z_j|^2}{2\sqrt{\mu}(1 + B_\gamma \sqrt{\mu})^2} + 0.3 \quad (48)$$

The ionic strength  $2\mu \approx \sum_i m_i z_i^2 = \sum_i a_i / \gamma_i z_i^2$  and reads

$$2\mu = (4.0 * a_{CO_3} / \gamma_2(\mu) + a_{HCO_3}(a_H, a_{CO_3}, T_{zero}) / \gamma_1(\mu) + a_{OH}(a_H, T_{zero}) / \gamma_1(\mu) + a_H / \gamma_1(\mu)), \quad (49)$$

where  $a_i$  is the activity of component  $i$  and  $\gamma_i$  is the activity coefficient and  $c_i = a_i / \gamma_i$  is the concentration.

Note that the concentrations  $c$  are related to the molalities  $m$  by  $c = \rho_w m$ , where  $\rho_w$  is the density of water. However this water density is always close to one. In high concentration salt solutions this no longer valid. The charge balance equation reads

$$\text{charge} = -2a_{CO_3} / \gamma_2(\mu) - a_{HCO_3}(a_H, a_{CO_3}, T_{zero}) / \gamma_1(\mu) - a_{OH}(a_H, T_{zero}) / \gamma_1(\mu) + a_H / \gamma_1(\mu) = 0. \quad (50)$$

We can, without approximations and using Eqs. (49) and (50), even get the exact expression

$$\mu \gamma_1(\mu) = \frac{3}{2} a_H - \frac{1}{2} (a_{OH} + a_{HCO_3})$$

We can use the charge balance equation to get an explicit expression for  $a_{CO_3}$

For all practical cases the concentration  $c_{CO_3} = a_{CO_3} / \gamma_2(\mu)$  of carbonate is much smaller than the concentration of the hydrogen plus ion. Therefore by adding the equations and observing that the charge is zero we find

$$\mu = a_H / \gamma_1(\mu) \approx m_H$$

and

$$\frac{d\mu}{d[H^+]} = 1.$$

### 4.3 Using equilibrium constants to express results in molalities

$$m_{OH} = \frac{10^{K_{ww}(T)}}{\gamma_1^2(\mu) m_H},$$

where  $m_i$  is the molality of species  $i$ . Note that the concentration  $c_i = \rho_w m_i$ .

$$m_{CO_2} = m_{CO_3} m_H^2 \gamma_2(\mu) \gamma_1^2(\mu) 10^{K_{ab}(T)}$$

where we use that the activity coefficient of carbon dioxide is one, and

$$m_{HCO_3} = m_{CO_3} m_H \gamma_2(\mu) 10^{K_{bb}(T)}$$

The equilibrium coefficients are given as functions of the temperature  $T$  expressed in  $K$  by

$$K_{aa}(T) = -356.309 - 0.06091964T + \frac{21834.37}{T} + 126.8339 \frac{\log(T)}{\log(10)} - \frac{1684915}{T^2}$$

and

$$K_{bb}(T) = 107.8871 + 0.03252849T - \frac{5151.79}{T} - 38.92561 * \frac{\log(T)}{\log(10)} + \frac{563713.9}{T^2}$$

and

$$K_{ab}(T) = 464.1965 + 0.09344813T - \frac{26986.16}{T} - 165.75951 \frac{\log(T)}{\log(10)} + \frac{2248628.9}{T^2}$$

and

$$K_{ww} = 293.29227 + 0.1360833T - \frac{10576.913}{T} - 123.73158 \frac{\log(T)}{\log(10)} + \frac{0.0}{T^2} - 6.996455 \times 10^{-5} T^2$$

We use for the temperature  $100^\circ F = 301.78K = 37.62^\circ C$  because the oil data are given at that temperature and we do not need to

Using the charge balance (Eq. (50)) we can derive an equation for  $a_{CO_3}$ , i.e., ( $a = \gamma c$ )

$$m_{CO_3} = -\frac{1}{2} m_{HCO_3}(m_H, m_{CO_3}, T_{zero}) - \frac{1}{2} m_{OH}(m_H, T_{zero}) + \frac{1}{2} m_H \text{ or}$$

$$m_{CO_3} = -\frac{1}{2} m_{CO_3} m_H \gamma_2(\mu) 10^{K_{bb}(T)} - \frac{1}{2} \frac{10^{K_{ww}(T)}}{\gamma_1^2(\mu) m_H} + \frac{1}{2} m_H$$

$$m_{CO_3} \gamma_2(\mu) \left( 1 + \frac{1}{2} m_H \gamma_2(\mu) 10^{K_{bb}(T)} \right) = -\frac{1}{2} \frac{10^{K_{ww}(T)}}{\gamma_1^2(\mu) m_H} + \frac{1}{2} m_H \text{ or}$$

$$m_{CO_3} = \frac{-\frac{1}{2} \frac{10^{K_{ww}(T)}}{\gamma_1^2(\mu) \gamma_2(\mu) m_H} + \frac{1}{2} \frac{m_H}{\gamma_2(\mu)}}{\left( 1 + \frac{1}{2} m_H \gamma_2(\mu) 10^{K_{bb}(T)} \right)}$$

Hence all the concentrations can be expressed in terms of the hydrogen ion concentration only.

The activity coefficients are given by the Davies expression, i.e.,

$$\ln \gamma_j(\mu) = -\frac{A_\gamma |z_j|^2 \sqrt{\mu}}{1 + B_\gamma \sqrt{\mu}} + 0.3\mu, \quad (51)$$

The mole fraction of carbon dioxide in the aqueous phase is given by

$$x_{a,CO_2} = \frac{m_{CO_2}}{m_{CO_2} + m_H + m_{OH} + m_{HCO_3} + m_{CO_3} + c_{H_2O}}$$

and the molality of water is  $m_{H_2O} = (1000/18.01528) = 55.508$  [mol/kg-water].

The activity of the carbonate ion  $a_{CO_3}$  is given by

$$\begin{aligned} a_{CO_3}/\gamma_2(\mu) &= -\frac{1}{2}a_{HCO_3}(a_H, a_{CO_3}, T_{zero})/\gamma_1(\mu) - \frac{1}{2}a_{OH}(a_H, T_{zero})/\gamma_1(\mu) + \frac{1}{2}a_H/\gamma_1(\mu) \text{ or} \\ a_{CO_3} \left( 1 + \frac{1}{2}a_H 10^{(Kbb(T))} \frac{\gamma_2(\mu)}{\gamma_1(\mu)} \right) &= -\frac{1}{2}10^{Kww(T)} \frac{1}{a_H} \frac{\gamma_2(\mu)}{\gamma_1(\mu)} + \frac{1}{2}a_H \frac{\gamma_2(\mu)}{\gamma_1(\mu)} \text{ or} \\ a_{CO_3} &= \frac{\left( -\frac{1}{2}10^{Kww(T)} \frac{1}{a_H} + \frac{1}{2}a_H \right) \frac{\gamma_2(\mu)}{\gamma_1(\mu)}}{\left( 1 + \frac{1}{2}a_H 10^{(Kbb(T))} \frac{\gamma_2(\mu)}{\gamma_1(\mu)} \right)} \\ c_{CO_3} &= \frac{-\frac{1}{2}10^{Kww(T)} \frac{1}{c_H} \frac{\gamma_2(\mu)}{\gamma_1(\mu)} + \frac{1}{2}c_H}{1 + \frac{1}{2}c_H 10^{(Kbb(T))} \gamma_2(\mu)} \end{aligned}$$

Substitution of the equilibrium expressions leads to

$$a_{CO_3} = \frac{\frac{1}{2}a_H - \frac{1}{2a_H} 10^{(Kww(T))}}{\left( \frac{\gamma_1(\mu)}{\gamma_2(\mu)} + \frac{1}{2}a_H 10^{(-Kbb(T))} \right)}$$

$$\begin{aligned} m_{tot} &= (10^{(Kww(T))}/a_H/\gamma_1(\mu) + 10^{(-Kaa(T)-Kbb(T))}a_{CO_3}a_Ha_H/\gamma_{co2}(\mu) \\ &\quad + a_{CO_3}a_H 10^{(-Kbb(T))}/\gamma_1(\mu) + a_{CO_3}/\gamma_2(\mu) + a_{H_2O} + a_H/\gamma_1(\mu)), \end{aligned} \quad (52)$$

which can be reduced by simplified notation and using that  $\gamma_{co2}(\mu(x)) = 1$ . Also we use that  $T = T_{zero}$ .

For the density mole fraction products we find

$$c_{a,H(1)} = \bar{\rho}_w \left( 10^{(K_{ww}(T))} / a_H / \gamma_1(\mu) + a_{CO_3} a_H 10^{(-K_{bb}(T))} / \gamma_1(\mu) + 2a_{H_2O} + a_H / \gamma_1(\mu(x, y)) \right) / m_{tot}(AH),$$

and

$$c_{a,O(-2)} = \bar{\rho}_w \left( \begin{array}{l} 10^{(K_{ww}(T))} / a_H / \gamma_1(\mu) + 3a_{CO_3} a_H 10^{(-K_{bb}(T))} / \gamma_1(\mu) \\ + 2 \times 10^{(-K_{aa}(T) - K_{bb}(T))} a_{CO_3} a_H a_H / \gamma_{co2}(\mu) \\ + a_{H_2O} + 3a_{CO_3} / \gamma_2(\mu) \end{array} \right) / m_{tot}(AH),$$

It is convenient to subtract the total hydrogen from twice the oxygen and to obtain

#### 4.4 Eliminating $H_2O$

In our ionic model (ICDOW) we employ equations of zero diffusion coefficients. We do so because it is well known that for upscaled equations the convection terms dominate the diffusion terms. The Riemann solution for this model can therefore be applied for upscaled transport processes in enhanced oil recovery involving geochemical aspects.

Leaving out the diffusion terms, we reformulate the system (40)- (43) in three conservation equations, in which we substitute regression expressions that are obtained by geochemical software PHREEQC. To do so, we use that one can verify that the balance equations (40)- (43) imply the charge conservation equation:  $x_{a,CO_3^{2-}} + x_{a,HCO_3^-} + x_{a,OH^-} - x_{a,H^+} = 0$ . We are therefore allowed to replace one balance equation by the charge conservation equation, which is an algebraic equation. Alternatively, we can combine the hydrogen and oxygen balance equations into a single equation, in such a way that the water concentration is eliminated, and use the charge conservation equation together with the combination of the hydrogen and oxygen balance equation to complete the system of equations. This replacement may to enhance stability in numerical simulations as the water concentration ( $\sim 55.5$  mole/liter) is much higher than the other concentrations, causing instability problems in the simulations. Thus, denoting by  $\rho_{a,O-H} = 2\rho_{a,O(2)} - \rho_{a,H(1)}$ , we reduce (40)- (43) without diffusion to a system of three conservation laws for total organic carbon, oxygen plus hydrogen and decane as

$$\partial_t (\varphi s_w \rho_{a,C(4)}) + \partial_x (u f_w \rho_{a,C(4)}) = 0, \quad (53)$$

$$\partial_t (\varphi (s_w \rho_{a,O-H} + 4s_o \rho_{o,CO_2})) + \partial_x (u (f_w \rho_{a,O-H} + 4f_o \rho_{o,CO_2})) = 0, \quad (54)$$

$$\partial_t (\varphi s_o \rho_{o,C(-4)}) + \partial_x (u f_o \rho_{o,C(-4)}) = 0, \quad (55)$$

where the unknowns are the water saturation, the  $y = pH$  and Darcy velocity, i.e.,  $(s_w, y, u)$ . We have that  $\rho_{a,C(4)}$ ,  $\rho_{a,O-H}$ ,  $\rho_{o,C(-4)}$  and  $\rho_{o,CO_2}$  are differentiable positive functions that depend only on the  $pH$ .

