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GEOCHEMICAL REACTIVE TRANSPORT MODELING IN OIL & GAS INDUSTRY— BUSINESS DRIVERS, CHALLENGES AND SOLUTIONS

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ABSTRACT

Geochemical reactive transport modeling (RTM) offers an integrated approach to understanding the dynamics of physical and chemical processes in the subsurface. It has been considered the most "realistic" approach to investigate coupled physical and chemical processes, such as fluid flow in porous media, phase behavior, and water-rock (WR) interaction through space and time.

Originally developed for environmental studies, early RTM applications inherently focused on thermo-hydro-geochemical (THGC) systems at low temperature and low pressure conditions. In contrast, the oil and gas industry deals with deep, high temperature/pressure/salinity THGC systems (i.e., reservoirs, source rocks and migration paths) to explore and extract hydrocarbons (HC) as well as to dispose of greenhouse gas and waste water. Water, steam, gas (e.g., N_2 and CO_2) or chemicals are commonly injected during HC production, especially for Enhanced Oil Recovery (EOR). Geochemical processes induced by these injections can lead to risks such as injectivity impairment and productivity decline by scaling (mineral precipitation) and/or clay/anhydrite swelling, fluid leakage, and wellbore instability by corrosion (dissolution of minerals) and reservoir souring. RTM is a unique tool that can be used to understand these processes and assess related risks during HC production.

A number of challenges remain for RTM application in the oil and gas industry: (1) pressure and temperature ranges in many fields exceed the range of available thermodynamic data; (2) the presence of hyper-saline reservoir brines requires modeling with dedicated simulators and thermodynamic data; (3) HC has to be considered not only as an additional phase but as a geochemical entity.

Dedicated experimental work and improvement to numerical simulators are needed to overcome these challenges. In the meantime, currently available simulators and thermodynamic data can be used with caution to gain valuable insight. This paper will discuss the business drivers, evaluate the challenges, and propose solutions for applications of RTM technology in the oil and gas industry, using real examples such as water injection, CO_2 injection (CCS or EOR), and water-alternate gas injection (WAG).

BUSINESS DRIVERS

The oil and gas industry typically deals with deep THGC systems at high temperature, high pressure, and high salinity conditions. A broad range of geochemical processes can take place in such systems, including organic processes, i.e., kerogen cracking (KC) and HC transformation, and inorganic processes, i.e., WR interactions. There are also interactions between the organic and inorganic systems: KC and HC transformation are affected by the inorganic system that provides the organic processes necessary conditions such as pH, Eh, salinity and catalytic effects from ionic and mineral compounds (Tannenbaum and Kaplan 1985, and Wei, et al, 2006); On the other hand, products from kerogen cracking can dissolve in water/brine, leading to changes in water/brine chemical composition. HC can coat the mineral surface, impacting mineral dissolution/ precipitation kinetics. During waterflood and enhanced HC recovery (EOR and EGR), water, gases (e.g., N_2 or CO_2), and other chemicals are injected into the reservoir. This fluid injection can lead to property changes in reservoir fluids, mineral dissolution/precipitation, and swelling/ shrinking

of clay and other minerals e.g., anhydrite. These processes can lead to changes in formation porosity and permeability, which can be favorable or unfavorable for HC recovery. Understanding such processes in the THGC systems is very important for evaluation of HC reserves, exploration, and production.

KC and HC transformation are normally simulated using "basin modeling" (BM) technology, which deals with the formation and evolution of sedimentary basins, including burial and thermal histories of the basin, the maturity progression of the source rocks, and the expulsion, migration, and trapping of hydrocarbons. However, processes taking place between kerogen cracking (including HC transformation) and WR interactions have traditionally not been thoroughly and rigorously considered in basin modeling exercises. These processes remain a challenge for basin modeling, in addition to the challenge of complex kinetics within the KC processes.

