EXPLICIT CONTINUUM-SCALE MODELING OF WATER-BASED IOR/EOR MECHANISMS

Kata Kurgyis¹, Bernd Flemisch², Rainer Helmig² and Holger Ott¹ ¹Department Petroleum Engineering, Montanuniversität Leoben, 8700 Leoben Austria ²Institut für Wasser- und Umweltsystemmodellierung, Universität Stuttgart, 70569 Stuttgart, Germany

This paper was prepared for presentation at the International Symposium of the Society of Core Analysts held in Vienna, Austria, 27 August – 1 September 2017

ABSTRACT

In this paper, we discuss first steps towards an explicit numerical description of waterbased chemical IOR/EOR processes on the continuum scale. Low-salinity-water and alkaline flooding belong to this family of water based methods. The mechanism governing additional oil production during low-salinity-water flooding is believed to be a combination of several physicochemical processes like multicomponent ion exchange and double layer expansion. These processes are captured in a complexed mechanistic model implemented in the open-source flow and transport simulator DuMu^{*}. Explicit description, in this context, means to implement the change of wetting properties due to the composition of the injected water by a set of chemical processes linked to concentrations and the concentrations to measured and interpolated flow properties such as relative permeability and capillary pressure saturation functions. The developed models are intended to be used for the design and interpretation of core-flood experiments, and will serve as a basis for upscaling.

INTRODUCTION

Many studies indicate that recovery of crude oil by water flooding (in secondary and tertiary recovery mode) can often be improved by simple and cost effective means through modifying the ionic composition of the injection water. Low salinity water flooding (LSWF) and alkaline flooding belong to this family of low-cost, water-based improved oil recovery (IOR) and enhanced oil recovery (EOR) methods. The recovery mechanisms of both deviate: while low saline water flooding modifies the wetting state of the reservoir as a result of reactions between constituents of the injected water and mineral-fluid interfaces, in alkaline flooding, surface active components are generated in-situ by contacting alkali solutions with specific crude oil components such as fatty acids, lowering interfacial tension between brine and crude. Nevertheless, both methods are not independent of each other and deserve a common investigation, however, in the present study, we primarily focus on LSWF.

The mechanisms governing low salinity effects are believed to be a combination of several physicochemical processes as in double layer expansion (DLE), multicomponent ion exchange (MIE), fine migration, emulsification and salting out among others. DLE and

SCA2017-056

MIE are the two most quoted phenomena extensively investigated in the past decades. Researchers investigated DLE on pore scale during LSWF and managed to accurately simulate the impact of electrical double layer on ionic diffusion behavior adjacent to a charged surface [1]. In another study [2], mass transfer equilibrium reactions characterizing ion exchange processes emerging during core flooding with diluted brine which was further confirmed by experimental evidence by a difference reported between divalent ion concentration of the injected brine and that of the effluent [3]. Their work has been further developed by several researchers [4, 5] through proposing equilibrium and kinetic reactions models to describe MIE during LSWF.

Additional recovery through the mobilization of fine particles is discussed controversially among researchers. Partial stripping of mixed wet particles alongside incremental oil recovery was reported as core flooding experiments had been executed with chemically modified injection water [6]. On the other hand, during a different study no fines migration or permeability reduction has been observed, although numerous core flood experiments were performed by LSWF [4]. The same conclusion can be derived based on studies inspecting alkaline like behavior of LSWF: results published by Lager et al. [4] indicate that despite the observed alkaline like behavior (water-in-oil emulsification, interfacial tension reduction) due to carbonate dissolution and cation exchange in several studies [7, 8], local pH increase in all probability is not the cause of incremental oil recovery.

Surface electrical potentials are responsible for wetting properties. Charged mineral surfaces are screened to a certain extend by dissolved ions of the aqueous phase forming an electrical double layer resulting in an effective electrical surface potential (zeta-potential). Lowering the ionic strength of the solvent, results in higher zeta potential yielding to an increase in the thickness of the double layer. If the double layer of two, similarly charged surfaces overlap, repulsive forces dominate over attractive forces, promoting desorption over adsorption. Under reservoir conditions, double layers form on the pore wall as a result of the charged mineral surfaces and the brine – crude oil interface caused by accumulation of polar organic components at the interface. Lowering the ion concentration of the brine yields a reduction in the ionic strength and gives rise to overlapping double layers. Therefore, electrical double layer expansion and as a consequence, desorption of polar organic compounds is a consequence of the interaction of Van der Waals forces in the crude oil – brine – rock system. [9]

Other than to double layer expansion, divalent ions contribute to multi-component ion exchange simultaneously. Polar organic compounds adsorb to charged solid surfaces by virtue of indirect bonds functioning as ion or ligand bridges. Upon injecting water with reduced divalent ion concentration, adsorbed carboxylic aggregates are stripped from the pore wall as ion and ligand bridging, and ion exchange processes emerge. [10]

STRATEGY

SCA2017-056

The objective of the here presented research is to develop the numerical capability for an explicit description of low-saline water flooding processes on the continuum scale. In this context, explicit description means that the change of wetting properties is linked to measured and interpolated flow properties. The developed model will be used for design and interpretation of core flood experiments and will serve as a basis for upscaling from the continuum-scale to field scale applications.