## 5 Riemann problem for ICROW model

The system of conservation laws (53)-(55), disregarding diffusion terms can be rewritten as:

$$\frac{\partial G(s_w, y)}{\partial t} + \frac{\partial(u\widehat{F}(s_w, y))}{\partial x} = 0, \quad (56)$$

where the accumulation and flux functions can be rewritten as  $G(s_w, y)$  and  $u\widehat{F}(s_w, y)$ , with

$$(G_1, G_2, G_3)^T = \varphi(s_w \rho_{a,C(4)}, s_w \rho_{a,O-H} + 4s_o \rho_{o,CO_2}, s_o \rho_{o,C(-4)})^T, \quad (57)$$

$$(\widehat{F}_1, \widehat{F}_2, \widehat{F}_3)^T = (f_w \rho_{a,C(4)}, f_w \rho_{a,O-H} + 4f_o \rho_{o,CO_2}, f_o \rho_{o,C(-4)})^T. \quad (58)$$

To simulate the injection of CO<sub>2</sub> in a reservoir, we are interested in solving the Riemann-Goursat problem associated with (56), i.e. the solution of (56) with piecewise constant initial and boundary data

$$\begin{cases} (s_{wl}, y_l, u_l) & \text{if } x = 0, t > 0, \\ (s_{wr}, y_r, \cdot) & \text{if } x > 0, t = 0. \end{cases} \quad (59)$$

We do not impose conditions on the downstream total velocity  $u_r$  because this quantity is obtained from the other variables and the solution of the system. In equation (59) the side  $r$  represents the initial conditions of the reservoir, while the side  $l$  represents the conditions of injection in the reservoir.

The method of characteristics (MOC) is appropriate for seeking analytical solutions of compositional models (see e.g. [111, 28, 25, 44, 83, 51]). The analytical solution is obtained by the concatenation of rarefaction and shock waves satisfying certain admissibility conditions. This method is the primary basis of the Buckley-Leverett theory ([58, 19]), which is the foundation work for Mathematical Modeling of Oil Recovery. In this paper, we obtain the analytic solution in the form of a Riemann solver by employing the Oleinik entropy condition, Liu's and Lax's criteria to ensure the existence of a unique solution of the Riemann-Goursat problem ([57, 74, 42, 60, 61]). In addition, the application of such a method allows to obtain loci in state space where the Riemann solution changes structure, such as the coincidence and inflection loci. These structures are useful both to build the analytical solution, and to determine the bifurcation curves where abrupt changes of the behavior of the solution are expected, which has significance in mathematical modeling of oil recovery. We, also provide the numerical solution by two numerical solvers.

The proposed model taking into account non constant Darcy velocity is important. It can be used for preliminary investigations of the behavior of injection of water of CO<sub>2</sub>

with brine water with two-phase homogeneous systems. The Riemann solver presented can be used to verify numerical solutions for compositional models; moreover the numerical method presented here also verified the accuracy of the Riemann solution. In this solver we described all the low and fast wave paths present in the solution in a unified manner.

## 5.1 Solving the Riemann-Goursat problem by MOC

The basis for MOC for Riemann problems is to assume that the independent variables  $(s_w, y, u)$  are functions of the variable  $\xi = x/t$ , which is possible because the Riemann solution are scale invariant under the map  $(t, x) \rightarrow (\alpha t, \alpha x)$ ; then we can take  $(s_w, y, u)(x, t) = (s_w, y, u)(x(\xi), t(\xi)) = (s_w, y, u)(\xi)$  with characteristic lines  $\xi = x/t$ .

## 5.2 Characteristic analysis

MOC allows to calculate the velocity at which the waves propagate through the porous medium. The basis of the method is to assume that the independent variables  $W = (s_w, y, u)$  are functions of the variable  $\xi = x/t$ . Along the characteristic curves we have

$$dW = \frac{\partial W}{\partial t} dt + \frac{\partial W}{\partial x} dx.$$

Using the system of conservation law (56-58), we obtain along characteristic curves for  $i = 1, 2, 3$

$$\frac{\partial G_i}{\partial W} \frac{dW}{dt} + \frac{\partial F_i}{\partial W} \frac{dW}{dx} = 0, \quad (60)$$

where

$$\frac{\partial G_i}{\partial W} = \frac{\partial G_i}{\partial s_w} \frac{ds_w}{d\xi} + \frac{\partial G_i}{\partial y} \frac{dy}{d\xi} + \frac{\partial G_i}{\partial u} \frac{du}{d\xi}, \quad \frac{\partial F_i}{\partial W} = \frac{\partial F_i}{\partial s_w} \frac{ds_w}{d\xi} + \frac{\partial F_i}{\partial y} \frac{dy}{d\xi} + \frac{\partial F_i}{\partial u} \frac{du}{d\xi}.$$

In matrix format equation (60) can be rewritten as

$$\left( -\xi \frac{\partial G}{\partial W} + \frac{\partial F}{\partial W} \right) \frac{dW}{d\xi} = 0, \quad (61)$$

where  $A = \frac{\partial F}{\partial W}$  and  $B = \frac{\partial G}{\partial W}$  with  $W = (s_w, y, u)$  are obtained as

$$\frac{\partial G}{\partial W} = \begin{pmatrix} \varphi \rho_{a,C(4)} & \varphi^{s_w} \rho'_{a,C(4)} & 0 \\ \varphi \rho_{a,O-H} & \varphi^{s_w} \rho'_{a,O-H} + 4\varphi(1-s_w) \rho'_{o,CO_2} & 0 \\ -\varphi \rho_{o,C(-4)} & \varphi(1-s_w) \rho'_{o,C(-4)} & 0 \end{pmatrix}, \text{ and}$$

$$\begin{aligned}
\frac{\partial F_1}{\partial s_w} &= u \frac{\partial f_w}{\partial s_w} \rho_{a,C(4)}, & \frac{\partial F_1}{\partial y} &= u f_w \rho'_{a,C(4)} + u \rho_{a,C(4)} \frac{\partial f_w}{\partial y}, & \frac{\partial F_1}{\partial u} &= f_w \rho_{a,C(4)}, \\
\frac{\partial F_2}{\partial s_w} &= u \frac{\partial f_w}{\partial s_w} (\rho_{a,O-H} - 4\rho_{o,CO_2}), & \frac{\partial F_2}{\partial u} &= f_w \rho_{a,O-H} + 4(1-f_w) \rho_{o,CO_2}, \\
\frac{\partial F_2}{\partial y} &= u f_w \rho'_{a,O-H} + 4u(1-f_w) \rho'_{o,CO_2} + u(\rho_{a,O-H} - 4\rho_{o,CO_2}) \frac{\partial f_w}{\partial y}, \\
\frac{\partial F_3}{\partial s_w} &= -u \frac{\partial f_w}{\partial s_w} \rho_{o,C(-4)}, & \frac{\partial F_3}{\partial y} &= u(1-f_w) \rho'_{o,C(-4)} - u \rho_{o,C(-4)} \frac{\partial f_w}{\partial y}, \\
\frac{\partial F_3}{\partial u} &= (1-f_w) \rho_{o,C(-4)}.
\end{aligned}$$

Let us denote

$$\rho_1 = \rho_{a,C(4)}, \rho_4 = \rho_{o,C(-4)}, \rho_5 = \rho_{o,CO_2}, \rho_6 = \rho_{a,O-H}, \text{ and}$$

$$\alpha_1 = f_w \rho'_1 + \rho_1 \frac{\partial f_w}{\partial y}, \quad \alpha_2 = s_w \rho'_1, \quad (62)$$

$$\beta_1 = f_w \rho'_6 + 4(1-f) \rho'_5 + (\rho_6 - 4\rho_5) \frac{\partial f_w}{\partial y}, \quad \beta_2 = s_w \rho'_6 + (1-s_w) \rho'_5, \quad (63)$$

$$\theta_1 = (1-f_w) \rho'_4 - \rho_4 \frac{\partial f_w}{\partial y}, \quad \theta_2 = (1-s_w) \rho'_4, \quad \Lambda = \frac{\phi}{u} \lambda. \quad (64)$$

To obtain the eigenvalues of (61), we solve  $\det(A - \lambda B) = 0$ , i.e.,

$$\det \begin{pmatrix} u \left( \frac{\partial f_w}{\partial s_w} - \Lambda \right) \rho_1 & u(\alpha_1 - \Lambda \alpha_2) & f_w \rho_1 \\ u \left( \frac{\partial f_w}{\partial s_w} - \Lambda \right) (\rho_6 - 4\rho_5) & u(\beta_1 - \Lambda \beta_2) & f_w \rho_6 + 4(1-f_w) \rho_5 \\ -u \left( \frac{\partial f_w}{\partial s_w} - \Lambda \right) \rho_4 & u(\theta_1 - \Lambda \theta_2) & (1-f_w) \rho_4 \end{pmatrix} = 0. \quad (65)$$

Substituting in (65), the second row by the sum of the first row multiplied by  $(\rho_6 - 4\rho_5)$  with second row multiplied by  $-\rho_1$ . Similarly, we substitute the third row by the sum of the first row multiplied by  $\rho_4$  with second third row multiplied by  $\rho_1$ . Also, denoting  $\gamma_2 = (\rho_6 - 4\rho_5)$ , we obtain that  $\det(A - \lambda B)$  is

$$u^2 \det \begin{pmatrix} \left( \frac{\partial f_w}{\partial s_w} - \frac{\varphi}{u} \lambda \right) \rho_1 & \left( \alpha_1 - \frac{\varphi}{u} \lambda \alpha_2 \right) & \widehat{F}_1 \\ 0 & \gamma_2 \left( \alpha_1 - \frac{\varphi}{u} \lambda \alpha_2 \right) - \rho_1 \left( \beta_1 - \frac{\varphi}{u} \lambda \beta_2 \right) & \gamma_2 \widehat{F}_1 - \rho_1 \widehat{F}_2 \\ 0 & \rho_1 \left( \alpha_1 - \frac{\varphi}{u} \lambda \alpha_2 \right) + \rho_4 \left( \theta_1 - \frac{\varphi}{u} \lambda \theta_2 \right) & \rho_4 \widehat{F}_1 + \rho_1 \widehat{F}_3 \end{pmatrix} \quad (66)$$