Normally, BM is conducted in a decoupled sequential manner, i.e., a simulation time step is started from burial calculation, accounting for subsidence and compaction, to simulate pressure distribution, followed by a thermal calculations of given boundary conditions to calculate temperature distribution. The pressure and temperature are then used as given conditions to calculate KC and expulsion with or without consideration of the diffusion process within the source rock. The generated HC is then assumed to migrate through possible pathways "directly" (i.e., no fluid dynamic controls considered) into targeted reservoirs when traps are present, or otherwise lost. BM is presently very comprehensive and robust in dealing with organic geochemical processes of large scale (basin scale) and long elapsed time (geologic time). It is very useful for evaluation of HC resources and helpful in exploration (sweetspotting). However, compared to RTM, it is limited in accuracy and precision, because deterministic principles and mechanisms are omitted to facilitate simulation with restricted computational power.

Reservoir simulation (RS) accounts for the multiphase fluid dynamics in HC reservoirs under isothermal or nonisothermal conditions. Geochemical processes are found, in many cases, as key controls during waterflood and EOR. Modeling the geochemical processes within the reservoir simulation is highly desired. Existing reservoir simulators, however, cannot practically handle the geochemical processes, because most of them have no such capability, while few of them can deal with geochemical systems with a limited number of unknowns, due to the numerical scheme normally deployed (i.e., fully implicit coupling). So far, there are only very limited successful reservoir simulations reported that truly incorporate geochemical reactions.

Reactive transport modeling tracks WR interactions under nonisothermal fluid dynamic conditions. Numerically, thermal, fluid dynamics, and geochemical reactions are all coupled in RTM using a direct substitution approach (DSA, fully implicit), a sequential iteration approach (SIA, implicit), or a sequential non-iteration approach (SNIA, explicitly). Most RTM simulators use SIA and thus can deal with large number of geochemical unknowns—essential for modeling "real" geochemical systems. In addition to WR interactions, KC and HC transformation is also considered in some RTM simulators, although not commonly handled in RTM practice. Geochemical reactions are handled in RTM using deterministic principles, i.e., the first (conservation of mass and energy) and second (mass action) law of thermodynamics. Compared to BM, RTM delivers results with higher accuracy and precision—however, to date, only for problems of a limited scale and time duration, due to restrictions in computational power. Parallel computing technology and the enormous, growing computational power of RTM will eventually bring RTM into problems of sufficient large scale, with reasonable detail in space and time.

Processes in hydrocarbon systems, including KC to generate HC in source rock, expulsion from the source rock, migration in flow paths, trapping in reservoirs and well production—can all be considered appropriate for RTM. Deployment of RTM technology in RS is ongoing. Geochemical processes will likely be well taken into account in future RS practices. Existing RTM simulators, e.g., TOUGHREACT, is still the first choice for modeling geochemical reactive transport of HC systems. Transplanta-

tion of RTM technology into BM, such as fluid-dynamics controls in HC migration, effects of WR interaction on KC, and the effects of KC on WR interaction, would be a great step forward for BM.

Theoretically, RTM can be conducted for systems of different scales (from basin, reservoir, well, core, to pore scale) and different time durations (from geologic to fractions of seconds), over a wide range of temperatures (nominally, up to 330°C or higher) and pressure (theoretically up to 5,000 bars or higher) depending on the availability of the required thermodynamic data of the T&P range. Data from oil and gas exploration, such as seismic, well logs, core analysis/measurements, fluid samples, and production logs, can all be utilized to construct an RTM. Appropriately designed RTMs can describe the interactions of competing processes at a range of spatial and time scales, and hence are critical for connecting the advancing capabilities for material characterization at the atomic scale, with the macroscopic behavior of complex earth systems (Steefel et al., 2005).

RTM numerical simulators have been developed over the last 20 years and have gradually been adopted by the oil and gas industry, through technology transfer or development inside the industry. TOUGHREACT (Xu et al., 2006; 2011) has been transferred to many organizations globally, including a number of major or independent oil companies. Applications with TOUGHREACT are rapidly increasing, and the user community has grown, leading to significant contributions in the oil and gas industry in multiple ways, such as reservoir characterization (Xiao and Jones, 2006), enhanced oil recovery (Zhang and Taberner, 2009) and disposal of greenhouse gas (Xu et al., 2005; Pruess and Muller 2009 and Zhang et al., 2010).