For these purposes, the relevant chemical mechanisms governing LSWF are coupled in a complex mechanistic model based on the work of Kuznetsov et al. [11]. In this work the physicochemical processes causing a change in the wetting state are described by a set of chemical reactions. Due to the complexity of the proposed mechanistic model, it is decomposed into three, superimposed problems in a manner that in each sub-model a new feature is introduced as shown in Figure 1.



Figure 1: Strategy of the mechanistic model construction

Model 1: Dissolved saline tracer

A core sample saturated with oil and brine is flooded with chemically modified water characterized by a lower salinity of the injection water with respect to the initial brine phase. Due to the change in the total dissolved solids in the brine phase, the thermodynamic equilibrium between the crude oil, brine and rock is disturbed resulting in a new wetting state expressed by modified relative permeability and the capillary pressure saturation function.



Figure 2: Basic model description

The first phenomenological model is illustrated in Figure 2. The salinity of the brine is specified as a primary variable. The relation between salinity and the wetting state (alteration) is established by a linear interpolation of fluid properties as function of salinity.



Figure 3: Interpolation scheme applied in the phenomenological models

Figure 3 demonstrates the interpolation workflow: relative permeability and capillary pressure data is provided as function of water saturation corresponding to the high saline water initially saturating the core and to the injected low saline water. As the low saline water imbibes into the core, the in-situ high saline water is displaced and maybe diluted leading to a variation of brine salinity in the simulation domain. At a given location, an interpolation coefficient is determined that defines the relative contribution of the two-phase flow properties corresponding to low and high salinity representing the flow properties at the actual salinity. Linear interpolation means the adaptation of this coefficient

into equation (1) - (3), which is executed in every cell and each time step during the simulation:

$$k_{rw}(S_w) = F(x_{salt})k_{rw}^{LS}(S_w) + (1 - F(x_{salt}))k_{rw}^{HS}(S_w)$$
(1)

$$k_{ro}(S_w) = F(x_{salt})k_{ro}^{LS}(S_w) + (1 - F(x_{salt}))k_{ro}^{HS}(S_w)$$
(2)

$$p_{c}(S_{w}) = F(x_{salt})p_{c}^{LS}(S_{w}) + (1 - F(x_{salt}))p_{c}^{HS}(S_{w})$$
(3)

Model 2: Adsorbed saline tracer

As the next step, adsorption is introduced by relating the wettability alteration to the total amount of adsorbed ion concentration. As low saline water enters the pore, polar hydrocarbon components bound to the rock surface desorb as ions dissolved in the brine adsorb to the mineral surface. Desorption of organic components, and hence, the concentration of adsorbed organic components, is proportional to the concentration of inorganic ions adsorbing from the aqueous phase. In the present model, the source of adsorption is not studied at this stage; therefore, the process is controlled by an isotherm coefficient relating the concentration of salt ions dissolved in brine to the adsorbate concentration. As a result of coupling adsorption with the low salinity displacement, it is necessary to adjust the interpolation function. For this adsorbed tracer model, the interpolation coefficient correlates with the adsorbate concentration.

Model 3: Mechanistic model

In the next development phase, the mechanisms acting behind the organic component desorption were analyzed. At this stage, low saline effects are assumed to result from the double layer expansion and multi-component ion exchange. On this account, the number of salt components in the brine phase is increased: instead of a single salt component, monovalent ions are represented by Na⁺ compound, whereas divalent ions are denoted as Ca²⁺ component.

$$Na^+ + \hat{S} \rightleftharpoons \widehat{Na} \sim K_{eq1}$$
 (4)

$$Ca^{2+} + 2\hat{S} \rightleftharpoons C\widehat{a_{VdW}} \sim K_{eq2}$$

$$Ca^{2+} + \hat{S} \rightleftharpoons C\widehat{a_{Y}} \sim K_{aa2}$$
(6)

$$Ca^{2+} + \hat{S} \rightleftharpoons \hat{Ca}_X \sim K_{eq3}$$

The adsorption of monovalent and divalent ions is described by equilibrium reactions given in equation (4) – (6) between the dissolved ions (Na⁺, Ca²⁺) and the solid surface (\hat{S}) resulting in adsorbed monovalent (\widehat{Na}) and divalent ($\widehat{Ca_{VdW}}$, $\widehat{Ca_X}$) ions. These chemical reactions are linked to the wetting properties through the total adsorbate concentration which determines the interpolation coefficient used to adjust multi-phase flow properties. The relative contribution of multi-valent ions to DLE and MIE [12], in addition to the impact of these two mechanisms on each other [13] are incorporated by an adjustment in the equilibrium constant of the chemical reactions capturing these phenomena.

