The effect of carbon dioxide in oil recovery from calcite reservoirs
Part II.[*]

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Abstract

We are interested in the effect of carbon dioxide in water flooding of light oil at high pressure in a calcite reservoir, representative for the presal formations off the coast of Brazil. We study this process initially in a 1-D setting in an oleic phase that includes carbon dioxide and an aqueous phase that contains all the ionic substances and dissolved mineral salts. By assuming chemical equilibrium we can describe the motion of all dissolved compounds in a limited number of transport equations of *master species*. Indeed, from the concentrations of the master species, chemical equilibrium determines the quantities of relevant solutes inclusive carbon dioxide, which is the only substance that is considered present in both phases. We use this model to determine the oil recovery when water is injected as a secondary recovery technique.To study this mechanism we formulate the conservation equations of hydrogen, twice oxygen minus hydrogen, chloride and decane. Therefore, we solve analytically and numerically these equations elucidating the effects of the injection of low salinity carbonated water into a reservoir containing oil equilibrated with high salinity carbonated water. We use PHREEQC (acronym of pH-REdox-Equilibrium C-program) to obtain the accurate equilibrium partition of neutral species that are soluble both in the oleic and the aqueous phase by application of the Krichevsky-Ilinskaya extension of Henry's law for solubility of gases in liquids. Using Gibbs phase rule it can be shown that the phase behavior only depends on the pH and the chloride concentration. The above mentioned equilibrium relations use Pitzer's activity coefficients to extend the validity up to 6M. We obtain the saturation, composition and the total Darcy velocity profiles. The significant new insight obtained is that by changing only the salinity in carbonated waterflooding the oil recovery can be enhanced.

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 [73] [74] supercritical gas injection, thermal methods [99] [112] [40] [110] and polymer [103] 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 [35], (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 (∼700 bars) make these reservoirs excellent candidates for high pressure miscible gas injection, e.g., CO_2 injection or carbonated water injection.

Recently much research has been done on low salinity water injection [7] [10] [62] [67] [95] [96] [104] [119] [118] [120] [116] 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% [41], but the effect of sulfate [106] depends on the chalk type and on the wettability of the rock [43]. 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 [78] [79] as a starting point.

There is also an increasing interest in the effect of injection of water minerals on the recovery efficiency [104]. Mixed-wet or weakly water-wet are often considered as optimum wetting conditions for oil recovery [58] [79]. The theory of wetting behavior is clearly explained in [55]. Contrary to sandstones, the majority of carbonate petroleum reservoirs are oil-wet [124]. The presence of asphaltenes [18] [19] [20] and their adsorption on kaolinite can render even a sandstone reservoir oil-wet [26]. The presence of a water film on the mineral surface may reduce the asphaltene adsorption [30], and induce more water-wet behavior. The presence of carboxylic acids [45] [46] [89] and amines in the oil determines the acid and base number [29]. 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 [14], [13]. 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 calaculations 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 equlibrium with each other. For the equilibrium in the aqueous phase with gaseouss 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 [90] model for activity coefficients. Some experimental methods are described in , [61]). The theory behind the calculations performed in ASPEN are summarized in chapter 8 of [90]. These experimental data can be used in ASPEN plus to obtain an optimal description of the phase behavior [122].

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 [25] [75] [87] [88] [101] [111]. An excellent data-base can be found in [42] and references cited therein (see also. Ananthaswamy and Atkinson [2]. Correct values are required if one extends geochemical behavior to other pressure and temperature regimes [11] [12]. An excellent overview of geochemistry can be found in [3] [64] and [109]. The general geochemical background is well explained in [5] [4] in combination with the accompanying software (PHREEQC) [84] [83] [98]. An overview of existing software for saturated and unsaturated transport problems in groundwater flow can be found in [114]. The solubility of carbon dioxide in electrolyte solutions can be found in [23] [94] [93] [92]. Extending Henry's law [97] requires the pressures to be replaced by fugacities [85] and the mole fractions to corrected for the activity coefficient [24] [115] .

Non-electrolyte solutions depend on the ionic strength as to their solubility [71]. The same coefficients can be used to determine the ionic strength dependence of the partial molar volume [53] [54] [77] [86]. Relevant coefficients can also be found in [83] [84]. 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 [49] [60].

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 [39]. Noh et al. [81], use fractional flow theory in order to give a mathematical formalism of combined geochemical and multiphase flow. Holstadt [56] gives a general framework for multi-species, multi-phase and non-isothermal flow, focusing on chemical reactions and transport. Evje et al. [37] propose a mathematical model for the weakening of chalk reservoirs due to chemical reactions. It consists of convection-diffusion transport coupled to dissolution/precipation processes. Evje and Hiorth [36], 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 [22]. In another paper [38], 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 [16] [17] [52].

In this paper, we obtain the analytic solution in the form of the Riemann solution, which consists basically in applying the method of characteristics (MOC). This method seeks analytical solutions of the CLICDOW Model similarly to the those treated in [28, 117, 21, 66, 91, 32, 51, 59]. The Riemann solution consists in a concatenation of rarefaction and shock waves implementing certain admissibility conditions ([65, 82, 47, 68, 69]). We, also provide comparisons obtained by means of the numerical solver COMSOL, which was useful for the verification of the analytical and numerical solutions.

In the CLICDOW model coefficient in the system of conservation laws are estimated by means of PHREEEQC program ([83, 84]). This procedure is extremely useful because allows to include in a unify manner the geochemistry, the equilibrium reactions and the charges balance. Also, the method employed is a robust recovery procedure that serves to study more complex situation as for example to include more chemical species in the system. In this way we reduce the mathematical complexity associated with considering the large number of physical constraints and parameters which are included in PHREEEQC program.

By means of numerical and analytical methods we aim in this paper at quantifying the recovery improvement when carbonated water equilibrated at low salinity is injected in a reservoir that contains carbonated brine in equilibrium with an oleic phase and carbon dioxide. Section 2 gives the physical model and uses Gibbs phase rule to show that there are only two degrees of freedom (e.g. pH and $^{-}$), which determine the composition. Section 3 gives some details about relative permeabilities. Section 4 gives the conservation equations in terms of an inorganic hydrogen balance, an organic carbon (decane) plus hydrogen balance, twice oxygen minus hydrogen (to eliminate the water) balance and the chloride balance. The flow is determined by two-phase Darcy's law. Section 5 gives the model results in terms of the pH, the chloride concentration, the water saturation and the total velocity. The calculation suggests that a low salinity carbonated water flood improves the recovery with respect to an iso-salinity carbonated water flood. Section 6 draw results obtained with COMSOL program. We end with some conclusions in Section 7.

Appendix A gives the definitions of activities and the equations for the activity coefficients. It also describes how to convert activities to molalities. Appendix B gives the temperature dependent expressions for the equilibriium constants for the dissolved components. The partition of carbon dioxide between the oleic and aqueous phase, using Henry's law can be found the first part of this report. 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 Langmuir adsorption isotherms of the surface complexes can be found the Part I of the presented report.

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 form 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., [76]) that the number of degrees of freedom is given by

$$N_f = N_s - N_r - N_c + 2 - p, \tag{1}$$

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 arbitrariness (judgment) in enumerating the relevant aqueous species; we follow Appelo and Parkhurst [83] and [4] 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. The programme tells us that when we add water, $CaCO_3\,(solid)$ and $NaCl$, 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 $CaCO3$ in the solid phase is denoted by $c_{r,CaCO_3}$, which is constant.

2.1.1 Equilibrium concentrations in the aqueous phase

We consider the following eight ($N_r = 8$) equilibrium reactions in the aqueous phase [63], [83].

$$\begin{gathered}
(CO_2)_{aq} + H_2O \rightleftharpoons HCO_3^- + H^+ \\
HCO_3^- \rightleftharpoons CO_3^{2-} + H^+ \\
H_2O \rightleftharpoons OH^- + H^+ \\
(CaCO_3)_{aq} \rightleftharpoons Ca^{2+} + CO_3^{2-} \\
Ca^{2+} + H_2O \rightleftharpoons CaOH^+ + H^+ \\
CO_3^{2-} + Ca^{2+} + H^+ \rightleftharpoons CaHCO_3^+ \\
Na^+ + CO_3^{2-} \rightleftharpoons NaCO_3^- \\
Na^+ + HCO_3^- = NaHCO_3
\end{gathered} \tag{2}$$

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 defined in Eqs. (**??** - **??**). The values of the equilibrium constants can be found in Section B. 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

$$\left(\begin{array}{c} 2m_{a,CO_3^{2-}} + m_{a,HCO_3^-} + m_{a,OH^-} + m_{a,NaCO3^-} + m_{a,Cl^-} \\ = 2m_{a,Ca^{2+}} + m_{a,H^+} + m_{a,Ca(HCO_3)^+} + m_{a,Na^+} + m_{a,CaOH^+} \end{array} \right), \tag{5}$$

The molal concentrations can be converted to molar concentrations as explained in Eq. (73) in Appendix A.3. Such conversions couple each concentration to all others.

The charge balance equation can be derived from the mass balance equations (see Appendix **??**). 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 (∼55.5 mole/liter) is much higher than the other concentrations, causing numerical problems in simulations.

3 Relative permeabilities

3.1 Relative permeabilities and viscosities

Relative permeabilities describe the reduction in permeability due to the presence of the other phase. Relative oil permeabilities [72] pp 82, [27] of strongly water-wet systems remain close to one, when the oil saturation drops to values of around 0.7, i.e., when the water saturation is 5-10% above connate water saturation $S_w \approx 0.20 - 0.25$ (highest water saturation at which water does not flow). On the other hand at residual oil saturation $S_o \approx 0.25$ the relative permeability to water can be as low as 10% of the single phase permeability. The cross-over point, i.e. the saturation at which the relative oil permeability and relative water permeability are equal is above 50% water saturation. For strongly oil-wet systems the oil permeability starts to reduce when the water saturation becomes higher than the connate water saturation. The relative permeability of water at residual oil saturation is greater than 50% and approaching 100%. The cross-over point when water and oil permeability are equal is less than 50%.

3.1.1 Relative permeabilities

There are a number of semi-empirical relations Reservoir engineering handbook, [1] that one can use when (more the rule than the exception) experimental data of relative permeabilities are lacking. We disregard the viscosity dependence of the relative permeabilities [31]; however, the lubrication effect at high oil viscosities can become significant [57]. General observations are that in water-wet media, oil will occupy the larger pores and obstruct the flow of water, leading to low relative water-permeabilities. A low relative water permeability leads to a favorable mobility ratio and more stable displacement. In oil-wet media oil will occupy the smaller pores and wet the pore walls of the larger pores, leading to a higher value of the relative water permeability[57]. Initial or connate water saturations in water-wet media are usually high, i.e., 20-25%, whereas initial water saturations in oil-wet media are small 10-15%. Consequently residual oil saturations in water-wet media are usually high, whereas they are low in oil-wet reservoirs. This leads to a lower ultimate recovery for water-wet media. The iso-permeability saturation point $S_{w,o=w}$ where the oil relative permeability is equal occurs at saturations below $S_{w,o=w} < 0.5$ for oil-wet media and at saturations $S_{w,o=w} > 0.5$ for water-wet media [55]. It is the purpose of this section to relate simple expressions of relative permeability to porous media properties, with the idea that they can be used to predict the consequence of these properties for 1-D recovery predictions.