The third column in (66) can be rewritten in terms of

$$\gamma_2 \widehat{F}_1 - \rho_1 \widehat{F}_2 = -4\rho_1 \rho_5, \quad \text{and} \quad \rho_4 \widehat{F}_1 + \rho_1 \widehat{F}_3 = \rho_1 \rho_4.$$

Now, we substitute the second row by the sum of the third row multiplied by  $4\rho_1 \rho_5$  with the second row multiplied by  $\rho_1 \rho_4$  in (66), we obtain that  $\det(A - \lambda B)$  is

$$u^2 \det \begin{pmatrix} \left( \frac{\partial f_w}{\partial s_w} - \frac{\varphi}{u} \lambda \right) \rho_1 & \left( \alpha_1 - \frac{\varphi}{u} \lambda \alpha_2 \right) & \widehat{F}_1 \\ 0 & \gamma_3 & 0 \\ 0 & \rho_4 \left( \alpha_1 - \frac{\varphi}{u} \lambda \alpha_2 \right) + \rho_1 \left( \theta_1 - \frac{\varphi}{u} \lambda \theta_2 \right) & \rho_4 \rho_1 \end{pmatrix}, \quad (67)$$

where

$$\begin{aligned} \gamma_3 = & \rho_1 \rho_4 \left( \gamma_2 \left( \alpha_1 - \frac{\varphi}{u} \lambda \alpha_2 \right) - \rho_1 \left( \beta_1 - \frac{\varphi}{u} \lambda \beta_2 \right) \right) + 4\rho_1 \rho_5 \rho_4 \left( \alpha_1 - \frac{\varphi}{u} \lambda \alpha_2 \right) + \\ & 4\rho_1 \rho_5 \rho_1 \left( \theta_1 - \frac{\varphi}{u} \lambda \theta_2 \right). \end{aligned} \quad (68)$$

Then equation (67) leads to the eigenvalues. One of the eigenvalues satisfies  $\frac{\partial f_w}{\partial s_w} - \frac{\varphi}{u} \lambda = 0$ , which implies that

$$\lambda_{s_w} = \frac{u \partial f_w}{\varphi \partial s_w}.$$

From (68) the second eigenvalue is given by  $\gamma_3 = 0$ . Using (62), (63) and (64), we obtain the second eigenvalue as

$$\begin{aligned} \lambda_H = & -\frac{u}{\varphi} \left( \frac{\rho_1 \gamma_2 \rho_4 \alpha_1 - \rho_1^2 \rho_4 \beta_1 + 4\rho_1 \rho_5 \rho_4 \alpha_1 + 4\rho_1^2 \rho_5 \rho_4' (1 - f_w) - \rho_1^2 \rho_5 \rho_4 (\partial f_w / \partial y)}{-\rho_1 \gamma_2 \rho_4 \alpha_2 + \rho_1^2 \rho_4 \beta_2 - 4\rho_1 \rho_5 \rho_4 \alpha_2 - 4\rho_1^2 \rho_5 \rho_4' (1 - s_w)} \right). \\ \lambda_H = & \frac{u}{\varphi} \left( \frac{-4\rho_1 \rho_4 \rho_5' + 4\rho_1 \rho_5 \rho_4' + (\rho_4 \rho_6 \rho_1' - \rho_1 \rho_4 \rho_6' + 4\rho_1 \rho_4 \rho_5' - 4\rho_1 \rho_5 \rho_4') f_w}{-4\rho_1 \rho_4 \rho_5' + 4\rho_1 \rho_5 \rho_4' + (\rho_4 \rho_6 \rho_1' - \rho_1 \rho_4 \rho_6' + 4\rho_1 \rho_4 \rho_5' - 4\rho_1 \rho_5 \rho_4') s_w} \right). \end{aligned}$$

Using Equations (62) and (63), Equations (5.2) can be rewritten in a more understandable way. Let us introduce

$$\Delta_1 = \rho_4 \rho_6 \rho_1' - \rho_1 \rho_4 \rho_6' + 4\rho_1 \rho_4 \rho_5' - 4\rho_1 \rho_5 \rho_4' \quad \text{and} \quad \Delta_2 = -4\rho_1 \rho_4 \rho_5' + 4\rho_1 \rho_5 \rho_4'. \quad (69)$$

Then we have

$$\lambda_H = \frac{u \Delta_1 f_w + \Delta_2}{\varphi \Delta_1 s_w + \Delta_2}$$

The first eigenvalue is associated to the eigenvector  $\vec{r}_s = (1, 0, 0)^T$  (saturation wave) and the second eigenvector  $\vec{r} = (r_1, r_2, r_3)$  (chemical composition waves) from (61) and (67) for  $\xi = \lambda_H$  and  $dW/d\xi = \vec{r}$  holds

$$u \left( \frac{\partial f_w}{\partial s_s} - \frac{\varphi}{u} \lambda_H \right) \rho_1 r_1 + u \left( \alpha_1 - \frac{\varphi}{u} \lambda_H \alpha_2 \right) r_2 + \widehat{F}_1 r_3 = 0, \quad (70)$$

and

$$\left( u \rho_4 \left( \alpha_1 - \frac{\varphi}{u} \lambda_H \alpha_2 \right) + u \rho_1 \left( \theta_1 - \frac{\varphi}{u} \lambda_H \theta_2 \right) \right) r_2 + \rho_1 \rho_4 r_3 = 0. \quad (71)$$

Taking  $r_3 = u$ , and denoting  $d\rho_1 = \rho'_1/\rho_1$ ,  $d\rho_4 = \rho'_4/\rho_4$  we obtain from (70)-(71) that

$$r_1 = \frac{-f_w - (d\rho_1(f_w - \Lambda_H s_w) + \frac{\partial f_w}{\partial y})r_2}{\left(\frac{\partial f_w}{\partial s_w} - \Lambda_H\right)}, \quad r_2 = -\frac{1}{(f_w - \Lambda_H s_w)(d\rho_1 - d\rho_4) + d\rho_4(1 - \Lambda_H)}. \quad (72)$$

Multiplying  $r_3$ ,  $r_1$  and  $r_2$  in (72), by a product of its denominators  $a$ , we obtain the eigenvector  $r_H = a(r_1, r_2, r_3) = (r_H^1, r_H^2, r_H^3)$

$$r_H^1 = ((-f_w((f_w - \Lambda_H s_w)(d\rho_1 - d\rho_4) + d\rho_4(1 - \Lambda_H))) - d\rho_1(f_w - \Lambda_H s_w) - \frac{\partial f_w}{\partial y}),$$

$$r_H^2 = -\left(\frac{\partial f_w}{\partial s_w} - \Lambda_H\right), \quad r_H^3 = u\left(\frac{\partial f_w}{\partial s_w} - \Lambda_H\right)((f_w - \Lambda_H s_w)(d\rho_1 - d\rho_4) + d\rho_4(1 - \Lambda_H)),$$

where  $\Lambda_H = (\varphi/u)\lambda_H$ .

Eigenvalues and eigenvector, can rewritten in original variable as

$$\lambda_s = \frac{u}{\varphi} \frac{\partial f_w}{\partial s_w}, \quad \text{and} \quad \lambda_H = \frac{u}{\varphi} \frac{\Delta_1 f_w + \Delta_2}{\Delta_1 s_w + \Delta_2}, \quad (73)$$

where

$$\Delta_1 = \rho_{o,C(-4)} \rho_{a,O-H} \rho'_{a,C(4)} - \rho_{a,C(4)} \rho_{o,C(-4)} \rho'_{a,O-H} - \Delta_2, \quad (74)$$

$$\Delta_2 = -4\rho_{a,C(4)} \rho_{o,C(-4)} \rho'_{o,CO_2} + 4\rho_{a,C(4)} \rho_{o,CO_2} \rho'_{o,C(-4)}. \quad (75)$$

Here  $\Delta_i$  with  $i = 1, 2$  depend only on  $y$ . Another solution of (61) is  $\xi$  equal to infinity, which is associated to perturbations of variable  $u$ . The eigenvector of system (61) for  $\xi = \lambda_s$  is  $\vec{r}_{s_w} = (1, 0, 0)^T$  (saturation wave) while the eigenvector for  $\xi = \lambda_H$  is  $\vec{r}_H =$

$(r_H^1, r_H^2, r_H^3)$  (chemical composition wave), i.e.:

$$\begin{aligned} r_H^1 &= ((-f_w((f_w - \Lambda_H s_w)(d\rho_{a,C(4)} - d\rho_{o,C(-4)}) + d\rho_{o,C(-4)}(1 - \Lambda_H))) \\ &\quad - d\rho_{o,C(4)}(f_w - \Lambda_H s_w) - \frac{\partial f_w}{\partial y}, \quad r_H^2 = -\left(\frac{\partial f_w}{\partial s_w} - \Lambda_H\right), \\ r_H^3 &= u\left(\frac{\partial f_w}{\partial s_w} - \Lambda_H\right)((f_w - \Lambda_H s_w)(d\rho_{a,C(4)} - d\rho_{o,C(-4)}) + d\rho_{o,C(-4)}(1 - \Lambda_H)), \end{aligned}$$

where  $\Lambda_H = (\varphi/u)\lambda_H$ ,  $d\rho_{a,C(4)} = \rho'_{a,C(4)}/\rho_{a,C(4)}$  and  $d\rho_{a,C(-4)} = \rho'_{a,C(-4)}/\rho_{a,C(-4)}$ .

The saturation rarefaction curves then are obtained by solving the ordinary differential equation  $d\mathcal{R}_S/d\xi = \vec{r}_{s_w}$  and  $d\mathcal{R}_H/d\xi = \vec{r}_H$ . Thus such waves are represented by curves with constant hydrogen concentration and it is possible to verify that along such a wave the velocity  $u$  is constant also. In this case, we reach the classical Buckley-Leverett rarefaction waves, which can also be obtained by the fractional flow method. It rarefaction curve in which only the saturation varies is denoted by  $\mathcal{R}_{s_w}$ ; it are associated to  $(\lambda_{s_w}, \vec{r}_{s_w})$ . The rarefaction curves in which, generically, all variables change are denoted as  $\mathcal{R}_H$ ; they are associated to  $(\lambda_H, \vec{r}_H)$ . The final step to obtain the chemical rarefaction wave consists of integration of the first order differential equations

$$ds_w/d\xi = r_H^1(s_w, y) \quad dy/d\xi = r_H^2(s_w, y) \quad \text{and} \quad du/d\xi = r_H^3(s_w, y, u). \quad (76)$$

Equations (76a) and (76b) must be solved before solving (76c) to find  $s_w(\xi)$  and  $y(\xi)$ . This decomposition is very useful from the numerical point of view as well. Notice that along such a compositional curve both saturation and hydrogen vary, so this wave is not trivial and it cannot be obtained by the fractional flow method.