Implementation

The introduced model concept was implemented into the numerical framework of the opensource porous media flow and transport simulator DuMu^X. DuMu^X can be applied to multiphase, -component, -scale and -physics fluid flow problems using continuum mechanical approaches. This software is a module of DUNE (Distributed and Unified Numerics Environment) that consists of several grid management, finite element shape function and iterative solver libraries resulting in fast computational performance, yet high flexibility and adaptivity [14].

The work presented here is based on a coupled, fully implicit 2-phase-N-component (2pnc) model capable to handle the number of components present in the fluid system with high flexibility, and solution-dependent flow properties. One of the extended versions of the 2pnc model coupling mineralization and evaporation processes to porous media flow providing a good foundation to realize organic compound ad- and desorption processes as well [15].

RESULTS

In the following section, simulation results are illustrated for the complex mechanistic model (Model 3), as during the development phase, Model 1 and 2 produced nearly identical results as Model 3.

Figure 4a illustrates saturation profiles for a secondary water flood scenario, when low saline water is injected into a core at connate water saturation. Simulation results (blue curve) were compared with analytical solution (red curve) based on the Buckley-Leverett fractional flow theory. The numerical results show a smearing out effect on the shock fronts leading to slight deviation from the analytical solution which is caused by numerical dispersion. This dispersion is amplified as a consequence of the linear interpretation implementation that is well illustrated in Figure 4a as one may observe more significant smearing out on the low saline shock front than on the high saline shock front. Since flow properties are functions of salinity, the salinity change across the core (green curve) has a severe impact on the flow profile: a gradual change in salinity results in high dispersion on the low saline shock front.

Figure 4b demonstrates the water and oil relative permeability curves for the high saline (dashed lines) and low saline water (dotted lines). The solid lines represent the relative permeability of Model 3 including the linear interpolation symbolized by the shift from the high saline permeability curve to the low saline lines. In the analytical solution, high saline flow properties change to low saline flow properties along a linear trend as a result of the abrupt change in the salinity on the interface of low saline and high saline water. In contrast to this, variation in the salinity and as a consequence, in the adsorbate concentration is a gradual change caused by a mixing zone between the high saline and low saline water.

The relative contribution of the dissolved ions to the different adsorption mechanisms are represented by the adsorbate concentration curves shown in Figure 4c. As all reactions are assumed to be in equilibrium, the initial adsorbate concentration values, which strongly

depends on the brine ionic composition, must be specified under equilibrium conditions. These values are not easy to measure and have a strong dependency on the equilibrium constants and the total surface site available for the ions to react. Currently the surface site is a prescribed value, thus providing a good foundation for further development by linking this value to pore surface area per volume ratio and shape factors characterizing the oil-brine-mineral contact area.



Figure 4a: Secondary water flood simulation from Model 3 compared with analytical solution



Figure 4c: Adsorbed ion concentrations expressed in mole fraction in secondary water flood



Figure 4b: Transition of relative permeability



Figure 4d: Tertiary water flood simulation from Model 3 compared with analytical solution

A tertiary recovery scenario was also simulated in order to evaluate the capability of the implemented model. In this case, a core with higher initial water saturation than connate water is flooded with the low saline water (Figure 4d). Similarly to the secondary water flood scenario, deviation between the analytical and the numerical results were observed due to the previously mentioned smearing out effect. Contrary to the secondary water flood scenario, where shock front heights determined by the simulation are identical to the analytical solution, in the case of the tertiary recovery, a difference was noted between the manner how oil bank forms based on the simulation and the analytical solution. Based on the Buckley-Leverett solution, oil bank height is constant, whereas in the model, oil bank height increases over time yielding to underestimation of the oil bank height at early simulation time, and overestimation at later simulation time caused by the fact that in case

of the analytical solution, constant injection rate is assumed, whereas in the simulation, due to current code limitations, constant pressure difference is applied over the core.