For illustration of the effect of only the viscosity the oversimplified relations (so-called power law relative permeabilities) can be used

$$\begin{aligned} k_{rw}\left(S_w\right) &= k_{rw}^{'} S_{we}^{n_w} \\ k_{ro}\left(S_w\right) &= k_{ro}^{'} S_{oe}^{n_o} \end{aligned} \tag{6}$$

where $S_{we} = (S_w - S_{wc})/(1 - S_{wc} - S_{or})$ and $S_{oe} = (S_o - S_{or})/(1 - S_{wc} - S_{or})$ and where k'_{rw} and k'_{ro} are the end-point permeabilities respectively for water and oil. Moreover the use of equation 6 requires an estimate of the connate water saturation S_{wc} and of the residual oil saturation S_{or}. We can find the connate water saturation from a plot of ln k_{rw} versus the water saturation and find the water saturation at which the relative permeability dramatically decreases. Indeed for water-wet media the relative permeability is never zero. The exponents n_w and n_o can assume values between one and seven.

Equations that honor more explicitly the sorting of grain sizes

$$k_{rw} = k^{'}_{rw} S_{we}^{2/\lambda+3}$$
$$k_{ro} = k^{'}_{ro} (1 - S_{we})^2 \left(1 - S_{we}^{2/\lambda+1}\right) \tag{7}$$

are called the Brooks-Corey relations, which are in fact a modified form of the Brooks-Corey relations [15]. In the original form Brooks (personal communication) and Corey preferred the effective saturation as $S_{we} = (S_w - S_{wc})/(1 - S_{wc})$ and used $k'rw = k'ro = 1$. In this equation λ is the sorting factor. Typical values are $0.2 < \lambda < 7$. The parameter λ can be obtained experimentally by plotting the logarithm of log S_{we} versus logarithm of the capillary pressure log (P_c), where $P_c = P_{cb} S_{we}^{-1/\lambda}$. Such a plot would also enable to observe for which value of the connate water saturation S_{wc}, the log-log plot will be closest to a straight line. The determination of the sorting factor λ does not depend on whether the residual oil saturation is considered zero or has some finite value. We will continue to discuss the modified form with non-zero residual oil saturation. The end point permeability k'_{rw} for water can be related to the initial water saturation S_{wi} or initial oil saturation S_{oi}. As intermediate step we relate the residual saturation S_{or} to the initial water S_{wi} saturation by the empirical relation [70]

$$S_{or} = (Z_{orw} + A_{orw} S_{wi}^{M_{orw}})(1 - S_{wi})^{L_{orw}}, \tag{8}$$

where $Z_{orw} = 0.1125$, $A_{orw} = 1.568$, $M_{orw} = 0.7321$ and $L_{orw} = 1.404$. The parameters are obtained by fitting Eq. (8) to data extracted from Fig. 5 in [34]. We use Eq. (A9) from [70] to obtain

$$k^{'}_{rw} = \frac{(1 - S_{or} - S_{wi})^{L_{wko}}}{(1 - S_{or} - S_{wi})^{L_{wko}} + E_{wko} S_{or}^{T_{wko}}},, \tag{9}$$

where $L_{wko} = 2.636$, $E_{wko} = 0.07667$, and $T_{wko} = 0.5413$. The parameters are obtained by fitting Eq. (9) to data extracted from Fig. 6 in [34]. The residual oil saturation S_{or} can also be expressed in terms of the USBM wettability index. Spiteri et al. [105] give a new model of trapping and relative permeability hysteresis for all wetting conditions. The parameters used here are borrowed from the so-called LET models of relative permeability named after its originators Lomeland, Ebeltoft, and Thomas [34], Lomeland et al. (2012)). In these models the connate water saturation S_{wc} is pragmatically similar to the initial water saturation S_{wir} that is established at high capillary pressure using a porous plate or centrifuge.

The USBM wetting index is determined by the 10-base logarithm of the ratio of area of the capillary pressure function above zero for the drainage curve and the area below zero for the imbibition curve. The system is water-wet when the index is between 0.3 and 1, weakly water wet when the index is between 0 and 0.3, weakly oil wet when the index is between -0.3 and 0, and oil wet when the Amott-Harvey index is between -1 and -0.3. The relative permeabilities using the LET correlation are

$$k_{ro} = k^{'}_{ro} \frac{(1 - S_{we})^{L_o}}{(1 - S_{we})^{L_o} + E_o S_{we}^{T_o}}$$
$$k_{rw} = k^{'}_{rw} \frac{S_{we}^{L_w}}{S_{we}^{L_w} + E_w (1 - S_{we})^{T_w}} \tag{10}$$

Only the connate water saturation S_{wc}, the residual oil saturation S_{or} and the end point permeabilities $k'_{rw}, k'_{ro} = 1$ have a physical meaning. The other six parameters determine the shapes of the curves.

Here L_w, L_o determine the behavior at low effective water- (oil-, $S_{oe} = 1 - S_{we}$) saturations, whereas T_w and T_o determine the behavior at high effective water (S_{we}) (oil, $S_{oe} = 1 - S_{we}$) saturations. The parameters E_w, E_o determine the transition point between high and low effective saturations.

4 Ionic Carbon Dioxide Oil Water with Salt (ClICDOW)

4.1 Physical model

We consider low salinity injection (0.01 $mol/liter$ NaCl, with CO_2 saturated at a $pH = 2.74$) into an inert rock (1D) filled with an oleic phase that contains both oil and dissolved carbon dioxide as well as a brine (0.3 $mol/liter$) phase also at $pH = 2.74$. Injection and initial fluids contain carbon dioxide, the ensuing ions and sodium chloride. The initial fluid also contains oil (decane). We assume chemical equilibrium in both the aqueous phase and the oleic phase and equilibrium of carbon dioxide between phases Eq. . The ions and water are only present in the aqueous phase, decane is only present in the oleic phase. Dissolution of oil (decane) in the aqueous phase is disregarded. Only carbon dioxide can be present both in the oleic phase and the aqueous phase. The injected fluid has a high carbon dioxide content, specified by the injection pH and salt concentration. The flow is governed by Darcy's law (Lorentz (1912), Muskat and Meres (1936), Hubbert (1956)) extended to two phase (Honarpour, (1986)) and conservation laws for chemical species (Appelo and Postma (2005), Holstad (2000)). We consider one dimensional incompressible flow.

4.2 Equation balance equations for the Ionic Carbon Dioxide-Oil-Water (ClICDOW) model

We derive the model equations from the conservation law for total inorganic carbon, the total hydrogen, the total oxygen and the total organic carbon. The conservation laws hold for the four lumped components (called master species) that do not convert into each other. As a result of the charge balance equation, which can be derived from the conservation laws we choose four of these equations, viz. the total hydrogen (H(1)), the twice oxygen minus hydrogen equation (to eliminate the H2O), the chloride ion equation and the total organic carbon (C(-4)) equation. The composition obtained with PHREEQC preserved the charge balance. The total molality of hydrogen can be expressed in terms of the other molalities $m_{a;j}$ $(a = phase, j = component)$ as follows $m_{a;H(1)}[mol/kgwater] = m_{a;HCO3} + m_{a;H} + m_{a;OH} + 2m_{a;H2O}$. The total molality of oxygen is given by $m_{a;O(-2)}[mol/kgwater] = 2m_{a;CO2} + 3m_{a;CO3} + 3m_{a;HCO3} + m_{a;OH} + m_{a;H2O}$.Taking the difference $m_{a,O-H} = m_{a;H(1)} - 2m_{a;O(-2)}$, we obtain $m_{a;O-H} = m_{a;H} - m_{a;OH} - 4m_{a;CO2} - 6m_{a;CO3} - 5m_{a;HCO3}$, an equation from which the H2O has been eliminated. We do not given the total carbon equation as it is already incorporated due to the conservation of charge. The total molar concentration in the aqueous phase is given by $m_{a;tot} = m_{a;CO2} + m_{a;CO3} + m_{a;HCO3} + m_{a;H} + m_{a;OH} + m_{a;H2O} + m_{a;Cl-}$ and we find the aqueous phase mole fractions $x_{a;i}$ as $x_{a;H(1)} = m_{a;H(1)}/m_{a;tot}$, $x_{a;O-H} = m_{a;O-H}/m_{a;tot}$, etc.

All mole fractions will be functions of only two concentrations, which we choose to be the pH and the chloride concentration. The molar concentrations of components j for the aqueous phase a;j are the product of the molar phase density w times the mole fractions of component j. The masterspecies equations include the total carbon, the total hydrogen, the total oxygen and the decane equation. The total hydrogen equation reads

$$\partial_t \left(\varphi S_w \rho_{a},_{H(1)}\right) + \partial_x \left(u f_w \rho_{a,H(1)}\right) = \partial_x \varphi D_m S_w \partial_x \rho_{a,H(1)}. + \partial_x D_{cap} \rho_{a,H(1)}. \partial_x S_w \tag{11}$$

where we include the molecular diffusion D_m and capillary diffusion D_{cap} term. We assume that the molecular and capillary diffusion term is constant. The hydrogen minus twice oxygen equation reads

$$\begin{aligned}\partial_t\left(\varphi S_w \rho_a,_{O-H}\right)+4\partial_t\left(\varphi S_o \rho_{o,CO_2}\right)+\partial_x\left(u f_w \rho_{a,O-H}\right)+4\partial_x\left(u f_o \rho_{o,CO_2}\right)=\\ \partial_x \varphi D_m S_w \partial_x \rho_{a,O-H}+\partial_x \varphi D_m S_o \partial_x \rho_{o,CO_2.}+\partial_x D_{cap} \rho_{a,C(4).} \partial_x S_w+\partial_x D_{cap} \rho_{o,CO_2.} \partial_x S_o\end{aligned} \tag{12}$$

where we again include the molecular diffusion D_m and capillary diffusion D_{cap} term. For the total organic carbon we have

$$\partial_t\left(\varphi S_o \rho_{o,C(-4)}\right)+\partial_x\left(u f_o \rho_{o,C(-4)}\right)=\partial_x \varphi D_o S_o \partial_x \rho_{o,C(-4).}+\partial_x D_c \rho_{o,C(-4).} \partial_x S_o \tag{13}$$

The organic carbon ($C(-4)$) equation (where in our case $C(-4) = decane$) reads

$$\begin{aligned}\partial_t\left(\varphi S_o \rho_o,_{C(-4)}\right)+\partial_x\left(\ u f_o \rho_{a,C(-4)}\right)=\\ \partial_x \varphi D_m S_w \partial_x \rho_{o,C(-4).}+\partial_x D_{cap} \rho_{o,C(-4).} \partial_x S_w+\partial_x D_{cap} \rho_{o,CO_2.} \partial_x S_o\end{aligned} \tag{14}$$

The chloride equation reads

$$\partial_t\left(\varphi S_w \rho_a,_{Cl(-1)}\right)+\partial_x\left(u f_w \rho_{a,Cl(-1)}\right)=\partial_x \varphi D_m S_w \partial_x \rho_{a,Cl(-1).}+\partial_x D_{cap} \rho_{a,Cl(-1).} \partial_x S_w \tag{15}$$

where $\rho_a,_{Cl(-1)}$ ([4]) is the molar concentration of the chloride ion in the aqueous phase. Initial conditions for all quantities X are given by

$$X = X_{init} + (1 - 0.5 * (1 + \tanh((x - 0.1)/0.05)))(X_{bound} - X_{init}), \tag{16}$$

where $pH_{init} = 2.74$, $Cl_{init} = 0.3[mol/liter]$, $Cl_{bound} = 0.01[mol/liter]$, $S_{init} = S_{wc} = 0.15$, $S_{bound} = 1 - S_{or} = 1.0$, and $u_{inj} = 10^{-5}[m/s]$.