In the oil and gas industry, the development of an RTM simulator has been carried out by normally, adding a geochemical solver into an existing reservoir simulator. Examples are CMG-GEM, Shell's MoReS-PHREEQC and GPRS (Fan, 2012) among a few others. This type of simulator will become mature if more applications can be successfully performed with it.

Limitations to RTM remain when dealing with a complex THGC system of large scale and long time duration, such as the proper treatment of coupled HC and WR system. Consideration of increasing complexity (coupling organic and inorganic systems) in RTM will require finer spatial resolution (more gridblocks), handling large numbers and different mechanisms of reactions over a long time period, i.e., geological time (thousands to millions of years) and thermodynamic database expansion. Numerical simulators accounting for such a coupled HC and WR system have not yet been achieved; their development is of great interest to the oil & gas industry. Temperature and pressure ranges of hydrocarbon systems are normally wider than that of other systems e.g., shallow groundwater systems. Thus, modeling coupled HC and WR systems requires sufficient data to cover wider T&P ranges. Currently available thermodynamic data do not cover these ranges. Dedicated experiments to this end are desired, and some are ongoing.

In the present paper, RTM challenges and possible solutions are discussed using some real examples, in addition to the business drivers discussed above.

CHALLENGES AND SOLUTIONS

Effects of high temperature, high pressure, high salinity and HC phases on geochemical processes

The pressure in typical HC reservoirs ranges from 100 to 30,000 psi (7–2070 bar). Temperature ranges between 10°C and 260°C (500 F) although most oil reservoirs are below 150°C and gas reservoirs below 250°C. Nevertheless, reservoirs can be heated up to 350°C or higher during *in situ* upgrading processes (IUP), *in situ* combustion processes (ICP) and thermal EOR. Water, steam, and/or gases are typically injected during EOR processes. Geochemical reactions induced at high temperature can have significant effects, such as souring due to H_2S generation from thermochemical reduction of sulfates (TSR) (Zhang et al., 2007), CO_2 generation from thermal decomposition of carbonates, scaling from enhanced precipitation of minerals under high temperature, and deformation from swelling/shrinking of clay and anhydrite. RTMs that can track these effects are highly desired, to

help understand these processes and evaluate the relevant risks. Effects of high pressure and high temperature on geochemical reactions must be considered when RTM is performed to properly characterize reservoir properties and evaluation of HC generation, migration, trapping and production.

HC coexists in reservoirs with high salinity water (brine). Salinity of reservoir brines, normally quantified using total dissolved solids (TDS), ranges from 10,000 ppm, translated to about 0.15 molal (*m*) of NaCl-equivalent ionic strength (*I*) up to 280,000 ppm (~1–6 m) or higher. A Na-Mg-Ca-Cl brine (Brine-1 in Table 1) was found from a Middle East carbonate reservoir having a salinity of about 382 g/L (*I* >10 *m*), and halite-saturated. A Na-Mg-Cl brine (Brine-2) was found in a reservoir hundreds of kilometers away from Brine-1, at about 375g/L and halite-saturated. Na-Mg-Ca-Cl or Na-Mg-Cl brine at halite saturation are frequently found in Middle East reservoirs, while halite-saturated Na-Cl type brines are common in HC reservoir and deep saline aquifers (e.g. Brine-3) in the North America basins such as the Gulf of Mexico and Alberta, Canada.

Table 1. Hypersaline brines found from HC reservoirs and saline aquifers (concentration in molality)

Component	Brine-1	Brine-2	Brine-3
Formation	dolostone	carbonate	sandstone
T (°C)	80	127	64
Density (kg/l)	1.28 at 33°C	1.22	1.19
TDS(g/l)	382	375	338
PH	3.8	5.6	5.9
Na^+	2.81	4.71	5.54
Ca^{+2}	1.18	1.7	0.056
Mg^{+2}	1.34	0.24	0.043
Fe^{+2}	9.0E-06	N.D.	5.88E-05
Ba^{+2}	N.D.	N.D.	4.08E-06
Sr^{+2}	N.D.	N.D.	4.98E-04
K^+	N.D.	0.135	3.46E-02
Cl^-	7.64	7.20	6.28
SO_4^{-2}	0.11	0.11	2.19E-02
HCO_3^-	N.D.	4.72E-06	1.38E-03
CO_3^{-2}	N.D.	N.D.	N.D.