### 5.3 Rankine Hugoniot conditions

Another possible type of solution for the system (53)-(55) represents discontinuities. They are shocks that satisfy the Rankine-Hugoniot relationships

$$\begin{aligned} u^- (f_w \rho_{a,C(4)})^- - u^+ (f_w \rho_{a,C(4)})^+ - \sigma \varphi \left( (S_w \rho_{a,C(4)})^- - (S_w \rho_{a,C(4)})^+ \right) &= 0, \\ u^- \left( f_w (\rho_{a,O-H} + 4\rho_{a,CO_2}) \right)^- - u^+ \left( f_w (\rho_{a,O-H} + 4\rho_{a,CO_2}) \right)^+ - \\ \sigma \varphi \left( \left( S_w (\rho_{a,O-H} + 4\rho_{a,CO_2}) \right)^- - \left( S_w (\rho_{a,O-H} + 4\rho_{a,CO_2}) \right)^+ \right) &= 0, \\ u^- (f_o \rho_{o,C(-4)})^- - u^+ (f_o \rho_{o,C(-4)})^+ - \sigma \varphi \left( (S_o \rho_{o,C(-4)})^- - (S_o \rho_{o,C(-4)})^+ \right) &= 0. \end{aligned}$$

To find a nontrivial solution for  $u^+$ ,  $u^-$  and  $\varphi\sigma$  the determinant

$$\begin{vmatrix} (f_w \rho_{a,C(4)})^- & (f_w \rho_{a,C(4)})^+ & ((S_w \rho_{a,C(4)})^- - (S_w \rho_{a,C(4)})^+) \\ (f_w \rho_A)^- & (f_w \rho_A)^+ & ((S_w \rho_A)^- - (S_w \rho_A)^+) \\ (f_o \rho_{o,C(-4)})^- & (f_o \rho_{o,C(-4)})^+ & ((S_o \rho_{o,C(-4)})^- - (S_o \rho_{o,C(-4)})^+) \end{vmatrix} = 0, \quad (77)$$

where  $\rho_A = \rho_{a,O-H} + 4\rho_{a,CO_2}$ . or

$$HL(s_w, y) := \det \begin{pmatrix} \widehat{F}_1^+ & -\widehat{F}_1^- & [G_1] \\ \widehat{F}_2^+ & -\widehat{F}_2^- & [G_2] \\ \widehat{F}_3^+ & -\widehat{F}_3^- & [G_3] \end{pmatrix} = 0. \quad (78)$$

Let us denote by  $[G] = G^+ - G^-$  and  $[F] = u^+ \widehat{F}^+ - u^- \widehat{F}^-$  i.e.,

$$\sigma(G_i^+ - G_i^-) - (u^- - u^+) \widehat{F}_i^+ - u^- (\widehat{F}_i^+ - \widehat{F}_i^-) = 0, \quad \text{with } i = 1, 2, 3, \quad (79)$$

where  $G_i^-$ ,  $F_i^-$  and  $G_i^+$ ,  $F_i^+$  are the accumulation and flux evaluated at the left ( $s_w^-, y^-, u^-$ ) and right ( $s_w^+, y^+, u^+$ ) states. Here  $\widehat{F}_1$ ,  $\widehat{F}_2$  and  $\widehat{F}_3$  are given in (58) and  $G_1$ ,  $G_2$  and  $G_3$  are given in (57).

Using (79) determinant in (78) can be rewritten as

$$HL(s_w, y) := \det \begin{pmatrix} -[F_1] & \widehat{F}_1^+ & [G_1] \\ -[F_2] & \widehat{F}_2^+ & [G_2] \\ -[F_3] & \widehat{F}_3^+ & [G_3] \end{pmatrix} = 0. \quad (80)$$

This is an equation in the variables  $S_w$  and  $y$ . Notice that if the classical *RH* condition is satisfied, so that the first column is proportional to the last one, then equation (80) is also satisfied. In other words, classical shocks belong to the *RH* curve, but there could be other discontinuities satisfying (80).

The curve found in  $(S_w, y)$  space gives the possible discontinuities that satisfy the Rankine-Hugoniot conditions. The shock curves in which only the saturation varies are denoted by  $\mathcal{S}_s$ . Shock curves in which, generically, all variables change are denoted as  $\mathcal{S}_H$ .

One can verified that Hugoniot locus is the union of two branches (see Figure 2 ), i.e.  $\mathcal{S}_s \cup \mathcal{S}_H$ , with

$$\mathcal{S}_s = \{(S_w^+, y^+) : y^+ - y^- = 0\}. \quad (81)$$

Along this branch we have that  $u = u^+ = u^-$  and  $\sigma = u[\widehat{F}_i]/[G_i]$ , with  $i = 1, 2, 3$ . Thus we call this curve as Buckley Leverett shock. And

$$\mathcal{S}_H = \{(S_w^+, y^+) : \frac{\partial HL}{\partial y}(S_w^-, y^-) + \frac{\partial^2 HL}{\partial y^2}(S_w^-, y^-)(y^+ - y^-) + \frac{\partial^3 HL}{\partial y^3}(S_w^-, y^-)(y^+ - y^-)^2 + O(y^+ - y^-)^3 = 0\},$$

where  $HL$  is given in (80).

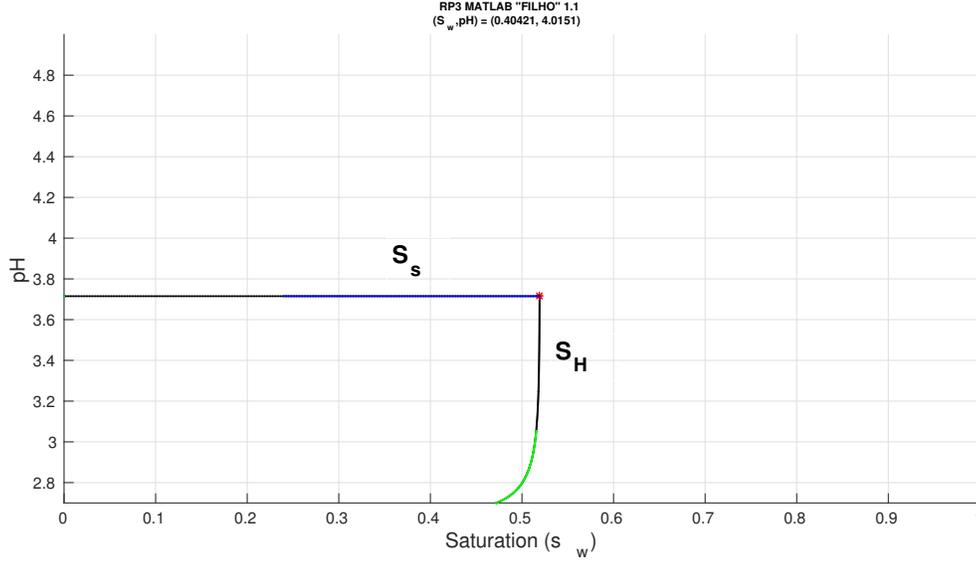


Figure 2: Branches of the Hugoniot locus.

Above statement is obtained using Taylor's Series for  $HL$  and that  $HL(s_w^-, y^-) = 0$  and  $\frac{\partial^k HL}{\partial s_w^k}(s_w^-, y^-) = 0$  hold, for  $k = 1, \dots$  we prove here  $\frac{\partial HL}{\partial s_w}(s_w^-, y^-) = 0$ , the rest is similar.

Derivation of (78) produces

$$\frac{\partial HL}{\partial s_w}(s_w^+, y^+) = \det \begin{pmatrix} \frac{\partial(\widehat{F}_1^+)}{\partial s_w} & -\widehat{F}_1^- & [G_1] \\ \frac{\partial(\widehat{F}_2^+)}{\partial s_w} & -\widehat{F}_2^- & [G_2] \\ \frac{\partial(\widehat{F}_3^+)}{\partial s_w} & -\widehat{F}_3^- & [G_3] \end{pmatrix} + \det \begin{pmatrix} \widehat{F}_1^+ & -\widehat{F}_1^- & \frac{\partial[G_1]}{\partial s_w} \\ \widehat{F}_2^+ & -\widehat{F}_2^- & \frac{\partial[G_2]}{\partial s_w} \\ \widehat{F}_3^+ & -\widehat{F}_3^- & \frac{\partial[G_3]}{\partial s_w} \end{pmatrix}, \quad (82)$$

or

$$\begin{aligned} \frac{\partial HL}{\partial s_w}(s_w^+, y^+) = & \det \begin{pmatrix} (\rho_{a,C(4)})^+ f'_w & -\widehat{F}_1^- & [G_1] \\ (\rho_A)^+ f'_w & -\widehat{F}_2^- & [G_2] \\ -(\rho_{o,C(-4)})^+ f'_w & -\widehat{F}_3^- & [G_3] \end{pmatrix} + \\ & \det \begin{pmatrix} \widehat{F}_1^+ & -\widehat{F}_1^- & (\rho_{a,C(4)})^+ \\ \widehat{F}_2^+ & -\widehat{F}_2^- & (\rho_A)^+ \\ \widehat{F}_3^+ & -\widehat{F}_3^- & -(\rho_{o,C(-4)})^+ \end{pmatrix}. \end{aligned} \quad (83)$$

Summing first and second column of second determinant in (83) we obtain

$$\begin{aligned} \frac{\partial HL}{\partial s_w}(s_w^+, y^+) = & \det \begin{pmatrix} (\rho_{a,C(4)})^+ f'_w & -\widehat{F}_1^- & [G_1] \\ (\rho_A)^+ f'_w & -\widehat{F}_2^- & [G_2] \\ -(\rho_{o,C(-4)})^+ f'_w & -\widehat{F}_3^- & [G_3] \end{pmatrix} \\ & + \det \begin{pmatrix} -[\widehat{F}_1] & -\widehat{F}_1^- & (\rho_{a,C(4)})^+ \\ -[\widehat{F}_2] & -\widehat{F}_2^- & (\rho_A)^+ \\ -[\widehat{F}_3] & -\widehat{F}_3^- & -(\rho_{o,C(-4)})^+ \end{pmatrix}. \end{aligned}$$

Applying properties of determinant we have,

$$\frac{\partial HL}{\partial s_w}(s_w^+, y^+) = \det \begin{pmatrix} (\rho_{a,C(4)})^+ & -\widehat{F}_1^- & [G_1]f'_w - [\widehat{F}_1] \\ (\rho_A)^+ & -\widehat{F}_2^- & [G_2]f'_w - [\widehat{F}_2] \\ -(\rho_{o,C(-4)})^+ & -\widehat{F}_3^- & [G_3]f'_w - [\widehat{F}_3] \end{pmatrix}, \quad (84)$$

or

$$\frac{\partial HL}{\partial s_w}(s_w^+, y^+) = (\lambda_{s_w} - \sigma) \det \begin{pmatrix} (\rho_{a,C(4)})^+ & -\widehat{F}_1^- & [G_1] \\ (\rho_A)^+ & -\widehat{F}_2^- & [G_2] \\ -(\rho_{o,C(-4)})^+ f'_w & -\widehat{F}_3^- & [G_3] \end{pmatrix}. \quad (85)$$

From (85) is obtained  $\frac{\partial HL}{\partial s_w}(s_w^-, y^-) = 0$ .