5 Riemann Solution for ClICDOW model

The transport equations disregarding the diffusion terms are

For the total hydrogen equation

$$\partial_t\left(\varphi S_w \rho_{a,H(1)}\right)+\partial_x\left(u f_w \rho_{a,H(1).}\right)=0. \tag{17}$$

Total chloride equation

$$\partial_t\left(\varphi S_w \rho_{a,Cl(-1)}\right)+\partial_x\left(u f_w \rho_{a,Cl(-1).}\right)=0. \tag{18}$$

If we subtract the hydrogen equation from twice the oxygen equation and denoting $\rho_{a,O-H} = 2\rho_{a,O(2)} - \rho_{a,H(1)}$, we obtain

$$\begin{aligned}&\partial_t\left(\varphi S_w \rho_{a,O-H}\right)+4\partial_t\left(\varphi S_o \rho_{o,CO_2}\right)\\ &+\partial_x\left(u f_w \rho_{a,O-H}\right)+4\partial_x\left(u f_o \rho_{o,CO_2.}\right)=0,\end{aligned} \tag{19}$$

and the organic carbon equation

$$\partial_t\left(\varphi S_o \rho_{o,C(-4)}\right)+\partial_x\left(u f_o \rho_{o,C(-4)}\right)=0, \tag{20}$$

Then the accumulation functions G are

$$G = (\varphi S_w \rho_{a,H(1)}, \varphi S_w \rho_{a,Cl(-1)}, \varphi S_w \rho_{a,O-H} + 4 S_o \rho_{o,CO_2}, \varphi S_o \rho_{o,C(-4)}), \tag{21}$$

and the flux function $F = u\widehat{F}$ as

$$\widehat{F} = (f_w \rho_{a,H(1)}, f_w \rho_{a,Cl(-1)}, f_w \rho_{a,O-H} + 4 S_o \rho_{o,CO_2}, f_o \rho_{o,C(-4)}). \tag{22}$$

5.1 System of conservation laws

Then the system of hyperbolic equations (17)-(20) for $\rho_{a,2O-H} = 2\rho_{a,O(2)} - \rho_{a,C(4)}$, $\rho_{a,H(1)}$ ρ_{o,CO_2}, $\rho_{a,Cl(-1)}$ and decane $(\rho_{a,C(-4)})$ disregarding the diffusion term are rewritten as:

$$\frac{\partial G(W)}{\partial t} + \frac{\partial uF(W)}{\partial x} = 0, \tag{23}$$

Taking $W = (U, u)$ with $U = (S_w, pH, [Cl])$ the accumulation functions can be written in separate variables as $G(\phi, U) = \varphi \widehat{G}(U)$, using the fact that the fluxes depend only on U, i.e., $F(U, u) = u\widehat{F}(U)$. So, we have $(S_w, [Cl-], [H+], u)$ unknowns and four equations.

5.2 Riemann problem

We are interested in the Riemann problem associated to (23), that is the solution of these equations with piecewise constant initial data

$$\begin{cases} (Sw_L, pH_L, Cl_L, u_L) & if \;\; x > 0, \\ (Sw_R, pH_R, Cl_R, \;\cdot\;) & \text{if } \; x < 0. \end{cases}$$

we do not impose conditions on the variable u_R because it is obtained from the other variables and the solution in the system

5.2.1 Method of characteristics

The method of characteristics 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 $W = (S_w, [Cl-], [H+])$ are functions of the variable $\xi = x/t$. Along the characteristic curves we have

$$dW = \frac{\partial W}{\partial t} dt + \frac{\partial W}{\partial x} dx. \tag{24}$$

Using the system of conservation law (17)-(20), we obtain along characteristic curves for $i = 1, 2, 3$

$$\frac{\partial G_i}{\partial W}\frac{dW}{dt} + \frac{\partial F_i}{\partial W}\frac{dW}{dx} = 0, \tag{25}$$

where

$$\frac{\partial G_i}{\partial W} = \frac{\partial G_i}{\partial s_w}\frac{ds_w}{d\xi} + \frac{\partial G_i}{\partial y}\frac{dy}{d\xi} + \frac{\partial G_i}{\partial u}\frac{du}{d\xi}, \quad \frac{\partial F_i}{\partial W} = \frac{\partial F_i}{\partial s_w}\frac{ds_w}{d\xi} + \frac{\partial F_i}{\partial y}\frac{dy}{d\xi} + \frac{\partial F_i}{\partial u}\frac{du}{d\xi}. \tag{26}$$

From now we rewrite above system of equations with another notation such that mathematical manipulation are more easily to do. Let us denote by $C_1 = \rho_{a,H(1)}$, $C_2 = 0$,$C_3 = \rho_{a,Cl(-1)}$, $C_4 = 4\rho_{o,CO_2}$, $C_5 = \rho_{a,O-H} = 2\rho_{a,O(2)}$, $C_6 = \rho_{o,C(-4)}$ and $C_7 = 0$. We consider a system evolving chemical species $\theta = (\theta_1, \theta_2) = ([Cl-], [H+])$, water saturation s and Darcy's velocity u. We denote our phase space as $\Omega = \{(s, \theta)\}$. Each concentration is given by $C_i = C_i(\theta)$, for $i = 1, \cdots, 7$ and the system of equations

(17)-(20) can rewritten as:

$$\frac{\partial}{\partial t}(S_wC_1)+\frac{\partial}{\partial x}(uf_wC_1)=0, \tag{27}$$

$$\frac{\partial}{\partial t}((1-S_w)C_2+S_wC_3)+\frac{\partial}{\partial x}u((1-f_w)C_2+f_wC_3)=0, \tag{28}$$

$$\frac{\partial}{\partial t}((1-S_w)C_4+S_wC_5)+\frac{\partial}{\partial x}u((1-f_w)C_4+f_wC_5)=0 \tag{29}$$

$$\frac{\partial}{\partial t}((1-S_w)C_6+S_wC_7)+\frac{\partial}{\partial x}u((1-f_w)C_6+f_wC_7)=0. \tag{30}$$

Denoting $A=\dfrac{\partial F}{\partial U}$ and $B=\dfrac{\partial G}{\partial U}$, the system of eigenvalues is written as $A\vec{r}=B\lambda\vec{r}$, where $r=(S_w,\theta,u)^T$ and B, A:

$$B=\begin{pmatrix} C_1 & S_w\frac{\partial C_1}{\partial\theta_1} & S_w\frac{\partial C_1}{\partial\theta_2} & 0\\ C_3-C_2 & (1-S_w)\frac{\partial C_2}{\partial\theta_1}+S_w\frac{\partial C_3}{\partial\theta_1} & (1-S_w)\frac{\partial C_2}{\partial\theta_2}+S_w\frac{\partial C_3}{\partial\theta_2} & 0\\ C_5-C_4 & (1-S_w)\frac{\partial C_4}{\partial\theta_1}+S_w\frac{\partial C_5}{\partial\theta_1} & (1-S_w)\frac{\partial C_4}{\partial\theta_2}+S_w\frac{\partial C_5}{\partial\theta_2} & 0\\ C_7-C_6 & (1-S_w)\frac{\partial C_6}{\partial\theta_1}+S_w\frac{\partial C_7}{\partial\theta_1} & (1-S_w)\frac{\partial C_6}{\partial\theta_2}+S_w\frac{\partial C_7}{\partial\theta_2} & 0 \end{pmatrix}, \tag{31}$$

$$A=\begin{pmatrix} uC_1\frac{\partial f_w}{\partial s} & uf\frac{\partial C_1}{\partial\theta_1} & uf\frac{\partial C_1}{\partial\theta_2} & f_wC_1\\ u(C_3-C_2)\frac{\partial f_w}{\partial s} & u(1-f_w)\frac{\partial C_2}{\partial\theta_1}+uf_w\frac{\partial C_3}{\partial\theta_1} & u(1-f_w)\frac{\partial C_2}{\partial\theta_2}+uf_w\frac{\partial C_3}{\partial\theta_2} & (1-f_w)C_2+f_wC_3\\ u(C_5-C_4)\frac{\partial f_w}{\partial s} & u(1-f_w)\frac{\partial C_4}{\partial\theta_1}+uf_w\frac{\partial C_5}{\partial\theta_1} & u(1-f_w)\frac{\partial C_4}{\partial\theta_2}+uf\frac{\partial C_5}{\partial\theta_2} & (1-f_w)C_4+f_wC_5\\ u(C_7-C_6)\frac{\partial f_w}{\partial s} & u(1-f_w)\frac{\partial C_6}{\partial\theta_1}+uf\frac{\partial C_7}{\partial\theta_1} & u(1-f_w)\frac{\partial C_6}{\partial\theta_2}+uf_w\frac{\partial C_7}{\partial\theta_2} & (1-f_w)C_6+f_wC_7 \end{pmatrix} \tag{32}$$

To obtain the eigenvalues we solve $det(A-\lambda B)=0$, where $A-\lambda B$ is:

$$\begin{pmatrix} C_1\xi_1 & \xi_3\frac{\partial C_1}{\partial\theta_1} & \xi_3\frac{\partial C_1}{\partial\theta_2} & f_wC_1\\ (C_3-C_2)\xi_1 & \xi_2\frac{\partial C_2}{\partial\theta_1}+\xi_3\frac{\partial C_3}{\partial\theta_1} & \xi_2\frac{\partial C_2}{\partial\theta_2}+\xi_3\frac{\partial C_3}{\partial\theta_2} & (1-f_w)C_2+f_wC_3\\ (C_5-C_4)\xi_1 & \xi_2\frac{\partial C_4}{\partial\theta_1}+\xi_3\frac{\partial C_5}{\partial\theta_1} & \xi_2\frac{\partial C_4}{\partial\theta_2}+\xi_3\frac{\partial C_5}{\partial\theta_2} & (1-f_w)C_4+f_wC_5\\ (C_7-C_6)\xi_1 & \xi_2\frac{\partial C_6}{\partial\theta_1}+\xi_3\frac{\partial C_7}{\partial\theta_1} & \xi_2\frac{\partial C_6}{\partial\theta_2}+\xi_3\frac{\partial C_7}{\partial\theta_2} & (1-f_w)C_6+f_wC_7 \end{pmatrix} \tag{33}$$

where

$$\xi_1=\left(u\frac{\partial f_w}{\partial S_w}-\lambda\right),\quad \xi_2=u(1-f_w)-\lambda(1-S_w)\quad\text{and}\quad \xi_3=uf_w-\lambda S_w.$$