N.D.: not detected or very low concentration

The origins of these brines have not been thoroughly investigated, although they are believed to be related to the adjacent salt deposition. Enrichment in Ca and/or Mg indicates that the brines or the related salt/evaporites must have been gone through an extreme evaporation as modeled in Zhang et al., (2009).

Simulations involving such hypersaline brines are required to deal with the short-distance ionic interactions using dedicated ionic activity models. Pitzer ion-interaction model (Pitzer, 1979; 1991 and Harvie et al., 1984) is normally used with proper ion–interaction parameters available for the P&T range, consistent with the thermodynamic equilibrium constants (K and usually given in form of log i.e. logK) used. The challenge is that the required ion–interaction parameters are not fully available for these P&T ranges. Compromise must be made, and thus uncertainties remain before appropriate data become available. Careful evaluation is highly recommended when using the current thermodynamic data under high-pressure, high-temperature and high-salinity conditions.

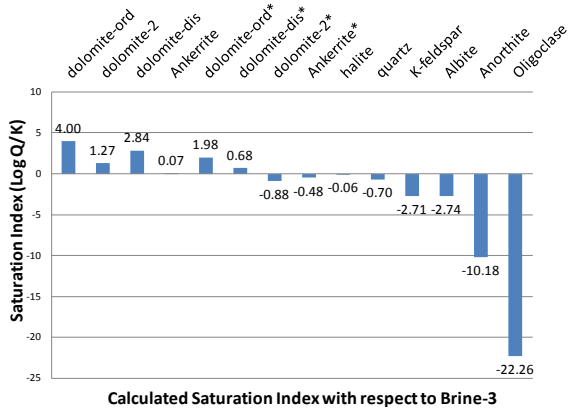

Figure 1. Calculated saturation indices of dolomite minerals with respect to brine-3 on Table 1, using logK data from the TOUGH-REACT database *TherAkin8.dat* and Pitzer ion interaction parameters from EQ3/6 Pitzer database *data0.ypf R2*.

As an evaluation example, calculated saturation indices (SI) of dolomite and other minerals with respect to brine-3 using different sets of thermodynamic equilibrium constants are compared in Figure 1. Different sets of thermodynamic equilibrium constants are represented by the name of "*dolomite-ord*" (ordered dolomite), "*dolomite-dis*" (disordered dolomite), and "*dolomite-2*" (representing a validated LogK value data set using measured data, Birkholzer et al., 2008; and Zheng et al., 2009), respectively. Along with these three sets of LogK's, Pitzer

ion–interaction parameters from Alai et al. (2005) have been used (*data0.ypf.r2*). Calculated saturation indices with most of these data are far higher than zero, which is not realistic because there is no dolomite detected in that formation (SEM and XRD measurements). Instead, an iron-rich dolomite, ankerite is present and the calculated SI of ankerite is just about zero, indicating this mineral is in equilibrium with respect to the brine. Based on the same logic, calculated SI of other dolomite members should be negative or close to zero, because of the absence of this mineral from the formation. In fact, only one set of logK data—the data represented by the name of *dolomite-2** assuming the brine is in equilibrium with respect to all major aluminosilicate phases of the formation—can derive a realistic SI, i.e., negative value (see column under caption *dolomite-2** in Figure 1). This test verifies that the logK data set represented by *dolomite-2* in the TOUGHREACT database *TherAkin8.dat* is the best data for dolomite under the high-salinity conditions of this case.