## 5.4 Regression expressions

In the equations below  $y = \ln[H^+]$ , where  $[H^+]$  is the concentration [*mol/liter*] of the hydrogen ion (here calculated at 39°C).

$$\ln [CO_3^{2-}] = 51242105.771024 * \exp(2.73572178786335 * y) + 6.69820568753213e - 14 * \sinh(2.02342646169015 * y) - 23.5002456098875 [mol/liter],$$

$$\ln [CO_3^{2-}] = 51242105.771024 \exp(2.73572178786335y) + 6.69820568753213e - 14 \sinh(2.02342646169015y) - 23.5002456098875,$$

$$\ln [CO_2] = 14.3412082339566 + 1.98420301521895 * y + 1.42894959991698e - 13 * \sinh(1.97397032954743 * y) [mol/liter],$$

$$\ln [HCO_3] = y - 3.72509519022871e - 17 * \sinh(-2.50221714601476 * y), [mol/liter]$$

$$\ln [HCO_3] = y - 3.72509519022871e - 17 * \sinh(-2.50221714601476 * y),$$

$$[H_2O] = 116798.454030875 + 486.844910347393 * \exp(y) - 116743.356027846 * \cosh(y * \exp(y)),$$

$$[H_2O] = 116798.454030875 + 486.844910347393 \exp(y) - 116743.356027846 \cosh(y \exp(y)),$$

$$\ln [OH^-] = -31.2 - y, [mol/liter],$$

$$\ln [OH^-] = -31.2 - y,$$

## 5.5 Bifurcation curves

Here some elements that determine the Riemann solution are presented: coincidence and inflection loci, which are region boundaries where rarefaction wave curves change. Moreover the procedure for building the analytical solution through admissible wave curves is shown.

### 5.5.1 Coincidence locus

Rarefaction wave solutions of the Riemann problem can suffer structural modifications along the surfaces where wave velocities coincide. In our case the coincidence locus in the projected state space  $(s_w, y)$  is given as the set where velocities  $\lambda_s$  and  $\lambda_H$  in (73) are equal, i.e.,

$$\mathcal{C} = \left\{ (s_w, y) : \frac{\partial f_w}{\partial s_w} = \frac{\Delta_1 f_w + \Delta_2}{\Delta_1 s_w + \Delta_2} \right\},$$

where  $\Delta_1$  and  $\Delta_2$  are given in (74) and (75), respectively. When the variables  $s_w$  and  $y$  vary, we have a coincidence surface. Choosing certain experimental data of interest obtained with the PHREEQC program, the coincidence locus consist of two curves in  $(s_w, y)$  space for fixed  $u$  (see Figure 3).

### 5.5.2 Inflection locus

Points on the inflection locus are those where genuine nonlinearity is not satisfied ([57]), i.e., we define the inflection locus for saturation waves and for composition waves as:

$$I_k = \left\{ (s_w, y, u) : \nabla \lambda_k \cdot r_k = \frac{\partial \lambda_k}{\partial s_w} r_k^1 + \frac{\partial \lambda_k}{\partial y} r_k^2 + \frac{\partial \lambda_k}{\partial u} r_k^3 = 0 \right\},$$

with  $k = \mathcal{S}_s, \mathcal{S}_H$ . It is possible to check the following fact: in the projected state space the inflection locus for the saturation wave is the curve

$$I_s = \{(s_w, y) : f_w''(s_w) = 0\},$$

for any fixed  $u$ , where  $f_w''$  is the second derivative of the flux  $f_w$  relatively to  $s_w$ . The inflection locus is important because it indicates where the rarefaction curves stop. For the examples discussed here the inflection locus for composition waves consist of four disconnected curves: one where the  $pH$  is approximately constant, one vertical line, where the saturation is constant and two other curves that are also coincidence curves for the eigenvalues. On the other hand (see Figure 3), the inflection locus for rarefaction wave consists of a line of constant saturation.

Figure 3 shows a typical example in experiments where the composition rarefaction waves have an inflection and necessarily have to stop.

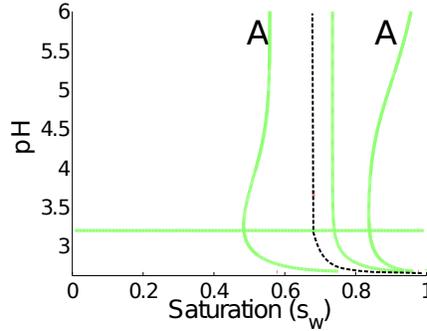


Figure 3: For the variable oil viscosity case. Dashed lines represents the inflection locus for the saturation wave, while the bold line represents the inflection locus for the case of composition waves. Here the coincidence curves are denoted by **A**, which are also inflection loci.

## 5.6 Numerical and Analytical solutions

By means of the analytical solution we study water and CO<sub>2</sub> flooding. Assuming that oil viscosity is constant, the structure of the Riemann solution for the examples with left (upstream) state ( $s_w = 0.8, pH = 2.7$ ) to right (downstream) state ( $s_w = 0.15, pH = 4$ ) consists of two rarefaction waves separated by a chemical shock; the latter is continued with a constant state and finally a fast Buckley-Leverett saturation shock. In the first rarefaction wave only the saturation changes, while in the second one both saturation and composition change. The connection point between the rarefaction waves can be constructed from a curve of states where the two characteristic velocities coincide.

In Figure 4 the analytical and numerical solutions obtained by software COMSOL and Riemann solver is shown. It shows that both solutions match almost indistinguishable. Comparing the results, we can clearly see the existence of a saturation rarefaction wave  $\mathcal{R}_s(J)$  connecting  $J$  to  $M_1$  then a chemical wave rarefaction wave  $\mathcal{R}_H(M_1, M_2)$  connecting  $M_1$  to  $M_2$ , then a chemical shock wave  $\mathcal{S}_H(M_2, M_3)$  connecting  $M_2$  to  $M_3$ , with the shock speed  $2.99 \times 10^{-5} m/s$  with the analytical method,  $2.9 \times 10^{-5} m/s$  from COMSOL simulation. After  $M_3$  there is a constant state and then a shock saturation wave  $\mathcal{S}_s(M_3, I)$  connecting  $M_3$  to  $I$ . This saturation shock speed is  $4.37 \times 10^{-5} m/s$  with analytical method, and  $4.33 \times 10^{-5} m/s$  with COMSOL simulation.

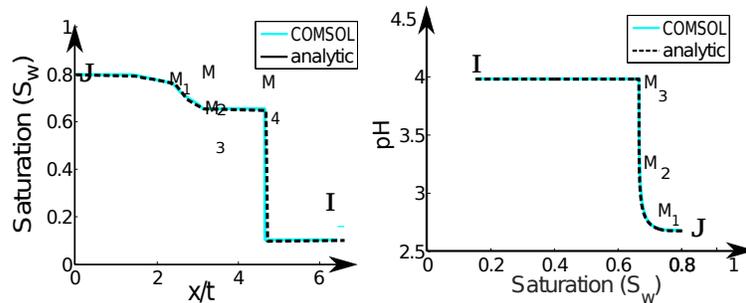


Figure 4: *a)- left* . The saturation profile from the COMSOL simulation (solid curve) a function of time scaled position compared with the analytical solution (dashed curve). *b)- right* . The  $pH$  profile from the COMSOL simulation (solid curve) compared with the analytical solution (dashed curve).

In the Figure 5 the hydrogen and saturation wave at different time instants is shown. The hydrogen concentration is characterized by a constant state, a shock like behavior

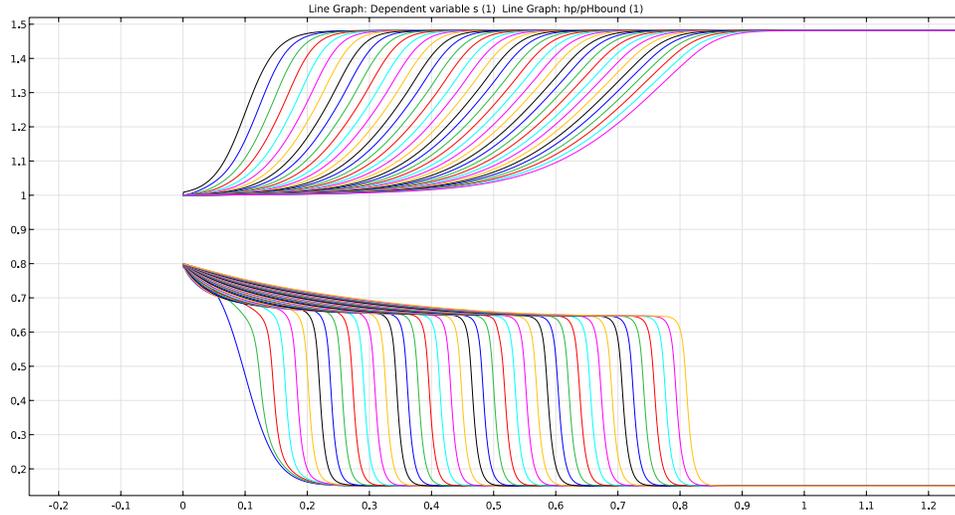


Figure 5: The saturation, inert tracer (chloride) and the hydrogen ion concentration in the ICDO model

and then a rarefaction. The saturation profile is a typically Buckley-Leverett profile.

In Fig. 6 we have added the decane concentration. We note that the behavior of decane at very low  $pH$  depends on a single data point and a literature search is required to get more data points. All the same the conclusion reached previously that the presence of carbon dioxide is strongly affecting the results still remains.

## 6 Conclusions

We developed a Riemann solver to obtain solutions for oil recovery problems including geochemical aspects. The methodology is adequate for one dimensional incompressible two-phase flow in porous media involving several chemical components.

As there is mass transfer between phases and the partial molar volume differs between phases, a variable total Darcy velocity ensues, so that fractional flow theory does not easily apply. For upscaled equations in reservoir flow, convection terms completely dominate the diffusion terms; this is why Riemann solutions, which use zero diffusion coefficients are usually better representations than numerical representations with non-zero diffusion coefficients on the reservoir scale. The Riemann solver for this model can therefore be applied for upscaling transport processes in enhanced oil recovery involving geochemical aspects.