Denoting each row of matrix $A-\lambda B$ by L_i, for $i=1,2,\cdots,4$, we can substitute each L_i, for $i=2,\cdots,4$

by $L_i(-C_1) + L_1(C_{2i-1} - C_{2i-2})$ and we obtain:

$$\begin{pmatrix} C_1\xi_1 & \xi_3\dfrac{\partial C_1}{\partial\theta_1} & \xi_3\dfrac{\partial C_1}{\partial\theta_2} & f_wC_1 \\ 0 & \xi_3\eta_{21} - \xi_2C_1\dfrac{\partial C_2}{\partial\theta_1} & \xi_3\eta_{22} - \xi_2C_1\dfrac{\partial C_2}{\partial\theta_2} & -C_1C_2 \\ 0 & \xi_3\eta_{31} - \xi_2C_1\dfrac{\partial C_4}{\partial\theta_1} & \xi_3\eta_{32} - \xi_2C_1\dfrac{\partial C_4}{\partial\theta_2} & -C_1C_4 \\ 0 & \xi_3\eta_{41} - \xi_2C_1\dfrac{\partial C_6}{\partial\theta_1} & \xi_3\eta_{42} - \xi_2C_1\dfrac{\partial C_6}{\partial\theta_2} & -C_1C_6 \end{pmatrix}, \tag{34}$$

where

$$\eta_{ij} = -\frac{\partial C_1}{\partial\theta_j}(C_{2i-1} - C_{2i-2}) + C_1\frac{\partial C_{2i-1}}{\partial\theta_j}$$

Using that $C_2 = 0$, we obtain

$$\begin{pmatrix} C_1\xi_1 & \xi_3\dfrac{\partial C_1}{\partial\theta_1} & \xi_3\dfrac{\partial C_1}{\partial\theta_2} & f_wC_1 \\ 0 & \xi_3\eta_{21} & \xi_3\eta_{22} & 0 \\ 0 & \xi_3\eta_{31} - \xi_2C_1\dfrac{\partial C_4}{\partial\theta_1} & \xi_3\eta_{32} - \xi_2C_1\dfrac{\partial C_4}{\partial\theta_2} & -C_1C_4 \\ 0 & \xi_3\eta_{41} - \xi_2C_1\dfrac{\partial C_6}{\partial\theta_1} & \xi_3\eta_{42} - \xi_2C_1\dfrac{\partial C_6}{\partial\theta_2} & -C_1C_6 \end{pmatrix}, \tag{35}$$

Substituting each L_3 by $L_3C_6 - L_4C_4$, we obtain:

$$\begin{pmatrix} C_1\xi_1 & \xi_3\dfrac{\partial C_1}{\partial\theta_1} & \xi_3\dfrac{\partial C_1}{\partial\theta_2} & fC_1 \\ 0 & \xi_3\eta_{21} & \xi_3\eta_{22} & 0 \\ 0 & \xi_3\chi_3 + \xi_2\chi_1 & \xi_3\chi_4 + \xi_2\chi_2 & 0 \\ 0 & \xi_3\eta_{41} - \xi_2C_1\dfrac{\partial C_6}{\partial\theta_1} & \xi_3\eta_{42} - \xi_2C_1\dfrac{\partial C_6}{\partial\theta_2} & -C_1C_6 \end{pmatrix}, \tag{36}$$

where

$$\chi_1 = C_1(C_4\frac{\partial C_6}{\partial\theta_1} - C_6\frac{\partial C_4}{\partial\theta_1}), \tag{37}$$

$$\chi_2 = C_1(C_4\frac{\partial C_6}{\partial\theta_2} - C_6\frac{\partial C_4}{\partial\theta_2}), \tag{38}$$

$$\chi_3 = C_6\eta_{31} - C_4\eta_{41}$$

$$\chi_4 = C_6\eta_{32} - C_4\eta_{42}$$

The determinant D of matrix in 36 is given by

$$D = -(C_1)^2C_6\xi_1\xi_3 det\begin{pmatrix} \eta_{21} & \eta_{22} \\ \xi_3\chi_3 + \xi_2\chi_1 & \xi_3\chi_4 + \xi_2\chi_2 \end{pmatrix}. \tag{39}$$

Thus the first eigenvalues satisfy $\xi_1 = 0$ so we have

$$\lambda_{S_w} = u\frac{\partial f_w}{\partial S_w}, \tag{40}$$

associated to the saturation wave. Second eigenvalue satisfy $\xi_3 = 0$, so we obtain

$$\lambda_{Cl} = u\frac{f_w}{S_w}. \tag{41}$$

This eigenvector $r_{Cl} = (r^1_{Cl}, r^2_{Cl}, r^3_{Cl}, r^4_{Cl})$ associated to λ_{Cl} satisfy

$$\begin{pmatrix} C_1(\lambda_{S_w} - \lambda_{Cl}) & 0 & 0 & fC_1 \\ 0 & 0 & 0 & 0 \\ 0 & \xi_2\chi_1 & \xi_2\chi_2 & 0 \\ 0 & -\xi_2 C_1\dfrac{\partial C_6}{\partial\theta_1} & -\xi_2 C_1\dfrac{\partial C_6}{\partial\theta_2} & -C_1C_6 \end{pmatrix} \begin{pmatrix} r^1_{Cl} \\ r^2_{Cl} \\ r^3_{Cl} \\ r^4_{Cl} \end{pmatrix} = 0. \tag{42}$$

Solving system in (42) we obtain

$$r^1_{Cl} = -fC_1\chi_2(uf_o - (f_w/S_w)S_o)\left(\frac{\partial C_6}{\partial\theta_2}(\chi_1/\chi_2) - \frac{\partial C_6}{\partial\theta_1}\right) \tag{43}$$

$$r^2_{Cl} = C_6\chi_2(\lambda_{S_w} - \lambda_{Cl}) \tag{44}$$

$$r^3_{Cl} = \chi_1 C_6(\lambda_{S_w} - \lambda_{Cl})\left(\frac{\partial C_6}{\partial\theta_2}(\chi_1/\chi_2) - \frac{\partial C_6}{\partial\theta_1}\right) \tag{45}$$

$$r^4_{Cl} = \chi_2(\lambda_{S_w} - \lambda_{Cl})\left(\frac{\partial C_6}{\partial\theta_2}(\chi_1/\chi_2) - \frac{\partial C_6}{\partial\theta_1}\right), \tag{46}$$

where χ_1 and χ_2 are given in (37) and (38).

Third eigenvalues satisfy:

$$det\begin{pmatrix} \eta_{21} & \eta_{22} \\ \xi_3\chi_3 + \xi_2\chi_1 & \xi_3\chi_4 + \xi_2\chi_2 \end{pmatrix} = 0, \tag{47}$$

We postulate that the eigenvalues have the general form:

$$\lambda_\Delta = u\frac{(1-f_w) - \Delta}{(1-S_w) - \Delta}. \tag{48}$$

In fact, substituting λ_Δ given by (48) in ξ_2 and ξ_3, we obtain:

$$\xi_2 = u(1-f_w) - \lambda(1-S_w) = -u\Delta\frac{(1-f_w) - (1-S_w)}{1 - S_w - \Delta}. \tag{49}$$

and

$$\xi_3 = uf_w - \lambda S_w = -u(1-\Delta)\frac{1 - f_w - (1-S_w)}{1 - S_w - \Delta} \tag{50}$$

Substituting ξ_2 and ξ_3 in (47), after some calculations we obtain:

$$det\begin{pmatrix} \eta_{21} & \eta_{22} \\ (1-\Delta)\chi_3 + \Delta\chi_1 & (1-\Delta)\chi_4 + \Delta\chi_2 \end{pmatrix} = 0, \tag{51}$$

since we assume that $(1 - f_w - (1 - S_w))/(1 - S_w - \Delta) \neq 0$. After some calculations we obtain

$$\Delta = \frac{\eta_{21}(C_6\eta_{31} - C_4\eta_{41}) - \eta_{22}(C_6\eta_{32} - C_4\eta_{42})}{\eta_{21}\chi_2 - \eta_{22}\chi_1 - (\eta_{21}(C_6\eta_{31} - C_4\eta_{41}) - \eta_{22}(C_6\eta_{32} - C_4\eta_{42}))}. \tag{52}$$

Denoting $\hat{\lambda}_{S_w} = (1/u)\lambda_{S_w}$ and $\hat{\lambda}_\Delta = (1/u)\lambda_\Delta$, the eigenvectors associated to λ_Δ is

$$\vec{r}_\Delta = \Big((f_w - S_w)r_1, (\hat{\lambda}_{S_w} - \hat{\lambda}_\Delta)r_2, (\hat{\lambda}_{S_w} - \hat{\lambda}_\Delta)r_3, u(\hat{\lambda}_{S_w} - \hat{\lambda}_\Delta)(f_w - S_w)r_4\Big), \tag{53}$$

where (r_2, r_3) are eigenvectors of matrix

$$\begin{pmatrix} \eta_{21} & \eta_{22} \\ (1-\Delta)\chi_3 + \Delta\chi_1 & (1-\Delta)\chi_4 + \Delta\chi_2 \end{pmatrix}, \tag{54}$$

moreover, $r_4 = \dfrac{f_w - S_w}{1 - S_w - \Delta}\hat{r}_4$, with

$$\hat{r}_4 = \left(\sum_{i=1}^{2} \Delta\left(\eta_{4i}C_2 - \eta_{2i}C_4\right) + (1-\Delta)C_1\left(\frac{\partial C_4}{\partial \theta_i}C_2 - \frac{\partial C_3}{\partial \theta_i}C_4\right)\right)$$

and

$$r_1 = \frac{u\Delta}{1 - S_w - \Delta}\left(\langle \nabla_\theta C_1, (r_2, r_3)\rangle + (1 - f_w)C_1\hat{r}_4\right),$$

here $\nabla_\theta C_1$ is the gradient of C_1 with respect to θ variable. The integral fields in the space θ does not depend on saturation.

5.2.2 Rarefaction Waves

We assume that W is a function of variable $\xi = x/t$, then, $W(x,t) = W(x(\xi), t(\xi)) = W(\xi)$, we obtain:

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

the first eigenvalue is $\lambda_{S_w} = uf'_w/\varphi$ associated to the eigenvector $\vec{r}_{S_w} = (1, 0, 0, 0)^T$ (saturation wave $\mathcal{R}_{S_w}$) and the second (chemical composition waves $\mathcal{R}_\Delta$) is $\lambda_\Delta = \dfrac{u}{\varphi}\dfrac{f_w - (\Delta - 1)}{S_w - (\Delta - 1)}$, where Δ depend on $(S_w, [Cl-], [H+])$ corresponding to the eigenvectors $\vec{r}_\zeta = ((u/\varphi)\zeta_1, (u/\varphi)\zeta_2, u\zeta_3)^T$, where the known functions ζ_1, ζ_2 depend on $(S_w, pH, [Cl])$ and ζ_3 on $(S_w, pH, [Cl])$ and third eigenvalue is $\lambda_3 = \dfrac{u}{\varphi}f_w/S_w$ which is a contact discontinuity (chloride wave $\mathcal{R}_{Cl}$) because $\nabla\lambda_{Cl} \cdot r_{Cl}$=0. The saturation waves are curves with constant hydrogen. The hydrogen curves can be obtained from the first order differential equations

$$dS_w/d\xi = r^1_\zeta((S_w, pH, [Cl]) = (f_w - S_w)r_1(\theta) \tag{55}$$

$$d[pH]/d\xi = r^2_\zeta(S_w, pH, [Cl]) = (\hat{\lambda}_{S_w} - \hat{\lambda}_\Delta)r_2(\theta) \tag{56}$$

$$d[Cl]/d\xi = r^3_\zeta(S_w, pH, [Cl]) = (\hat{\lambda}_{S_w} - \hat{\lambda}_\Delta)r_3(\theta) \tag{57}$$

split from ODE

$$du/d\xi = r_\zeta^4(S_w, pH, [Cl], u) = u(f_w - S_w)(\hat{\lambda}_{S_w} - \hat{\lambda}_\Delta)r_4; \tag{58}$$

splitting is very useful from the numerical point of the view.