Calculated SI of halite is just about zero, representing reality. The SI of quartz is slightly below zero—still believed realistic because as the dominant mineral, quartz undergoes very slow dissolution. SI's of major aluminosilicate phases in the formation are all negative, because the measured aluminum concentration is not realistic and assumptions of equilibrium or realistic thermodynamic status on one or more major aluminosilicate phases must be made to better simulate the brine-rock system.

The calculated SI of dolomite with respect to brine-1 in Table 1 stays negative (< -5) under the measured reservoir CO_2 partial pressure, no matter which set of the data is used. This situation implies uncertainties in the thermodynamic equilibrium constants ion–interaction parameters, the consistencies of logK and ion–interaction parameters, T- and P- dependence of all parameters at the hypersaline condition, and of course, possible uncertainties in measurements.

The temperature dependence of logK is commonly incorporated into most geochemical simulators. The temperature range of the thermodynamic database of PHREEQC (Parkhurst, and Appelo, 1999) is 0–60°C and that of EQ3/6 (Wolery and Daveler, 1992) is 0-300°C. Most of others lie between. Uncertainties in the temperature dependence of logK have been evaluated (André, et al., 2006); they are believed to be the most significant source of uncertainty in most thermodynamic databases. Similar evaluations have been done on the ion-interaction parameters from Alai et al. (2005) (Zhang and Sturmer, 2011). Uncertainties in the T-dependence significantly impact model results.

Pressure-dependence of logK is generally less than the T-dependence. For pressure variation less than 10 bars, logK can be assumed to be P-independent. For example, Sawamura (2007) studied halite solubility and found that for constant temperatures 37°C, solubility increases from 6.13 *m* at 1 bar, to 6.38 *m* at 500 bar, 6.41 *m* at 1000 bar, 6.61 *m* at 2,000 bar and 6.69 *m* at 3,000 bar. In addition, Morse and MacKenzie (1990), in studying the pressure dependence of CO_2 solubility, found that the equilibrium constant of CO_2 dissolution in pure water changes 0.31 log units, near-linearly, when pressure increases from 1 bar up to 600 bar at constant temperature. However, this value changes 0.27 log units, from 0°C to 25°C, at constant pressure.

These examples illustrate the strong dependence of logK on temperature and weak dependence on pressure. Temperature dependence in an HC system can never be ignored, while pressure dependence can be omitted if pressure variation is not very large and the logK's are calibrated for that pressure range.

Handling high-salinity brines requires not only an appropriate ionic activity model, but also considering the effects on other reactions, such as cation exchange and sorption. Simulation of the geochemical steady-state condition of a high salinity WR interaction system of an Eocene formation (smectite-dominated clay and quartz sandstone interlayer at I ~3 m) requires calibrating the cation exchange selectivity coefficients to the high-salinity conditions. The calibrated values deviate from the normal ranges of literature values used in Zheng et al. (2009) (Table 2) although the mechanism causing the salinity dependence of the selectivity coefficient has not been thoroughly investigated. A new constitutive cation exchange model is needed to account for the salinity effects on cation exchange.

Table 2. Calibrated selectivity coefficients (Gaines-Thomas convention) to high salinity condition and literature value available to low salinity condition (typically $I < 0.1$ m)

Cation	Value calibrated to high salinity	Value available to low salinity
Master	H^+	Na^+
H^+	1.00	1.00
Na^+	0.24	1.00
Ca^{+2}	0.76	0.40
Mg^{+2}	0.88	0.45
K^+	0.27	0.20
Ba^{+2}	0.46	0.35
Sr^{+2}	0.45	n/a

Generally speaking, an RTM involved in problems of high-salinity brine under high P and high T conditions needs to carefully select an ionic activity model and evaluate the thermodynamic data including ion-interaction parameters, as well as the consistency of the parameter sets. Calibration is strongly recommended to reduce the uncertainties.

High-salinity conditions may also be encountered in other situations in an HC system, such as cement corrosion leading to wellbore degradation, especially when CO_2 is injected for the purpose of geological sequestration and/or EOR. RTM of cement corrosion has not been much studied, but still ought to attract attention from both experimental and modeling aspects.