The performance of our Riemann solver is illustrated for carbonated water injection in

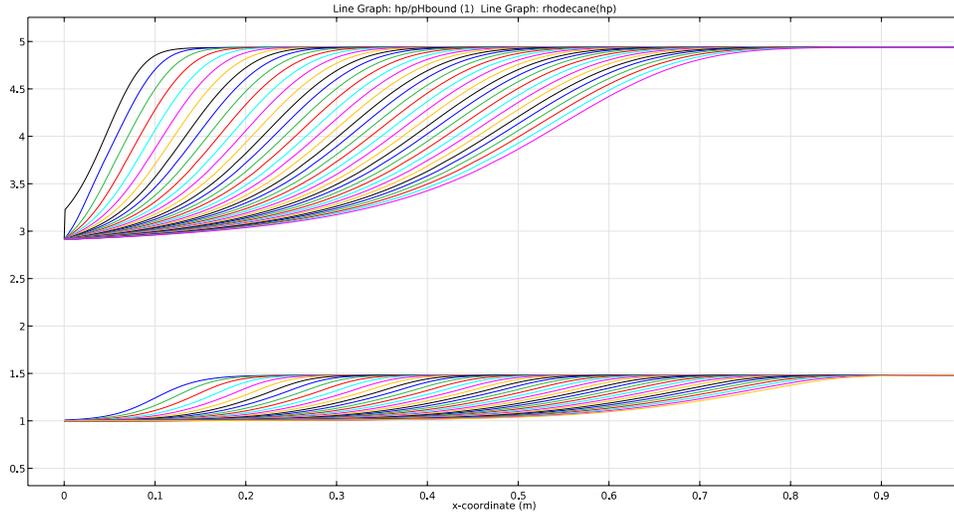


Figure 6: Oil concentration and hydrogen equation in the ICDOW model

a rock containing oil and carbon dioxide. The salinity is zero everywhere. We formulate three conservation equations, in which we substitute expressions that are obtained from geochemical software (PHREEQC) by regression. Gibbs phase rule together with charge balance shows that all compositions can be written in terms of the pH only.

The Riemann solution can be compared with a numerical solution, which can include capillary and diffusion effects. We use the initial and boundary conditions for carbonated water injection in an oil reservoir containing connate water with some carbon dioxide. Two numerical procedures were used (1) an in house developed upstream finite difference simulator (IVUP) (2) implementation of the model equations into COMSOL. There is good agreement between the numerical solutions and the Riemann solution except that COMSOL shows a slightly lower total velocity than IVUP and the Riemann solution.

The structure of the Riemann solution from left (upstream) to right (downstream) consists of two rarefaction waves connected by a chemical shock; the latter is continued with a constant state and finally a fast Buckley-Leverett saturation shock. In the first rarefaction wave only the saturation changes, while in the second one both saturation and composition change. The connection point between the rarefaction waves can be constructed from a curve of states where the two characteristic velocities coincide.

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## A Activity coefficients

### Molalities, molarities and mole fractions

The chemical potential of a component does not depend on whether the concentrations are measured in molar, molal or mole fractions. Therefore we obtain

$$\begin{aligned}\mu &= \mu_X^0 + RT \ln (\gamma_{H,x} X) \\ &= \mu_m^0 + RT \ln (\gamma_{H,m} m) \\ &= \mu_c^0 + RT \ln (\gamma_{H,c} c) \\ &= \mu^0 + RT \ln a\end{aligned}$$

where  $\mu_X^0$  is the chemical potential of pure solute having the properties of an infinitely dilute solution,  $\mu_m^0$  is the chemical potential of the solute in the ideal one molal solution and  $\mu_c^0$  is the chemical potential (Anderson and Crerar) of the ideal one molar solution. Anderson and Crerar show that difference between the activity coefficients  $\gamma$  except for very high concentrations are extremely small, i.e.,

$$\ln \gamma_{H,x} = \ln \gamma_{H,m} + \Gamma_\gamma = \ln \gamma_{H,m} + \ln (1 + 0.0180153m) \quad (86)$$

The unit of the activity depends on the reference state that determines  $\mu^0$ .

The equilibrium constants express the values with respect to a reference state, e.g., an ideal one molar solution with activity coefficient one, which corresponds to an activity equal to one. The equilibrium constants tabulated in Appelo, are referring to one molal ideal solutions, which have thus an activity equal to one. So all activities computed from the equilibrium relations are with respect of an ideal solution of one mol/kg-water, which has an activity one.

Division by these activities by the activity coefficients give us the value of the concentrations. The activity coefficients are derived in the Debye-Hückel theory, which uses the Electrostatic Poisson equation, where the charge density is expressed in charge per unit volume. Hence it appears that the activity coefficients are formally correct only for concentrations expressed in mol/liter. All the same many authors still use molalities (concentrations in mol/ kg-water) based on the fact that the difference between the

activity coefficients based on molarities, molalities or even mole fractions are extremely small.

### Activity coefficients for charged molecules; extended Debye Hückel law

The extended Debye-Hückel theory for calculating the activity coefficient of an ion reads [1]

$$\ln \gamma_j(\mu) = -\frac{A_\gamma |z_j|^2 \sqrt{\mu}}{1 + B_\gamma \hat{a}_j \sqrt{\mu}} + b_j \mu \quad (87)$$

where  $\mu = \frac{1}{2} \sum_i (c_i z_i^2)$  [mol/liter] is the ionic strength of the solution,  $z_i$  is the charge of the ion, in water. Finally  $\hat{a}_j$  is the effective diameter of an ion  $j$  in Ångstrom see Appelo and Postma, [3], page 125. For small ions we use a value of 3 Ångstrom.

$$B_\gamma = \left( \frac{8\pi N_A q_e^2 \rho_0}{1000 \varepsilon_r k_B T} \right)^{1/2} = \frac{50.29158649 \rho_0^{1/2}}{(\varepsilon_r T)^{1/2}} \quad (88)$$

where  $N_A$  is the Avogadro number ( $6.225 \times 10^{23}$ ) molecules per mole,  $q_e = 4.803 \times 10^{-10}$  esu (electrostatic unit of charge),  $\rho_0$  is the density of pure water water in  $[g/cm^3]$ ,  $\varepsilon_r$  is the relative dielectric coefficient,  $k_B = 1.38054 \times 10^{-16}$  erg/K is the Boltzmann constant,  $T$  is the temperature in  $K$ ,  $P$  is the pressure in atmosphere. and the compressibility  $\kappa_0 = (atm^{-1})$ . For the definition of  $B$  in Eq. (25) we need to express Å in Ångström.

Moreover we can express the Debye-Hückel parameter for the activity coefficients as [95]

$$A_\gamma = \frac{(2\pi N_A)^{1/2} q_e^3 \sqrt{\rho_0}}{\sqrt{1000} (\varepsilon k_B T)^{3/2}} = \frac{1824829.238 \sqrt{\rho_0}}{(\varepsilon T)^{3/2}} [(mol/kg)^{0.5}] \quad (89)$$

At room temperature ( $25^\circ C$ ) and atmospheric pressure  $A_\gamma / \ln(10) = 0.5085$  and  $B = 0.3281$ . Finally  $\hat{a}_j$  is the effective diameter of an ion  $j$  in Ångstrom [4] [3], page 125. For small ions we use a value of 3 Ångstrom. The ionic strength can be written in terms of activities as

$$\mu = \frac{1}{2} \sum_i (c_i z_i^2) = \frac{1}{2} \sum_i \left( \frac{a_i}{\gamma_i(\mu)} z_i^2 \right) \quad (90)$$

### Converting molalities into concentrations

For more or less dilute solutions we can take the activity of water  $a_{H_2O} = 1$ . ([56] [2]). For sea water  $a_{H_2O} = 0.98$ . The concentrations are expressed in moles per unit mass

of water. Indeed, if we divide the activities by activity coefficients  $\gamma_{w,j}$  we obtain the concentration in molalities, simply because Appelo [4] defines the reference state as the activity of one molal of ideal solution. The molarities are proportional to the molalities and the conversion is given by the equation

$$c_{a,j} = \frac{\rho_a}{\sum_{i=1}^N (m_{w,i} M_i)} m_{w,j} = [M_w c_{a,w}] m_{w,j}, \quad (91)$$

where we have used that  $M_w c_{a,w} = \rho_a / \sum_{i=1}^N (m_{w,i} M_i)$ , and that the molality of water  $m_{w,j} = 1000/M_w$ . The density of the aqueous solution is  $\rho_a$ .

## B Partition of carbon dioxide into the aqueous and oleic phases

By comparing the Henry coefficient of carbon dioxide between the oleic phase and the gas phase to the Henry coefficient between the aqueous and the gas phase it is possible to derive the equilibrium of carbon dioxide between an oleic phase and the aqueous phase.

Henry's law describes the ratio between the activity of carbon dioxide in the aqueous phase and in the gas phase. We obtain

$$K_{w-g}^H = a_{w,CO_2}/a_{g,CO_2} = m_{a,CO_2} \gamma_{a,CO_2} / f_{g,CO_2}, \quad (92)$$

where  $m_{a,CO_2}$  is the molality of carbon dioxide in the water phase,  $\gamma_{a,CO_2(aq)}$  the activity coefficient, and  $f_{CO_2(g)}$  is the fugacity of carbon dioxide in the gas phase.

We can also relate the equilibrium of carbon dioxide in the oil phase [116] [71] and the gas phase by

$$K_{o-g}^H = a_{o,CO_2}/a_{g,CO_2} = m_{o,CO_2} \gamma_{o,CO_2} / f_{g,CO_2}. \quad (93)$$

The procedure to get activities in neutral molecules in the aqueous phase is given in [87].

Therefore the ratio of the Henry coefficients give the ratio of the molalities

$$\frac{K_w^H}{K_o^H} = \frac{m_{a,CO_2} \gamma_{a,CO_2}}{m_{o,CO_2} \gamma_{o,CO_2}} \approx \frac{m_{a,CO_2}}{m_{o,CO_2}} \quad (94)$$

The approximation is valid for low ion concentrations. In practice there will be an effect for natural brine reservoirs. For the simplified model we use that  $\gamma_{a,CO_2} = \gamma_{o,CO_2}$ .

For crude estimates we can use that the mole fraction of CO<sub>2</sub> in oil (2,2,4-trimethyl pentane) at 40 bar is [71] of the order of  $x_{o,CO_2} = 0.2$ . The Henry coefficient in water is 0.034 mol/liter/atm [91] [118], which would be approximately 1.38 mol / liter at 40 bar. This corresponds to a mole fraction of  $x_{w,CO_2} = 0.025$ . Hence the solubility ratio  $R_{CO_2}$  between oil and water is of the order of 8, i.e.,

$$R_{CO_2} = \frac{c_{o,CO_2}}{c_{a,CO_2}} \approx 8 \quad (95)$$

Therefore we can also relate the concentration of the carbon dioxide in oleic phase  $c_{o,CO_2}$  to the hydrogen ion concentration and the chloride concentration as the other concentrations. Using Eq.

$$\frac{\rho_{o,C(-4)}}{\rho_{O,C(-4)}} + \frac{\rho_{o,CO_2}}{\rho_{O,CO_2}} = 1, \quad (96)$$

we can also calculate  $c_{o,oil}$  and relate it to the hydrogen ion concentration and the chloride concentration.