Assumption 1. *Partial molar volume parameters are such that for chemical composition wave* R_Δ *holds* $r_\zeta^3(S_w, pH, [Cl]) \equiv 0$.

Proposition 1. *Under Assumption 1 chemical composition wave* R_Δ *is invariant on the planes constant chloride,* $Cl = const.$

Assumption 2. *Partial molar volume parameters are such that for chloride wave* R_{Cl} *holds* $r_{Cl}^3(S_w, pH, [Cl]) \neq 0$.

Proposition 2. *Under Assumption 5.4 Chloride wave* S_{Cl} *is transversal to the planes constant chloride,* $Cl = const.$

Assumptions 1 and 5.4 are satisfied approximately for the data set studied here.

5.2.3 Rankine-Hugoniot curve

One possible type of solution appears when discontinuities appear. They are shocks in the flow; that satisfy the Rankine-Hugoniot relationships (RH)

$$\sigma[G] = [F] = (u^+ - u^-)\widehat{F}_i^{\,+} + u^-(\widehat{F}_i^{\,+} - \widehat{F}_i^{\,-}), \tag{59}$$

where $W^- = (s_w^-, y_1^-, y_2^-, u^-)$ and $W^+ = (s_w^+, y_1^+, y_2^+, u^+)$ are the states on the left and the right side of the discontinuity, with $[G] = G^+ - G^-$ and $[\widehat{F}] = u^+\widehat{F}^+ - u^-\widehat{F}^-$. Given W^- the set of of W^+ states that satisfy the RH relation defines the RH curves. Here $\widehat{F_1}$, $\widehat{F_2}$ and $\widehat{F_3}$ are given in (22).

A sufficient condition for the existence of a non-trivial solution u^+, u^- and σ for (59) is that the following determinant condition must be satisfied

$$HL_1(S_w, Cl, pH) = det \begin{vmatrix} -[\widehat{F_1}] & \widehat{F_1}^{\,+} & [G_1] \\ -[\widehat{F_2}] & \widehat{F_2}^{\,+} & [G_2] \\ -[\widehat{F_3}] & \widehat{F_3}^{\,+} & [G_3] \end{vmatrix} = 0, \tag{60}$$

and

$$HL_2(S_w, Cl, pH) = det \begin{vmatrix} -[\widehat{F_1}] & \widehat{F_1}^{\,+} & [G_1] \\ -[\widehat{F_2}] & \widehat{F_2}^{\,+} & [G_2] \\ -[\widehat{F_4}] & \widehat{F_4}^{\,+} & [G_4] \end{vmatrix} = 0. \tag{61}$$

This is equation in the variables S_w, $[Cl-]$ and $[H+]$. The curve found in $(S_w, [Cl-], [H+])$ space gives the possible discontinuities that satisfy the shock conditions. Shock curves in which only saturation varies is denoted by $\mathcal{S}_s$.

Since equations (60) and (61) determine the locus of two surfaces, it intersection (Hugoniot locus) is a curve in three dimensional space determinate by the variables $(S_w, [Cl-], [H+])$.

One can verified that Hugoniot locus is the union of three branches (see Figure 1), i.e. $\mathcal{S}_s \cup \mathcal{S}_H$, with

$$\mathcal{S}_s = \{(S_w^+, Cl^+, pH^+) : Cl^+ - Cl^- = 0, \quad pH^+ - pH^- = 0\}. \tag{62}$$

Along this branch we have that $u = u^+ = u^-$ and $\sigma = u[\widehat{F}_i]/[G_i]$, with $i = 1, 2, 3, 4$. Thus we call this curve as Buckley Leverett shock. And the intersection of the surfaces

$$\begin{aligned}
\mathcal{S}_H^1 = \{(S_w^+, Cl^+, pH^+) : & \frac{\partial HL_1}{\partial Cl}(S_w^-, Cl^-, pH^-) + \\
& \frac{\partial^2 HL_1}{\partial Cl^2}(S_w^-, Cl^-, pH^-)(Cl^+ - Cl^-) + \frac{\partial^3 HL_1}{\partial Cl^3}(S_w^-, Cl^-, pH^-)(Cl^+ - Cl^-)^2 + \\
& \frac{\partial HL_1}{\partial pH}(S_w^-, Cl^-, pH^-) + \frac{\partial^2 HL_1}{\partial pH^2}(S_w^-, Cl^-, pH^-)(pH^+ - pH^-) + \\
& \frac{\partial^3 HL_1}{\partial pH^3}(S_w^-, Cl^-, pH^-)(pH^+ - pH^-)^2 + O(Cl^+ - Cl^-)^3 + O(pH^+ - pH^-)^3 = 0\},
\end{aligned}$$

and

$$\begin{aligned}
\mathcal{S}_H^2 = \{(S_w^+, Cl^+, pH^+) : & \frac{\partial HL_2}{\partial Cl}(S_w^-, Cl^-, pH^-) + \\
& \frac{\partial^2 HL_2}{\partial Cl^2}(S_w^-, Cl^-, pH^-)(Cl^+ - Cl^-) + \frac{\partial^3 HL_2}{\partial Cl^3}(S_w^-, Cl^-, pH^-)(Cl^+ - Cl^-)^2 + \\
& \frac{\partial HL_2}{\partial pH}(S_w^-, Cl^-, pH^-) + \frac{\partial^2 HL_2}{\partial pH^2}(S_w^-, Cl^-, pH^-)(pH^+ - pH^-) + \\
& \frac{\partial^3 HL_2}{\partial pH^3}(S_w^-, Cl^-, pH^-)(pH^+ - pH^-)^2 + O(Cl^+ - Cl^-)^3 + O(pH^+ - pH^-)^3 = 0\},
\end{aligned}$$

where HL_1 and HL_2 are given in (60) and (61), respectively. Above statement is obtained using Taylor's Series for HL_1 and HL_2 and $HL_1(S_w^-, Cl^-, pH^-) = 0$, $HL_2(S_w^-, Cl^-, pH^-) = 0$ $\dfrac{\partial^k HL_1}{\partial s_w^k}(S_w^-, Cl^-, pH^-) = 0$ and $\dfrac{\partial^k HL_2}{\partial s_w^k}(S_w^-, Cl^-, pH^-) = 0$, hold for $k = 1, \ldots$.

We prove here $\dfrac{\partial HL_1}{\partial s_w}(S_w^-, Cl^-, pH^-) = 0$, the rest is similar.

Derivative of (**??**) produces

$$\frac{\partial HL}{\partial s_w}(S_w^+, Cl^+, pH^+) = det \begin{pmatrix} \partial(\widehat{F_1}^+)/\partial s_w & -\widehat{F_1}^- & [G_1] \\ \partial(\widehat{F_2}^+)/\partial s_w & -\widehat{F_2}^- & [G_2] \\ \partial(\widehat{F_3}^+)/\partial s_w & -\widehat{F_3}^- & [G_3] \end{pmatrix} + det \begin{pmatrix} \widehat{F_1}^+ & -\widehat{F_1}^- & \partial[G_1]/\partial s_w \\ \widehat{F_2}^+ & -\widehat{F_2}^- & \partial[G_2/\partial s_w \\ \widehat{F_3}^+ & -\widehat{F_3}^- & \partial[G_3]/\partial s_w \end{pmatrix}, \tag{63}$$

or

$$\frac{\partial HL}{\partial s_w}(S_w^+, Cl^+, pH^+) = det \begin{pmatrix} \left(\rho_{a,C(4)}\right)^+ f_w' & -\widehat{F_1}^- & [G_1] \\ \left(\rho_A\right)^+ f_w' & -\widehat{F_2}^- & [G_2] \\ -\left(\rho_{o,C(-4)}\right)^+ f_w' & -\widehat{F_3}^- & [G_3] \end{pmatrix} + det \begin{pmatrix} \widehat{F_1}^+ & -\widehat{F_1}^- & \left(\rho_{a,C(4)}\right)^+ \\ \widehat{F_2}^+ & -\widehat{F_2}^- & \left(\rho_A\right)^+ \\ \widehat{F_3}^+ & -\widehat{F_3}^- & -\left(\rho_{o,C(-4)}\right)^+ \end{pmatrix}, \tag{64}$$

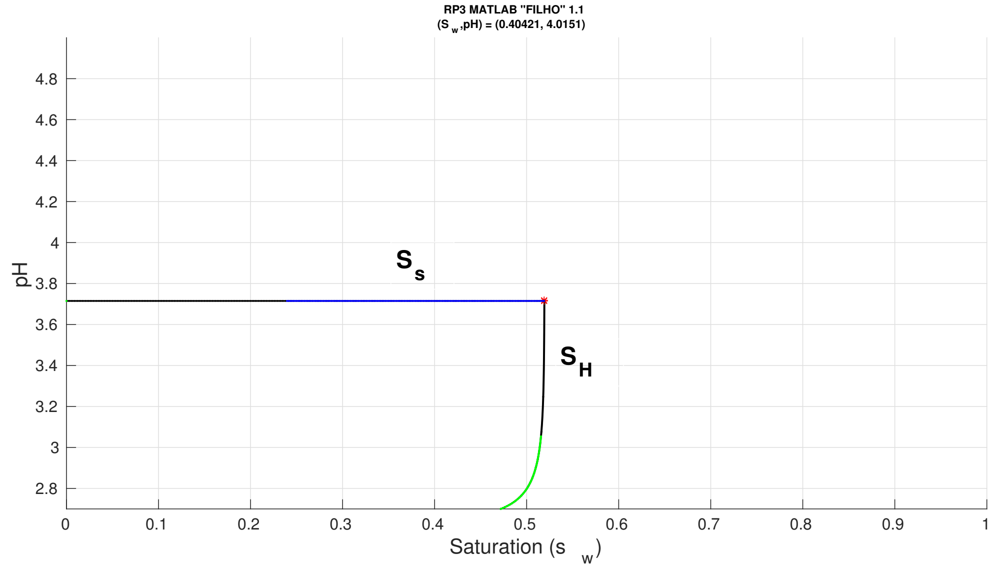

Figure 1: Branches of the Hugoniot locus.

Summing first and second column od second determinant in (64) we obtain

$$\frac{\partial HL}{\partial s_w}(s_w^+, y^+) = det\begin{pmatrix} \left(\rho_{a,C(4)}\right)^+ f'_w & -\widehat{F_1}^- & [G_1] \\ \left(\rho_A\right)^+ f'_w & -\widehat{F_2}^- & [G_2] \\ -\left(\rho_{o,C(-4)}\right)^+ f'_w & -\widehat{F_3}^- & [G_3] \end{pmatrix} + det\begin{pmatrix} -[\widehat{F_1}] & -\widehat{F_1}^- & \left(\rho_{a,C(4)}\right)^+ \\ -[\widehat{F_2}] & -\widehat{F_2}^- & \left(\rho_A\right)^+ \\ -[\widehat{F_3}] & -\widehat{F_3}^- & -\left(\rho_{o,C(-4)}\right)^+ \end{pmatrix}, \tag{65}$$

Applying properties of determinant we obtain,

$$\frac{\partial HL}{\partial s_w}(S_w^+, Cl^+, pH^+) = det\begin{pmatrix} \left(\rho_{a,C(4)}\right)^+ & -\widehat{F_1}^- & [G_1]f'_w - [\widehat{F_1}] \\ \left(\rho_A\right)^+ & -\widehat{F_2}^- & [G_2]f'_w - [\widehat{F_2}] \\ -\left(\rho_{o,C(-4)}\right)^+ & -\widehat{F_3}^- & [G_1 3f'_w - [\widehat{F_3}] \end{pmatrix}, \tag{66}$$

or

$$\frac{\partial HL}{\partial s_w}(S_w^+, Cl^+, pH^+) = (\lambda_{s_w} - \sigma)det\begin{pmatrix} \left(\rho_{a,C(4)}\right)^+ & -\widehat{F_1}^- & [G_1] \\ \left(\rho_A\right)^+ & -\widehat{F_2}^- & [G_2] \\ -\left(\rho_{o,C(-4)}\right)^+ f'_w & -\widehat{F_3}^- & [G_3] \end{pmatrix}. \tag{67}$$

From (67) we obtain $\dfrac{\partial HL}{\partial s_w}(S_w^-, Cl^-, pH^-) = 0$.