Effects of HC phase on geochemical reactions

As discussed above, HC affects WR systems through dissolution of HC components, such as organic acids. Geochemical modeling of these reactions is not challenging from a numerical perspective; however, not many examples exist. In addition, the HC phase can act as a barrier to WR interaction by coating the solid surface. This effect reduces the effective surface area of minerals for dissolution and precipitation, and can impose a saturation window (Xu et al., 2006). For example, calibrated effective specific surface area of minerals in the same Eocene formation (I ~3 m and oil saturation 40–80%) is 3 to 5 orders of magnitudes lower than the normal ranges of literature values (Table 3).

Table 3. Calibrated effective surface area (cm^2/g) of minerals (along with kinetic rates from Palandri & Kharaka, 2004) to account for the effects of HC coating in dissolution and precipitation and compared to literature values

Mineral	Calibrated to account for the HC effect	Initial Estimate based on SEM	Ranges of literature value*
Quartz	0.255	1.132	$10\text{-}10^4$
K-feldspar	0.185	1.0	$10^2\text{-}10^3$
Albite	0.185	1.2	$10^2\text{-}10^3$
Smectite	55.23	1008	$10^5\text{-}10^7$
Illite	10.22	431	$10^5\text{-}2\text{x}10^6$
Muscovite	32.25	1000	$10^4\text{-}3\text{x}10^4$
Kaolinite	8.03	560	$10^4\text{-}10^5$
Chlorite	18.1	1000	$10^3\text{-}10^5$
Pyrite	1.992	1.1	$10^3\text{-}10^4$

*Literature values are from Yuang and Shen (2005), Xu et al. (2009), Hamilton et al. (2000), Gaines (1957), Zhou and Gunter (1992), Aylmore et al. (1970), Chirita (2003), and Wolfe et al. (2007), and some of the reference therein.

The coating effects of HC in WR interaction, also characterized as "wettability" in the industry, are complex, and normally a function of phase saturation. There is so far no appropriate relationship useable in the RTM. Developing such a model to actually simulate HC wettability effects on mineral dissolution and precipitation remains a challenge.

Effects of geochemical processes on injectivity and productivity

Charged by injection or extraction of fluid and heat, the near-wellbore region experiences more significant geochemical processes. The major drivers are (1) changes in temperature and pressure, (2) mutual solubility of fluid phases, e.g., injected CO_2 evaporates into formation water, and (3) incompatibility of injection fluid and formation fluids, e.g., contrasts in pH and/or Eh between the injected water and the formation water during waterflood and hydraulic fracturing. Results of associated geochemical reactions are (1) drastic changes in water chemical composition, leading possibly to fluid dynamic property changes, corrosion potential to wellbore, and clay swelling; and (2) changes in porosity and permeability due to dissolution and/or precipitation of minerals/salts and clay swelling/shrinking. Effects of these geochemical

reactions become key issues in risk assessment for HC extraction and CCS projects.

Injection of large amounts of water or gas (mainly CO_2) into an HC reservoir for water-flood or enhanced oil/gas recovery will induce precipitation of minerals, mainly calcite, if the injected water (normally seawater with pH >8.0) is geochemically "incompatible" with the formation water (normally hypersaline with pH ~6 or lower). Precipitation of other minerals (e.g., barite) also contributes to scaling. Scaling is normally modeled using batch geochemical simulators in the industry, such as "Geochemist Workbench" (Bethke and Yeakel, 2012) and Oli "ScaleChem" (2011). Batch calculations cannot give results with spatial variation; nevertheless, the spatial variation is very important for evaluation of scaling potential.

RTM is the right tool to predict mineral dissolution and precipitation in a given time- and space-domain. Variation in time and space are well tracked in RTM simulations. The strong capability of RTM becomes better recognized in the production geology and production technology communities.

TOUGHREACT RTM results show that, during a 20-year waterflood of a hypersaline reservoir using untreated seawater, precipitated calcite will accumulate at the wellbore in significant amounts, causing a volume-averaged porosity reduction in the near-wellbore region, about 2 porosity units (0.02) at the end of the injection, while barite will precipitate at the moving front of the injected seawater and will not be accumulated at a single location.