The calculation of activity coefficients of neutral molecules (CO<sub>2</sub> (aq), SiO<sub>2</sub> (aq), H<sub>2</sub>S(aq)) is usually much simpler than the calculation of activity coefficients of ions [2]. The first ionization constant is usually small, so that species other than the neutral substances can usually be disregarded. We will consider



for which the Henry coefficient can be written as

$$K_H = a_{CO_2(aq)} / a_{CO_2(g)} = m_{CO_2(aq)} \gamma_{CO_2(aq)} / f_{CO_2(g)}, \quad (98)$$

where  $f_{CO_2}$  is the fugacity of carbon dioxide,  $\gamma_{CO_2}$  is the activity coefficient of CO<sub>2</sub> in the aqueous phase and  $m_{CO_2}$  is the molality of carbon dioxide. The activity coefficient,  $\gamma_{CO_2(aq)}$ , in pure water is usually close to one.

The Setchénow coefficient  $k_S$  relates the activity coefficient of interest to the ionic strength of the solution, e.g., for carbon dioxide

$$\log \gamma_{CO_2(aq)} = k_S \mu = \frac{1}{2} k_S \sum_{i=1}^N c_i Z_i^2. \quad (99)$$

where the logarithm has base ten. Similar relations hold for the other non-charged components (see Table ??)

For single salt solutions, values can be found in [102]. Byrne et al. [21] use the equation

$$\log \frac{m_0}{m_s} = \sum_i k_{mi} I, \quad (100)$$

for salt mixtures, where  $m_0$  and  $m_s$  are the solubilities in distilled water and salt solutions, at  $T, P$  and the fugacity of interest. Solubilities of methane are not much affected by the presence of clay [101]. For an overview of activity coefficients for neutral molecules in ionic solutions we refer to [87] [86] [85]. We will not explicitly use it, but the Eq. (??) has already been implemented in PHREEQC [75].

However, to add the individual values is cumbersome and we can approximate the values using that  $k_s = 0.1$  ([62]) ([101]), even if these values can vary.

## C Partial molar volume

The regression expressions for the density and the dielectric constant are given in Appendix A

Following Redlich and Mayer (1964), it is convenient to introduce Traube's apparent molal volume defined by the volume  $V$  of a solution containing  $n_1$  moles of solvent (molal volume)  $v_{10}$  and  $n_2$  moles of solute according to (see Redlich and Meyer, 1964).

$$V = n_1 v_{10} + n_2 \phi \quad (101)$$

Usually the apparent molal volume is computed from the molal weight of the solute  $w_2$ , its concentration  $c$  (moles/l.), and the densities  $s$  of the solution and  $s^0$  of the solvent by

$$\phi = \frac{w_2}{s^0} - 1000 (s - s^0) / (cs^0) \quad (102)$$

The theory of electrolytes furnishes the limiting relation

$$\phi = \phi^0 + kw^{1.5}c^{0.5} \quad (103)$$

It shows the usual linear dependence on the square root of the concentration and the influence of the valence factor  $w$ , which is given by the number  $\nu_i$  of ions of species  $i$  formed by one molecule of the electrolyte and the valence  $z_i$  according to

$$w = \frac{1}{2} \sum_i \nu_i z_i^2 \quad (104)$$

-Millero—Alternative formulation for calculating the specific volume for the aqueous species (Millero, 2000) by convention relative to the volume of  $H^+$  at a ionic strength of 0. The specific volume for species  $i$  is calculated according to the formula , where  $\bar{V}_i$  is the specific volume at infinite dilution;  $A_v$  is the Debye-Hückel limiting slope, and  $I$  is the ionic strength. The volume at infinite dilution is parameterized as  $\bar{V}_{i,inf}$  and the coefficient is parameterized as  $\beta_i$ , where  $T$  is °C. If both  $-Vm$  and -Millero are defined for a species, the numbers from  $-Vm$  are used. Warning: the applicability of the Millero formulas is limited to  $T < 50$  °C, and the calculated densities may be incorrect at ionic strengths  $> 1.0$  except for NaCl solutions. Optionally, Millero or -Mi[llero]. a, b, c, d, e, f—Numerical values for parameters a to f in the specific volume equation.

### The density

The density  $\rho_w$  can be expressed as the inverse molar volume, i.e.,

$$\rho_w = \frac{1}{V} = \frac{1}{\sum_i n_i \bar{V}_i} \quad (105)$$

where

$$\bar{V}_i = \bar{V}_{i,inf} + \frac{1}{2} z_i^2 A_v \frac{\sqrt{\mu}}{1 + \overset{\circ}{a} B \sqrt{\mu}} + \beta_i \mu^{i_4}, \quad (106)$$

where  $\beta_i = i_1 + i_2 / (T_K - 228) + i_3 (T_K - 228)$  and  $\mu$  is the ionic strength. The partial molar volume  $\bar{V}_{i,inf}$  at infinite dilution is

$$\bar{V}_{i,inf} = 41.84 \left( a_1/10 + \frac{100a_2}{2600 + P_b} + \frac{a_3}{T_K - 228} + \frac{10000a_4}{(2600 + P_b)(T_K - 228)} - W Q_{Born} \right), \quad (107)$$

where  $Q_{Born} = -\partial_P (1/\epsilon_r)^2$ . The constants in *cal/mole/bar* are a1, a2, a3, a4,  $\overset{\circ}{a}$  W, i1, i2, i3, i4  $a_1 = 8.615$ ,  $a_2 = 0$ ,  $a_3 = -12.21$ ,  $a_4 = 0$   $\overset{\circ}{a} = 1.667$ ,  $W = 0$ ,  $i_1 = 0$ ,  $i_2 = 264$ ,  $i_3 = 0$  and  $i_4 = 1$  for the reaction  $CO_3^{2-} + H^+ \rightarrow HCO_3^-$ . Using the factor 41.84, leads to a volume of  $cm^3/mol$ . The factor 4.184 converts calorie to Joule.

The constant  $A_v$ , the Debye limiting slope, can be expressed as [10]

$$A_v = 2RT \sqrt{\frac{2\pi N_A \rho_0}{1000}} \left( \frac{q_e^2}{\epsilon kT} \right)^{3/2} \left[ \left( \frac{\partial \log \epsilon_r}{\partial P} \right)_T + \frac{\kappa_0}{3} \right] [(cm^3/mol)(mol/kg)^{-0.5}], \quad (108)$$

where  $N_A$  is the Avogadro number ( $6.225 \times 10^{23}$ ) molecules per mole,  $q_e = 4.803 \times 10^{-10}$  esu (electrostatic unit of charge),  $\rho_0$  is the density of pure water in  $[g/cm^3]$ ,  $\varepsilon_r$  is the relative dielectric coefficient,  $k_B = 1.38 \times 10^{-16}$  erg/K is the Boltzmann constant,  $T$  is the temperature in  $K$ ,  $P$  is the pressure in atmosphere. and the compressibility  $\kappa_0 = (atm^{-1})$ .

$$B = \frac{8\pi N_A q_e^2 \rho_0}{\varepsilon_r k_B T} \quad (109)$$

## D Sorption isotherms

In this section as we assume for the simple model, that the activity coefficients of the surface complexes are equal to one. Indeed, the conversion of activities to concentration of surface complexes is not easy [3] and activity coefficients of surface complexes are usually taken equal to one. However, the equilibrium coefficients  $K_{i,\kappa}$  have been corrected for charge effects. Usually in surface chemistry one uses activities for the dissolved ions. The activity coefficients of the surface complexes are usually one, i.e., we do not discern different values of the activity coefficients of the surface complexes. This is generally done as currently there is no model to derive the activity coefficients of surface complexes [3]. We distinguish again weak and strong binding sites. The total charge is the charge on the weak binding sites added to the charge on the strong binding sites. This determines the surface potential of the sorbent phase. The number of strong binding sites are for instance 1% of the number of weak binding sites.. From Eqs. (??) we obtain

$$K_{-11} = \frac{m_{H^+}(oil_{s,N})}{(oil_{s,NH^+})} = \frac{m_{H^+} \left( m_{oil_{s,NH^+}}^{tot} - m_{oil_{s,NH^+}} \right)}{m_{oil_{s,NH^+}}} \quad (110)$$

where we used that the total number of surface sites of per kilogram of oil is  $m_{oil_{s,NH^+}} + m_{oil_{s,N}} = m_{oil_{s,NH^+}}^{tot}$ . Hence we obtain

$$m_{oil_{s,NH^+}} = \frac{m_{H^+} m_{oil_{s,NH^+}}^{tot}}{K_{-11} + m_{H^+}} \quad (111)$$

$$m_{oil_{s,N}} = m_{oil_{s,NH^+}}^{tot} - m_{oil_{s,NH^+}} \quad (112)$$

The total number of binding sites of the surface complexes per mol of adsorbent, e.g., the cationic surfactant concentration  $m_{oil_{s,NH^+}}^{tot}$  per mole of oil is given. In addition

we give the average molar weight of the surfactant molecule and the surface area of the adsorbent in  $[m^2/g - \text{sorbent}]$ . The concentration of amines and carboxylic acids in the ioil are implicitly given by the base number and acid number respectively. It concerns the mass of  $KOH$  that is necessary to neutralize the solution and is an indicator of the amount of carboxylic acids. Conversely the base number the mass of perchloric / glacial acetic acid required to neutralize the solution. It is mentioned [26] that many standard methods are not able to determine the weak acid concentration.

In the same way we obtain

$$m_{oil_w, COOH} = \frac{m_{oil_w, COOH}^{tot} m_{H^+}}{K_{-21} + m_{H^+} + K_{22} m_{Ca^{2+}} m_{H^+}} \quad (113)$$

$$m_{oil_w, COO^-} = \frac{K_{-21} m_{oil_w, COOH}^{tot}}{K_{-21} + m_{H^+} + K_{22} m_{Ca^{2+}} m_{H^+}} \quad (114)$$

$$m_{oil_w, COOCa^+} = \frac{K_{22} m_{Ca^{2+}} m_{oil_w, COOH}^{tot} m_{H^+}}{K_{-21} + m_{H^+} + K_{22} m_{Ca^{2+}} m_{H^+}} \quad (115)$$

where we have defined  $m_{oil_w, COOH}^{tot} = (m_{oil_w, COOH}) + (m_{oil_w, COO^-}) + (m_{oil_w, COOCa^+})$ . Here the molalities are given in terms of [mol/kg-oil]

$$m_{Cal_s, OH} = \frac{m_{Cal_s, OH}^{tot}}{K_{33} m_{HCO_3^-} + K_{13} m_{H^+} + 1} \quad (116)$$

$$m_{Cal_s, CO_3^-} = \frac{m_{Cal_s, OH}^{tot} K_{33} a_{HCO_3^-}}{K_{33} m_{HCO_3^-} + K_{13} m_{H^+} + 1} \quad (117)$$

$$m_{Cal_s, OH_2^+} = \frac{m_{Cal_s, OH}^{tot} K_{13} m_{H^+}}{K_{33} m_{HCO_3^-} + K_{13} m_{H^+} + 1} \quad (118)$$

$$m_{Cal_w, CO_3H} = \frac{m_{Cal_w, CO_3H}^{tot}}{(1 + K_{-14} m_{H^+} + K_{24} m_{Ca^{2+}})} \quad (119)$$

$$m_{Cal_w, CO_3^-} = \frac{K_{-14} m_{H^+} m_{Cal_w, CO_3H}^{tot}}{(1 + K_{-14} m_{H^+} + K_{24} m_{Ca^{2+}})} \quad (120)$$

$$m_{Cal_w, CO_3Ca^+} = \frac{K_{24} m_{Cal_w, CO_3H}^{tot} m_{Ca^{2+}}}{(1 + K_{-14} m_{H^+} + K_{24} m_{Ca^{2+}})}, \quad (121)$$

where the molalities are given in [moles per kg-calcite].