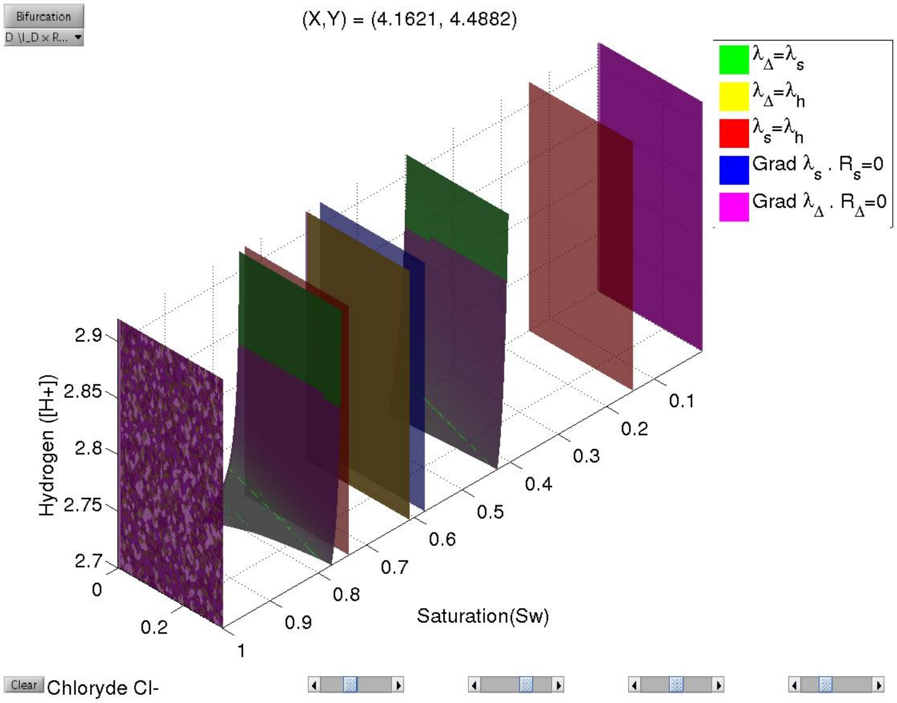

Figure 2: Bifurcation and Inflection surfaces depend on eigenvalues ($\lambda_i = \lambda_j$) and $\nabla\lambda_j \times r_j$=0, j=1,2,3. These surfaces have almost constant saturation ($S_w = C$)

5.3 Inflection surfaces

Surface of the inflection locus are those where genuine nonlinearity is not satisfied ([65]), 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 $k = \mathcal{S}_s, \mathcal{S}_H$. Here we are able to prove some important results connecting the coincidence between the eigenvalues and, for non linearly degenerated field, we can obtain some inflection surfaces.

Our first remark is about the relationship between the states where $\lambda_{S_w} = \lambda_\Delta$. We have the following result:

Lemma 3. *The states in the space Ω such that $\lambda_{S_w} = \lambda_\Delta$ and $f_w = S_w$ are in the inflection locus of Δ field. Moreover, The saturation change the direction for states satisfying $f_w = S_w$, and θ_i change the direction for states satisfying $\lambda_s = \lambda_\Delta$.*

Proof: Using $\vec{r}$ given in Equation (53) and $\nabla\lambda$ given in (**??**), it is easy to see that we can factor the quantity $(f - s)(\hat{\lambda}_s - \hat{\lambda}_\Delta)$, thus $\nabla\lambda \cdot \vec{r} = 0$ if $f = s$ or $\hat{\lambda}_{S_w} = \hat{\lambda}_\Delta$. The remain result follows from the system (**??**)-(**??**). $\square$. **Region for characteristic analysis**

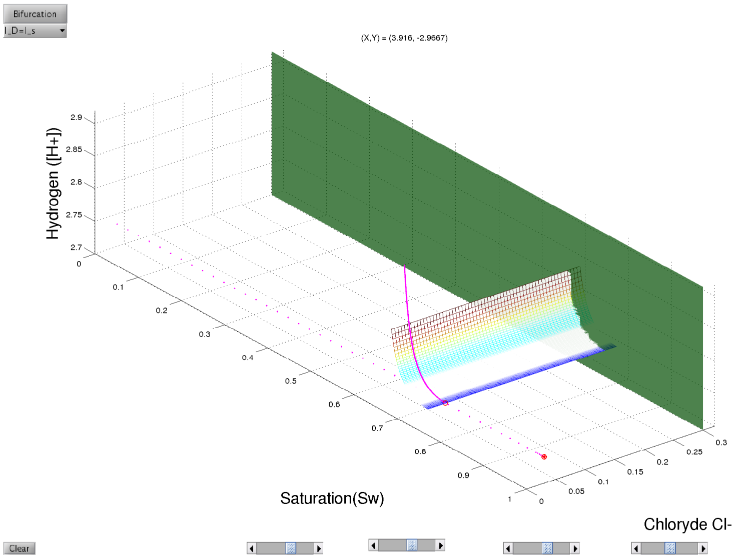

Figure 3: Wave curve admissibility and transitional surface(foliation generated by contact curve transversal to the plane of constant Chloride ($[Cl] = C$)).

5.4 Strategy in the Riemann Solver

The general procedure to solve the Riemann problem consists in the following step: First we take waves along constant chlorine planes, i.e. admissible rarefaction waves R_Δ, R_{S_w}, or shock curves. Second we use the transitional waves R_{Cl} (contact wave), to go to other constant chlorine planes where right state belongs.

For example, we are going to construct the Riemann solution assuming that the left state (S_w^-, Cl^-, pH^-) belongs to a locus where $\lambda_{S_w} \leq \lambda_\Delta \leq \lambda_{Cl}$ holds. We assume also that the left and right sides are such that Cl^- is different from Cl^+. Then the solution is obtained with following step: First we take a saturation wave R_{S_w}, to the point where $\lambda_{S_w} = \lambda_\Delta$ (See Figure 3). From this point an admissible rarefaction R_Δ is take until the physical boundary. Second, we extend this R_Δ rarefaction by using transitional rarefaction waves R_{Cl}. That is to say, using as initial points of this R_Δ rarefaction we construct a contact wave, which has constant velocity characteristic. This construction determines a foliation of rarefaction curve which we call transitional surface (See Figure 3).

Subsequently, we draw backward waves that come out of the right state point (S_w^+, Cl^+, pH^+). And now we look for the intersection point of the transitional surface with all backward curves coming on. We check the compatibility condition at the point of intersection i.e. if the speed characteristic of the wave is less than or equal to the speed of the backward wave at the intersection point (see Figure 4).

5.5 Examples of Numerical and analytical solutions

In this section an relevant example in oil recovery is presented. We show the analytic solution from Riemann solver and the numerical solution for COMSOL. This comparison serves as verification of both

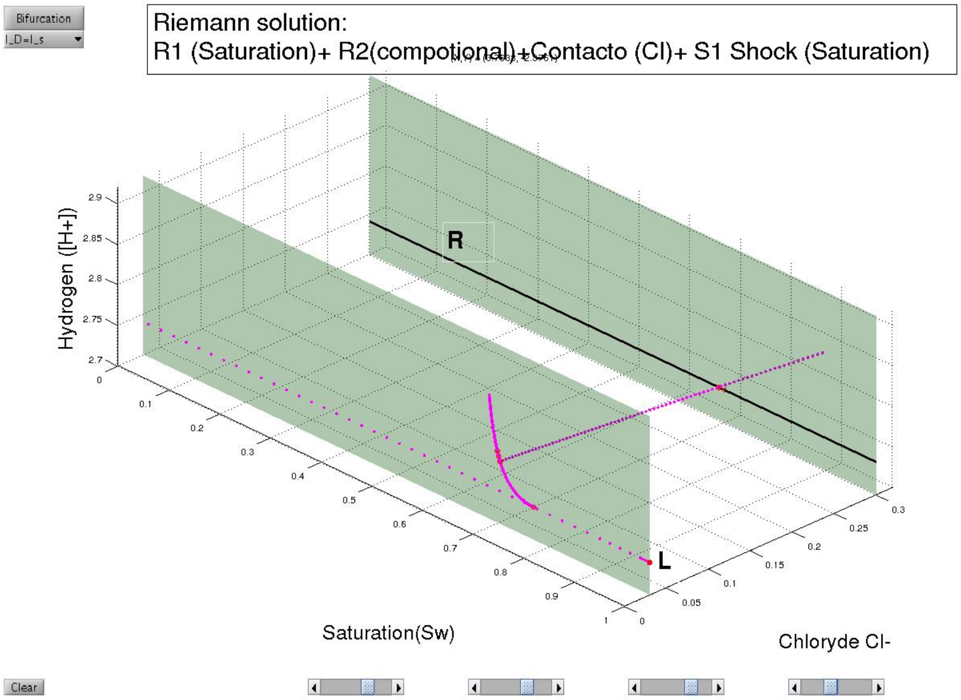

Figure 4: Saturation wave associated to λ_1

solutions. In particular, we can verified that step hydrogen solution obtained with COMSOL is not a numerical artificial to the convergence of the solution.

In Figure 5

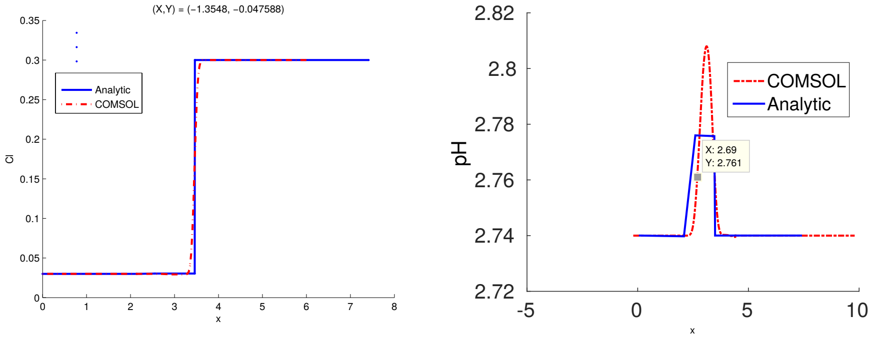

Figure 5: Profile of Clhoride and Hydrogen wave for Analytic method and COMSOL solution. (bold curve) Analytic (dashed curve) COMSOL. We have excellent agreement for both chemical waves.