Injection of CO_2 into a saline aquifer for CCS or saline reservoir for EOR can induce precipitation of halite within a dryout zone near the wellbore, due to the solubility of water in CO_2. The precipitated salt will be accumulated at the moving dryout front, while dissolved salt is supplied by imbibition flow of formation brine from an outer brine-CO_2 mixing zone. This type of process has been simulated using TOUGHREACT-Pitzer (Zhang et al., 2006) for several applications (Zhang et al., 2011). A recent such model effort has been carried out on a sandstone aquifer of halite-saturated brine (brine-3 in Table 1) at 64°C and 2100 m deep. Model-predicted salt precipitation accumulates at the dryout front, up to 70 kg/m^3, higher than the salt contained in the in-place brine, because the imbibition brings salt back toward the dryout front where salt precipitates. Salt has been observed precipitating at the inlet of a similar sandstone core with similar brine while injecting supercritical CO_2 in a lab experiment (Wang et al., 2010). This observation is consistent with the effects of imbibition on salt precipitation observed from the RTM results.

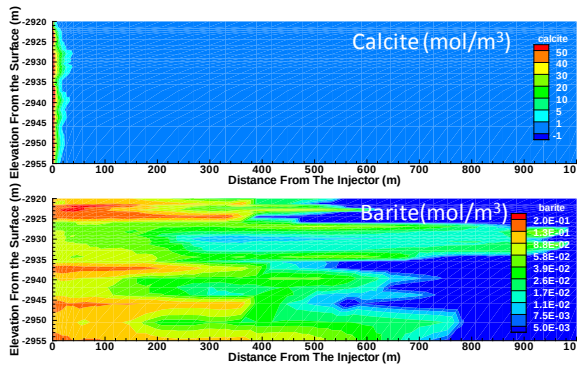

Figure 2. TOUGHREACT RTM predicted accumulative precipitation (mol/m^3 rock) of calcite and barite during 20-years injection of seawater into a hypersaline oil reservoir for secondary oil recovery. Note that the injector is on the left on the figure.

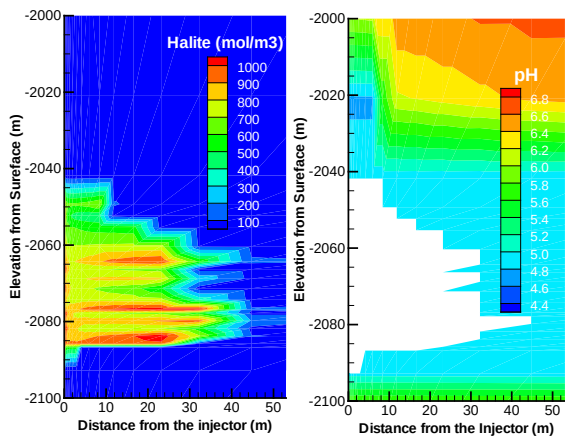

Figure 3. TOUGHREACT RTM predicted halite precipitation and pH at the end of a 25-year injection of CO_2 into a sandstone formation for storage. Blank area represents the near-wellbore dryout zone. Note that the injector is on the left of the figure.

Such a large amount of salt precipitation will likely clog pores, leading to injectivity impairment. Model results indicate that salt will

preferably precipitate in high-permeability layers (Figure 3), tending to even out the permeability over the dryout zone. This phenomenon can be verified by some experimental observations, i.e., during a coreflood experiment, salt first precipitates within the fracture or pore space (Wang et al., 2010) although the hypothesis of salt preferably precipitating at the pore throat has also been accepted by some investigators. However, it is a complicated situation, because in reality, the distribution of salt can also be affected by the injection rate, i.e., CO_2 flux. But, the mechanism that the CO_2 velocity affects the salt distribution is not known. Permeability changes as a function of porosity change adds another challenge, although various models have been suggested and implemented (Pruess et al., 1999). Still, much more efforts in pore or nanoscale research are very much welcomed.