The molalities can be converted to concentrations using the Eq. A.

The total concentrations are given by

$$\begin{aligned} c_{oil_w,COOH,tot} &= 1.3 \times 10^{-3} \text{ mol/m}^3, \\ c_{oil_s,N,tot} &= 1.3 \times 10^{-3} \text{ mol/m}^3, \\ c_{Ca_s,OH,tot} &= 1.1 \times 10^{-2} \text{ mol/m}^3, \\ c_{Ca_w,CO3H,tot} &= 1.1 \times 10^{-2} \text{ mol/m}^3. \end{aligned}$$

## E Charge neutrality

### E.1 Mathematical derivation

**Remark: We did not consider the surface complexes, but the idea is similar**

We consider that we have the  $n$  possible different atoms to obtain  $m$  possible chemical species. We denote these atoms as

$$X_1, X_2, \dots, X_n.$$

We suppose that atom  $X_i$ , for  $i = 1, 2, \dots, n$ , has the valence  $\theta_i$ .

The  $j$ -th chemical species is denoted as

$$((X_1)_{\gamma_{1j}}(X_2)_{\gamma_{2j}} \cdots (X_n)_{\gamma_{nj}})^{\xi_j}. \quad (122)$$

Here  $\xi_j$  is the ion charge of the  $j$ -th component; if the  $j$ -th chemical species is not a ion, then  $\xi_j = 0$ . For the constant  $\gamma_{ij}$ , the index  $i$  is associated to the particular atom  $X_i$ , and the index  $j$  is associated to the chemical species. Moreover, it is possible that  $\gamma_{ij} = 0$  if the atom is absent in chemical species.

Using the charge balance of each  $j$ -th chemical species, we have that:

$$\sum_{i=1}^n \gamma_{ij} \theta_i = \xi_j. \quad (123)$$

We denote the concentration of  $j$ -th chemical species as:

$$c((X_1)_{\gamma_{1j}}(X_2)_{\gamma_{2j}} \cdots (X_n)_{\gamma_{nj}})^{\xi_j} \quad (124)$$

We define the total charge as:

$$\sigma = \sum_{j=1}^m \xi_j c((X_1)_{\gamma_{1j}}(X_2)_{\gamma_{2j}} \cdots (X_n)_{\gamma_{nj}})^{\xi_j}. \quad (125)$$

When  $\sigma = 0$  we say that there is *charge neutrality*.

**Theorem 1.** *The charge neutrality is conserved by the evolution equations, i.e., if  $\sigma = 0$  for the initial value, it remains  $\sigma = 0$  for all  $t > 0$ .*

*Proof:*

The conservation law for the  $i$ -th atom in the water phase is given by the concentration of each chemical species:

$$\begin{aligned} & \frac{\partial}{\partial t} \left( \sum_{j=1}^m \gamma_{ij} c \left( (X_1)_{\gamma_{1j}} (X_2)_{\gamma_{2j}} \cdots (X_n)_{\gamma_{nj}} \xi_j \right) \right) + \frac{\partial}{\partial x} u \left( \sum_{j=1}^m \gamma_{ij} c \left( (X_1)_{\gamma_{1j}} (X_2)_{\gamma_{2j}} \cdots (X_n)_{\gamma_{nj}} \xi_j \right) \right) \\ &= \frac{\partial}{\partial x} \left( \varphi D_w \frac{\partial}{\partial x} \left( \sum_{j=1}^m \gamma_{ij} c \left( (X_1)_{\gamma_{1j}} (X_2)_{\gamma_{2j}} \cdots (X_n)_{\gamma_{nj}} \xi_j \right) \right) \right) \end{aligned} \quad (126)$$

To obtain the conservation of charge, notice that we can multiply the equation for the  $i$ -th atom by his respective valence,  $\theta_i$ . Notice that there are  $n$  equations. We add all equations and we obtain:

$$\begin{aligned} & \sum_{i=1}^n \theta_i \frac{\partial}{\partial t} \left( \sum_{j=1}^m \gamma_{ij} c \left( (X_1)_{\gamma_{1j}} (X_2)_{\gamma_{2j}} \cdots (X_n)_{\gamma_{nj}} \xi_j \right) \right) + \\ & \sum_{i=1}^n \theta_i \frac{\partial}{\partial x} u \left( \sum_{j=1}^m \gamma_{ij} c \left( (X_1)_{\gamma_{1j}} (X_2)_{\gamma_{2j}} \cdots (X_n)_{\gamma_{nj}} \xi_j \right) \right) \\ &= \sum_{i=1}^n \theta_i \frac{\partial}{\partial x} \left( \varphi D_w \frac{\partial}{\partial x} \left( \sum_{j=1}^m \gamma_{ij} c \left( (X_1)_{\gamma_{1j}} (X_2)_{\gamma_{2j}} \cdots (X_n)_{\gamma_{nj}} \xi_j \right) \right) \right) \end{aligned} \quad (127)$$

Changing the order of sum in  $i$  and  $j$  we obtain

$$\begin{aligned} & \frac{\partial}{\partial t} \left( \sum_{j=1}^m \left( \sum_{i=1}^n \theta_i \gamma_{ij} \right) c \left( (X_1)_{\gamma_{1j}} (X_2)_{\gamma_{2j}} \cdots (X_n)_{\gamma_{nj}} \xi_j \right) \right) + \\ & \frac{\partial}{\partial x} u \left( \sum_{j=1}^m \left( \sum_{i=1}^n \theta_i \gamma_{ij} \right) c \left( (X_1)_{\gamma_{1j}} (X_2)_{\gamma_{2j}} \cdots (X_n)_{\gamma_{nj}} \xi_j \right) \right) \\ &= \frac{\partial}{\partial x} \left( \varphi D_w \frac{\partial}{\partial x} \left( \sum_{j=1}^m \left( \sum_{i=1}^n \theta_i \gamma_{ij} \right) c \left( (X_1)_{\gamma_{1j}} (X_2)_{\gamma_{2j}} \cdots (X_n)_{\gamma_{nj}} \xi_j \right) \right) \right) \end{aligned} \quad (128)$$

Using (123), we finally obtain:

$$\begin{aligned} & \frac{\partial}{\partial t} \left( \sum_{j=1}^m \xi_j c \left( (X_1)_{\gamma_{1j}} (X_2)_{\gamma_{2j}} \cdots (X_n)_{\gamma_{nj}} \right)^{\xi_j} \right) + \frac{\partial}{\partial x} u \left( \sum_{j=1}^m \xi_j c \left( (X_1)_{\gamma_{1j}} (X_2)_{\gamma_{2j}} \cdots (X_n)_{\gamma_{nj}} \right)^{\xi_j} \right) \\ &= \frac{\partial}{\partial x} \left( \varphi D_w \frac{\partial}{\partial x} \left( \sum_{j=1}^m \xi_j c \left( (X_1)_{\gamma_{1j}} (X_2)_{\gamma_{2j}} \cdots (X_n)_{\gamma_{nj}} \right)^{\xi_j} \right) \right). \end{aligned} \quad (129)$$

Notice that (129) is an equation for the unknown  $\sigma$ :

$$\frac{\partial}{\partial t} (\sigma) + \frac{\partial}{\partial x} u(\sigma) = \frac{\partial}{\partial x} \left( \varphi D_w \frac{\partial}{\partial x} (\sigma) \right). \quad (130)$$

If  $\sigma = 0$  initially, from the uniqueness of solution of partial differential equation, we prove that  $\sigma = 0$  is the only solution.  $\square$

## F Basic programs for calculation of the density and dielectric properties

### F.1 Program for $A_V$ obtained from Table in Donald Archer and Pelming Wang

Function AVeps(T, P)

rem T in K and P in MPa

coef3 = -1.63521E-15 \* T \* T \* T + 1.66821E-12 \* T \* T -  
- 0.000000000587862 \* T + 0.0000000664581

coef2 = 9.26251E-13 \* T \* T \* T - 0.000000000912623 \* T \* T -  
+ 0.000000341581 \* T - 0.00004174

coef1 = 5.53046E-11 \* T \* T \* T - 0.000000101197 \* T \* T -  
+ 0.000023077 \* T - 0.001447951

coef0 = -0.0000000716544 \* T \* T \* T + 0.0000929356 \* T \* T -  
- 0.027716004 \* T + 2.530009631

AVeps = coef3 \* P \* P \* P + coef2 \* P \* P -  
+ coef1 \* P + coef0

End Function

Function rhotp(T, P)

```

rem P in MPa and T in K, density in kg/m^3
Rem Experimental study of the p, V, T properties
Rem For temperatures in the range
' 323.15 to 773.15 K and pressures up to 200 MPa
' I. TANISHITA, K. WATANABE, J. K. IIMA, H. ISHII,
' K. OGUCHI, and M. UEMATSU"
Rem J. Chem. Thermodynamics (1976) 8 pp 1-20
Rem partial molar volume
aone = 0.000768687 * T + 0.14162221
atwo = -0.692035118 * T + 1213.365007
rhotp = aone * P + atwo
End Function

```

## F.2 Program for dielectric coefficient $\epsilon$ , obtained from Table in Donald Archer and Pelming Wang

```

Function epsi(T, P)
rem T in K and P in Mpa
coef3 = 1.21462E-14 * T * T * T - 1.36106E-11 * T * T -
+ 0.00000000512099 * T - 0.000000624514
coef2 = -0.000000000012255 * T * T * T + 0.0000000140519 * T * T -
- 0.0000054587 * T + 0.000684648
coef1 = 0.00000000264951 * T * T * T - 0.00000266152 * T * T -
+ 0.000859081 * T - 0.0529549
coef0 = -0.000000955266 * T * T * T + 0.00165457 * T * T -
- 1.09166 * T + 282.114
epsi = coef3 * P * P * P + coef2 * P * P -
+ coef1 * P + coef0
End Function

```

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