Low salinity water flood is believed to cause economical increase in the recovery factor, only in cases where significant shift in the wettability condition is achieved. Literature states an optimum salinity value for this in a range of 4000 - 5000 ppm. [11, 16] This effect is accounted for by an optimal adsorbate concentration (or salinity in the earlier models) in the interpolation function, where adsorption rate is the fastest. Related to the interpolation function, it means that low salinity effects are enhanced if adsorbate concentration (salinity) is at this optimum value or below. Figure 5a shows the saturation profile for the same secondary low salinity water flood scenario with different linear interpolation function definition. In one case, a linear interpolation is applied neglecting this optimal salinity value (blue line): amplified smearing out effect on the low saline shock front. In the second case, where an interpolation considering this optimal value is used (Figure 5b – red line), the smearing out of the low saline water front is weakened, an oil bank forms and a spreading wave forms between the oil bank and the high saline water shock front.



i igure sui seesiidui y

CONCLUSION

In the presented work a complex mechanistic model is proposed that implements low salinity effect by correlating the change in the wetting conditions with salinity controlled flow properties. The obtained simulation results are in good agreement with analytical solution. Deviations are caused by numerical dispersion. The simulation model exhibits high sensitivity to the captured phenomena as well as to the realization of the interpolation function.

A combination of experimental research and the explicit numerical description could provide essential information on the equilibrium constants, total surface site concentration and finally to the interpolation function, leading to an accurate model description for LSWF.

REFERENCES

 Joekar Niasar, V., Mahani, H., "Nonmonotonic Pressure Field Induced by Ionic Diffusion in Charged Thin Films" *Industrial & Engineering Chemistry Research*, (2016) 55(21), 6227-6235 Formatted Table

- Hill, H.J., "Cation exchange in Chemical Flooding: Part 3 Experimental", SPE Journal, (1978) 18(6), 445-457
- Valocchie, A.J., Street, R.L. and Roberts, P.V., "Transport of ion exchanging solutes in groundwater: Chromatographic theory and field simulation" *Water Resources Research*, (1981) 17(5), 1517-1527
- Lager, A., Webb, K.J., Black, C.J.J., Singleton, M., Sorbie, K.S., "Low Salinity Oil Recovery – An Experimental Investigation" *Petrophysics*, (2008) 49, 28-35
- Suijkerbuijk, B.M.J.M, Kuipers, H.P.C.E., Al-Quarshubi, E.C.M. et al. "The Development of a Workflow to Improve Predictive Capability of Low Saline Response" presented at the *International Petroleum Technology Conference* in Beijing, China, 26-28 March 2013
- Tang, G.-Q. and Morrow, N.R., "Influence of brine composition and fines migration on crude oil/brine/rock interactions and oil recovery" *Journal of Petroleum Science and Engineering*, (1999) 24, 99-111
- Al-Attar, H.H., Mahmoud, M.Y., Zekri, A.Y., Almehaideb, R., Ghannam, M.T., "The Impact of LoSalTM on Oil Recovery from a Selected Carbonate Reservoir in Abu Dhabi – An Experimental Approach", SPE (2013) SPE-164331-MS
- Yousef, A.A., Al-Saleh, S.M., Al-Jawfi, M., "New Recovery Method for Carbonate Reservoirs through Tuning the Injection Water Salinity – Smart Water Flooding" SPE (2011) SPE143550-MS
- Lee, S.Y., Webb, K.J., Wang, X. et al., "Low Salinity Oil Recovery Increasing Understanding of the Underlying Mechanisms" SPE (2010) SPE-129722-MS
- Ligthelm, D.J., Gronsveld, J., van der Linde, H.A. et al., "Novel Waterflooding Strategy by Manipulation of Injection Brine Composition", SPE (2009) SPE-119835-MS
- Kuznetsov, D., Cotterill, S., Giddins, M.A., Blunt, M.J. "Low-Salinity Waterflood Simulation: Mechanistic and Phenomenological Models" SPE (2015) SPE-174615-MS
- Arnarson, T.S., and Keil, R.G., "Mechanisms of pore water organic matter adsorption to montmorillonite", *Marine Chemistry*, (2000) 71, 309-320
- Mahani, H., Berg, S., Illic, D., Bartels, W.-B., Joekar Niasar, V., "Kinetics of Low-Salinity-Flooding Effect" SPE (2015) SPE-165255-MS
- Flemisch, B., Darcis, M., Helmig, R. et al., "DuMuX: DUNE for multi-{phase, component, scale, physics,...} flow and transport in porous media" *Advances in Water Resources*, (2011) 34, 1102-1112
- Jambhekar, V.A., Helmig, R., Schröder, N., Shokri, N., "Free-Flow-Porous-Media Coupling for Evaporation-Driven Transport and Precipitation of Salt and Soil" *Transport in Porous Media*, (2015) 110(2), 251-280
- Austad, T., Rezazidoust, A., Puntervold, T., "Chemical Mechanism of Low Salinity Water Flooding in Sandstone Reservoirs" SPE (2010) SPE-129767-MS