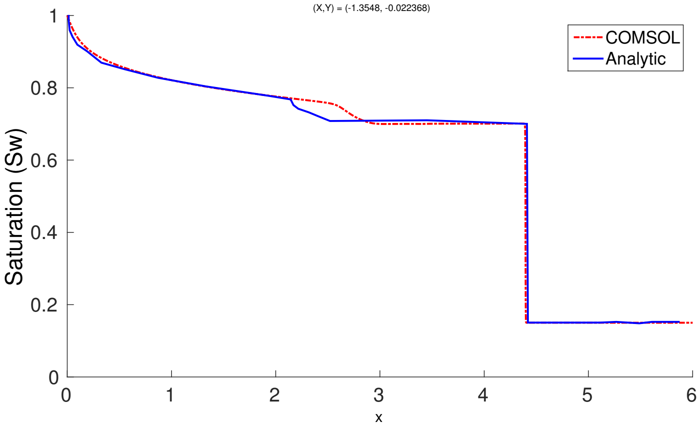

Figure 6: Saturation profile for Analytic method and COMSOL solution. (bold curve) Analytic (dashed curve) COMSOL. We have good agreement between both solutions.

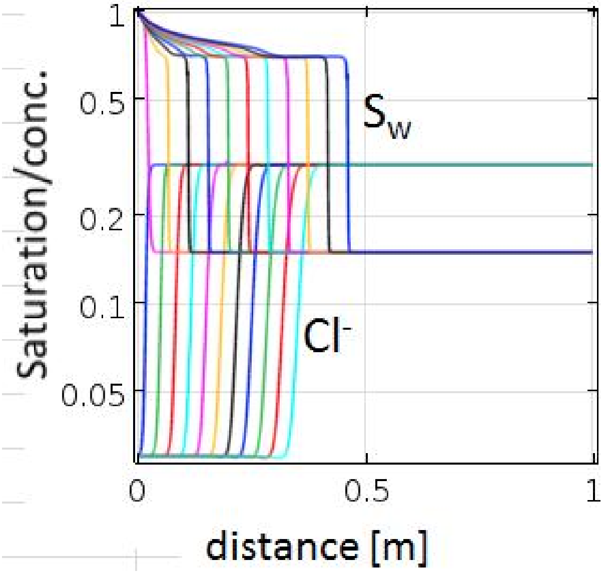

Figure 7: Saturation and $Cl-:=\rho_{a,Cl}$ profiles. Initial and boundary $pH=2.74$. Initial $Cl_{init}=0.3[mol/liter]$ and $Cl_{bound}=0.01[mol/liter]$ at the boundary. From left to right: $t=(0,20000[s])$ with $\Delta t=2000[s]$. In this and all calculations below we use the porosity is $\phi=0.37$, $\mu_w=1.0e-3[Pas]$, $\mu_o=2.0e-3[Pas]$, $\lambda=3$, $D_m=1e-9[m^2/s]$, $D_{cap}=1.0e-8[m^2/s]$.

6 Results of CLICDOW model

Figure 7 plots the weak formulation results of the water saturation and the chloride concentration as a function of distance at times $(0.20000[s])$ with intervals $\Delta t=2000[s]$. The saturation (S_w) profile is similar to the Buckley-Leverett profile except that it shows a constant state between the Buckley-Leverett shock and the rarefaction part. The chloride $(Cl-:=\rho_{a,Cl})$ profiles occur downstream of the rarefaction part ([52, 17, 16, 63, 81]). Figure 8 shows the weak formulation method results of the relative Darcy velocity u change, the saturation S_w, the chloride concentration Cl and the pH change versus distance for time $(20000[s])$. The advantage of the weak formulation option in COMSOL is that it does not require the addition of an artificial $DTdu/dt$ term to obtain the total Darcy velocity profile. As the initial and boundary concentration of the $pH=2.74$, we do not expect a pH wave and at the time that we submitted the paper it was not clear to us whether this is an artifact due to the high sensitivity of the solution to low

Figure 8 plots the weak formulation method results of the carbon dioxide concentration and decane concentration in the oleic phase. The figure shows that the low salinity injection gives an increased carbon dioxide concentration and a decreased decane concentration upstream leading to improved recovery.

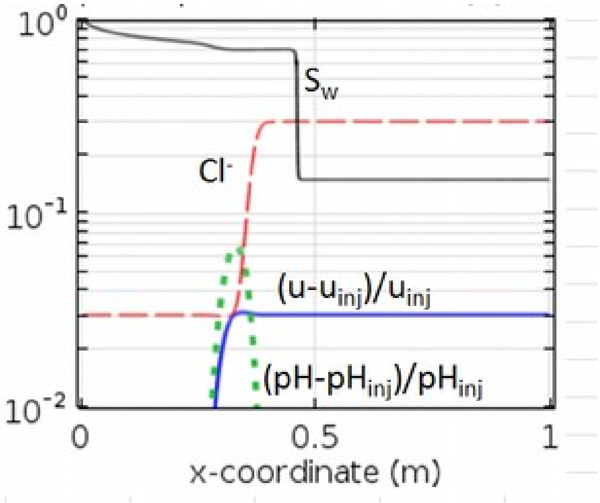

Figure 8: Molar densities $[mol/liter]$ in the oleic phase at $t = 10000[s]$.

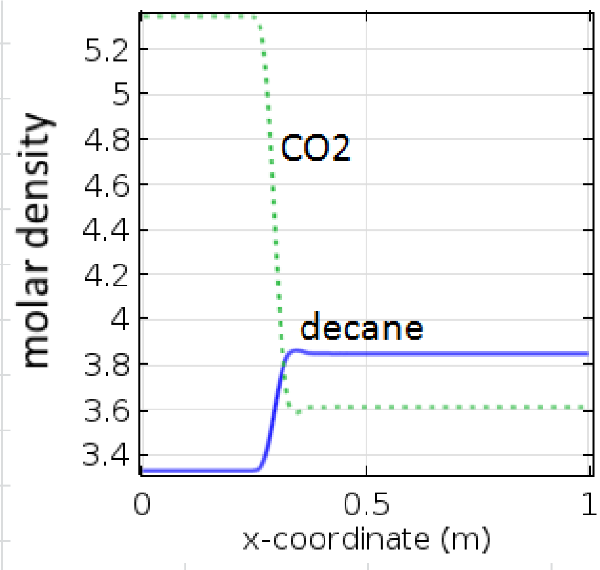

Figure 9: Molar densities $[mol/liter]$ in the oleic phase at $t = 10000[s]$.

7 Conclusion for CLICDOW model

- Developed a Riemann solver for oil recovery problems for low salinity carbonated waterflooding model including geochemical aspects. The methodology is adequate for one dimensional incompressible two-phase flow in porous media with several chemical components.
- As between phases there is mass transfer and the partial molar volume differs, a variable Darcy velocity ensues.
- The performance of our Riemann solver is illustrated for carbonated water injection in a rock containing oil, brine water and carbon dioxide. We formulate four balance equations, in which we substitute expressions that are obtained from geochemical software (PHREEQC) by regression. All compositions can be written in terms of the pH and Cl only.
- There is acceptable agreement between the numerical solutions and the Riemann solution except that COMSOL shows a slightly lower total velocity than IVUP and the Riemann solution.
- This shows that the Riemann solver can effectively and accurately solve the carbonated waterflooding with low salinity injection problem and elucidate the mechanism for enhancement of oil recovery.

A Activity coefficients

A.1 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

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

where μ_X^0 is the chemical potential of pure solute having the properties of an infinitely dilute solution, μ_m^0 is the chemical potential of the solute in the ideal one molal solution and μ_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 γ except for very high concentrations are extremely small, i.e.,

$$\ln\gamma_{H,x} = \ln\gamma_{H,m} + \Gamma_\gamma = \ln\gamma_{H,m} + \ln\left(1 + 0.0180153m\right) \tag{68}$$

The unit of the activity depends on the reference state that determines μ^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 molalilties (concentrations in mol/ kg-water) based on the fact that the difference between the activity coefficients based on molarites, molalities or even mole fractions are extremely small.

A.2 Activity coefficients for charged molecules; extended Debye H$\ddot{u}$ckel law

The extended Debye-H$\ddot{u}$ckel theory for calculating the activity coefficient of an ion reads [2]

$$\ln\gamma_j\left(\mu\right) = -\frac{A_\gamma|z_j|^2\sqrt{\mu}}{1 + B_\gamma\mathring{a}_j\sqrt{\mu}} + b_j\mu \tag{69}$$

where $\mu = \frac{1}{2}\sum_i\left(c_i z_i^2\right)$ $[mol/liter]$ is the ionic strength of the solution, z_i is the charge of the ion, in water. Finally $\mathring{a}_j$ is the effective diameter of an ion j in Ångstrom see Appelo and Postma, [4], page 125. For small ions we use a value of 3 Ångstrom.

$$B_\gamma = \left(\frac{8\pi N_A q_e^2\rho_o}{1000\varepsilon_r k_B T}\right)^{1/2} = \frac{50.29158649\rho_0^{1/2}}{\left(\varepsilon_r T\right)^{1/2}} \tag{70}$$

where N_A is the Avogadro number (6.225×10^{23}) molecules per mole, $q_e = 4.803 \times 10^{-10}$ esu (electrostatic unit of charge),ρ_0 is the density of pure water water in $\left[g/cm^3\right]$,ε_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 compressibilty $\kappa_0 = \left(atm^{-1}\right)$. For the definition of B in Eq. (**??**) we need to express å in Ångström.

Moreover we can express the Debye-Hückel parameter for the activity coefficients as [101]

$$A_\gamma = \frac{(2\pi N_A)^{1/2}\, q_e^3 \sqrt{\rho^0}}{\sqrt{1000}\,(\varepsilon k_B T)^{3/2}} = \frac{1824829.238\sqrt{\rho^0}}{(\varepsilon T)^{3/2}} \quad \left[(mol/kg)^{0.5}\right] \tag{71}$$

At room temperature ($25^o C$) and atmospheric pressure $A_\gamma / \ln(10) = 0.5085$ and $B = 0.3281$. Finally $\mathring{a}_j$ is the effective diameter of an ion j in Ångstrom [5] [4], page 125. For small ions we use a value of 3 Ångstrom.The ionic strength can be written in terms of activities as

$$\mu = \frac{1}{2}\sum_i \left(c_i z_i^2\right) = \frac{1}{2}\sum_i \left(\frac{a_i}{\gamma_i(\mu)} z_i^2\right) \tag{72}$$

A.3 Converting molalities into concentrations

For more or less dilute solutions we can take the activity of water $a_{H_2O} = 1$. ([64] [3]). 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 [5] 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

$$c_{a,j} = \frac{\rho_a}{\sum_{i=1}^{N}(m_{w,i} M_i)} m_{w,j} = [M_w c_{a,w}]\, m_{w,j}, \tag{73}$$

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 ρ_a.

B Equilibrium constants for the aqueous species

The equilibrium constants and other data relevant to the simulation of geochemical aspects have been obtained from PHREEQC [83] and MINTEQ, e.g., phreeqc.dat, wateq4f.dat, llnl.dat, pitzer.dat, sit.dat and minteq.dat and [49] [60].

Remark 4. *The relation between the activity $a_{a,CaCO_3}$ of $CaCO_3$ in the aqueous phase and the activity in the solid phase $a_{r,CaCO_3}$ can be written as $K_{CaCO3} = \frac{a_{a,CaCO_3}}{a_{r,CaCO_3}}$, where $\log_{10}(K_{CaCO3}) = -1400.6385 - 0.377433T + 3835$*

Remark 5. *The data for $NaHCO3$ and $NaCO3^-$ are obtained with MINTEQ*

Remark 6. *It is sometimes convenient to use $K_c := \hat{K}_c a_{a,CaCO_3} = \widehat{K}_c K_{CaCO_3} = \frac{a_{a,Ca}\, a_{a,HCO_3}}{a_{a,H}}$, with $\log_{10}(K_c) = -64.0194 - 0.04546451T - 2312.471/T + 32.66939\log(T)/\log(10) + 563713.9/T^2$ and*

$K_a{=}\dfrac{a_{a,HCO3}\ a_{a,H}}{a_{a,CO_2}a_{a,H_2O}}$	$\log_{10}\left(K_a\right) = -356.309 - 0.06092T + 21834.37/T$ $+126.8339\log\left(T\right)/\log\left(10\right) - 1684915/T^2$
$K_b{=}\ \dfrac{a_{a,CO_3}a_{a,H}}{a_{a,HCO_3}}$	$\log_{10}\left(K_b\right) = \ -107.8871 - 0.03252849T + 5151.79/T +$ $38.92561\log\left(T\right)/\log\left(10\right) - 563713.9/T^2$
$K_w{=}\dfrac{a_{a,OH}a_{a,H}}{a_{a,H_2O}}$	$\log_{10}\left(K_w\right) = \ 293.29227 + 0.1360833T - 10576.913/T$ $-123.73158\ \log\left(T\right)/\log(10) - 6.996455*10^{-5}*\left(T^2\right)$
$K_{calc}{=}\dfrac{a_{a,CO3}\ a_{a,Ca}}{a_{a,CaCO3}}$	$\log_{10}\left(K_{calc}\right) = \ +1228.732 + 0.299440T$ $-35512.75/T - 485.818\log\left(T\right)/\log\left(10\right)$
$K_{ca}{=}\dfrac{a_{a,CaOH}\ a_{a,H}}{a_{a,Ca}a_{a,H_2O}}$	$\log_{10}\left(K_{Ca}\right) = -12.78 + 60814.44/R_B \times (1/T_0 - 1/T)/\log(10)$
$K_{hca}{=}\dfrac{a_{a,CaHCO_3}}{a_{a,CO_3}a_{a,Ca}\ a_{a,H}}$	$\log_{10}\left(K_{hca}\right) = \ 1317.0071 + 0.345468894T - 39916.84/T$ $-517.70761\log\left(T\right)/\log\left(10\right) + 563713/T^2$
$K_{CaCO3}{=}\dfrac{a_{a,CaCO_3}}{a_{r,CaCO_3}}$	$\log_{10}\left(K_{CaCO3}\right) = \ -1400.6385 - 0.377433T + 38352.069/T$ $+557.413\log\left(T\right)/\log\left(10\right)$
$K_{N_aCO_3}{=}\dfrac{a_{a,NaCO_3}}{a_{a,Na}a_{a,CO_3}}$	$\log_{10}\left(K_{NaCO_3}\right) = \ 1.268 -$ $20350/R_B \times (1/T_0 - 1/T)/\log(10)$
$K_{NaHCO_3}{=}\dfrac{a_{a,NaHCO_3}}{a_{a,Na}\ a_{a,HCO_3}}$	$\log_{10}\left(K_{NaHCO3}\right) = \ -0.25 -$ $13730/R_B \times (1/T_0 - 1/T)/\log(10)$

Table 1: Equilibrium constants for dissolved species

$\log_{10}\left(\widehat{K}_c\right) = 1336.6191 + 0.33196849T - 40664.54/T - 524.74361\log(T)/\log(10) + 563713.9/T^2$. *This equilibrium equation can be obtained from the equilibrium equtions already shown in Table 1. Note that we have to use* $K_c := \hat{K}_c a_{a,CaCO_3}$
and eliminate $\widehat{K}_c$.

C Partial molar volume

The regression expressions for the density and the dielectric constant are given in Appendix A.2

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).

$$V = n_1 v_{l0} + n_2 \phi \tag{74}$$

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

$$\phi = \frac{w_2}{s^0} - 1000 \left(s - s^0\right) / \left(cs^0\right) \tag{75}$$

The theory of electrolytes furnishes the limiting relation

$$\phi = \phi^0 + kw^{1.5} c^{0.5} \tag{76}$$

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

$$w = \frac{1}{2} \sum_i \nu_i z_i^2 \tag{77}$$

-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 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 and the coefficient is parameterized as , 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.

C.1 The density

The density ρ_w can be expressed as the inverse molar volume, i.e.,

$$\rho_w = \frac{1}{V} = \frac{1}{\sum_i n_i \overline{V}_i} \tag{78}$$

where

$$\overline{V}_i = \overline{V}_{i,\text{inf}} + \frac{1}{2} z_i^2 A_V \frac{\sqrt{\mu}}{1 + \mathring{a} B \sqrt{\mu}} + \beta_i \mu^{i_4}, \tag{79}$$

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

$$\overline{V}_{i,\text{inf}} = 41.84 \left(a_1/10 + \frac{100 a_2}{2600 + P_b} + \frac{a_3}{T_K - 228} + \frac{10000 a_4}{\left(2600 + P_b\right)\left(T_K - 228\right)} - W Q_{Born} \right), \tag{80}$$

where $Q_{Born} = -\partial_P \left(1/\varepsilon_r\right)^2$. The constants in $cal/mole/bar$ are a1, a2, a3, a4, å W, i1, i2, i3, i4 $a_1 = 8.615$, $a_2 = 0, a_3 = -12.21$, a_4 =0 $\mathring{a} = 1.667$, $W = 0$, $i_1 = 0$. $i_2 = 264$, $i_3 = 0$ 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 [11]

$$A_V = 2RT\sqrt{\frac{2\pi N_A \rho_0}{1000}}\left(\frac{q_e^2}{\epsilon kT}\right)^{3/2}\left[\left(\frac{\partial \log \varepsilon_r}{\partial P}\right)_T + \frac{\kappa_0}{3}\right]\left[(cm^3/mol)(mol/kg)^{-0.5}\right], \tag{81}$$

where N_A is the Avogadro number (6.225×10^{23}) molecules per mole, $q_e = 4.803\times10^{-10}$ esu (electrostatic unit of charge), ρ_0 is the density of pure water water in $\left[g/cm^3\right]$, ε_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 $\kappa_0 = \left(atm^{-1}\right)$.

$$B = \frac{8\pi N_A q_e^2 \rho_o}{\varepsilon_r k_B T} \tag{82}$$

D Derivation of simplified model equations

E Combination of the hydrogen and chloride equation and oxygen minus carbon with the chloride equation

Equation (**??**) can be extended to

$$\partial_t \left(S_w\right) + S_w \partial_t \ln \rho_{a,H(1)} + u f_w \partial_x \ln \rho_{a,H(1)} + \partial_x \left(u f_w\right) = 0, \tag{83}$$

and Eq. (**??**) and obtain

$$\partial_t S_w + S_w \partial_t \ln \rho_{a,Cl(-1)} + u f_w \partial_x \ln \rho_{a,Cl(-1)} + \partial_x u f_w = 0 \tag{84}$$

After subtraction we find

$$S_w \partial_t \left(\ln \rho_{a,Cl(-1)} - \ln \rho_{a,H(1)}\right) + u f_w \partial_x \left(\ln \rho_{a,Cl(-1)} - \ln \rho_{a,H(1)}\right) = 0 \tag{85}$$

In the same way we find after subtraction of Eq. (Eq. (**??**))

$$\partial_t \left(\ln\left(\rho_{a,O-H} + 4\rho_{a,C(4)}\right) - \ln \rho_{a,Cl(-1)}\right)\right) + u f_w \partial_x \left(\ln\left(\rho_{a,O-H} + 4\rho_{a,C(4)}\right) - \ln \rho_{a,Cl(-1)}\right) = 0 \tag{86}$$

We define $A\left(H^+, Cl^-\right) = \ln \rho_{a,Cl(-1)} - \ln \rho_{a,Cl(-1)}$ and $B\left(H^+, Cl^-\right) = \left(\ln\left(\rho_{a,O-H} + 4\rho_{a,C(4)}\right) - \ln \rho_{a,Cl(-1)}\right)\right)$ and find

$$S_w d_{H^+} A\left(H^+, Cl^-\right) \partial_t \left(H^+\right) + S_w d_{Cl^-} A\left(H^+, Cl^-\right) \partial_t \left(Cl^-\right)$$
$$+ u f_w d_{H^+} A\left(H^+, Cl^-\right) \partial_x H^+ + u f_w d_{Cl^-} A\left(H^+, Cl^-\right) \partial_x Cl^- = 0 \tag{87}$$

$$S_w d_{H^+} B\left(H^+, Cl^-\right) \partial_t \left(H^+\right) + S_w d_{Cl^-} B\left(H^+, Cl^-\right) \partial_t \left(Cl^-\right)$$
$$+ u f_w d_{H^+} B\left(H^+, Cl^-\right) \partial_x H^+ + u f_w d_{Cl^-} B\left(H^+, Cl^-\right) \partial_x Cl^- = 0 \tag{88}$$

or

$$d_{H^+} A\left(H^+, Cl^-\right) \left(S_w \partial_t \left(H^+\right) + u f_w \partial_x H\right) + d_{Cl^-} A\left(H^+, Cl^-\right) \left(S_w \partial_t \left(Cl^-\right) + u f_w \partial_x Cl^-\right) = 0 \tag{89}$$

In the same way we find

$$d_{H^+} B\left(H^+, Cl^-\right) \left(S_w \partial_t \left(H^+\right) + u f_w \partial_x H\right) + d_{Cl^-} B\left(H^+, Cl^-\right) \left(S_w \partial_t \left(Cl^-\right) + u f_w \partial_x Cl^-\right) = 0 \tag{90}$$

Unless the determinant is zero we find

$$\left(S_w \partial_t \left(H^+\right) + u f_w \partial_x H\right) = \left(S_w \partial_t \left(Cl^-\right) + u f_w \partial_x Cl^-\right) = 0 \tag{91}$$

Backsubstituting into Eq. (83) leads to

$$\partial_t S_w + \partial_x u_w = 0 \tag{92}$$

E.1 Total velocity equation

Combinattion with the total velocity equation leads to

$$S_o \partial_t \left(\ln \rho_{o,C(-4)}\right) + \partial_t S_o + u f_o \partial_x \left(\ln \rho_{o,C(-4)}\right) + \partial_x \left(u f_o\right) = 0. \tag{93}$$

Addition of Eq. (92) leads to

$$S_o \partial_t \left(\ln \rho_{o,C(-4)}\right) + u f_o \partial_x \left(\ln \rho_{o,C(-4)}\right) + \partial_x \left(u\right) = 0. \tag{94}$$

$$S_o \partial_t \left(\ln \rho_{o,C(-4)}\right) + u f_o \partial_x \left(\ln \rho_{o,C(-4)}\right) + \partial_x \left(u\right) = 0. \tag{95}$$

and using that $\partial_t = -u f_w / S_w \partial_x$ we obtain

$$u\left(f_o - f_w \, \frac{S_o}{S_w}\right) \partial_x \left(\ln \rho_{o,C(-4)}\right) + \partial_x \left(u\right) = 0. \tag{96}$$

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