Injectivity/productivity issues can also arise when clay swells during the injection of low-salinity water into a high-salinity formation. Clay swelling can be accounted for in TOUGHREACT, but in a pragmatic way, calculating the porosity change due to clay swelling as an empirical function of salinity. The Gouy-Chapman diffuse-double-layer theory (Wayllace, 2008 and Zheng et al., 2011) considers the chemical controls of water activity and the hydration process of clay interlayer, and calculates the excess pressure (called swelling pressure) caused by the hydration of the interlayer. If coupled with a geomechanical simulator, clay swelling can be better simulated in support of evaluation of well injectivity, productivity, and stability. We hope that this model can be available soon in TOUGHREACT.

A Scheuerman diagram (Scheuerman and Bergersen, 1990) is often used to evaluate the swelling potential of a given clay mineral in contact with a water of known chemical composition. The swelling potential of the given clay mineral is evaluated in a two-dimensional Cartesian domain defined by concentration of total cations (as the Y-axis) and the fraction of divalent cations over total cations (as the X-axis). Giving the chemical composition, water can be mapped on a diagram of a given clay; therefore, the combination of water and clay can be qualitatively evaluated as Zone A, "compatible," meaning no risk of swelling; Zone B, "impairing," meaning a risk of definite swelling, Zone C, "acceptable," meaning slight swelling but not a showstopper, and Zone D, "need more data," meaning the swelling potential cannot be evaluated using this diagram, and more data and more studies are needed, i.e., the swelling risk can no longer be simply viewed as a function of salinity and the ion ratio of the water.

One example is given in Figure 4 for evaluating a clay swelling risk using the Scheuerman diagram, for a case of injecting low-salinity water (I <0.04 m) into a high-salinity reservoir (I ~3 m). Water chemical composition was predicted using a TOUGHREACT RTM, considering the injection of the low-salinity water, mixing with the high-salinity formation brine, dissolution and precipitations of relevant minerals, and, most importantly, cation exchange.

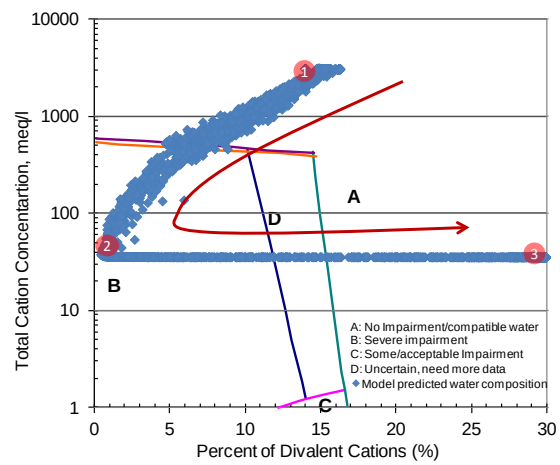

Figure 4. Mapping TOUGHREACT RTM predicted water composition of the whole domain and duration of injection of a low salinity water into a high salinity reservoir on Scheuerman diagram for evaluation of smectite swelling potential.

Both injected low-salinity water and the high-salinity formation brine are located within Zone A (1 and 3), no swelling. However, water composition at a given location through which the injected low salinity water will pass evolves from the initial composition of formation brine into a final composition defined by the equilibrium between the injection water and the formation rock. In between, water composition is transient (e.g., 2) and characterized by

coupled mixing, cation exchange, and mineral dissolution/precipitation under the injection conditions. However, water 2 falls within Zone B, where there is high potential of swelling. The transient water moves away from the injector wellbore. Swelling in the formation can enhance productivity by pressurizing the reservoir, if sufficient effective permeability can still be maintained and the swelling does not take place at or very close to the wellbore. Results of this study can be used to optimize well placement towards maximum productivity.

The coupling between the swelling and flow had to be omitted in the RTM because there is no such capability in the current version of TOUGHREACT. In some other cases, challenges have also arisen because clay is found to swell when CO_2 is involved. The mechanism has not been outlined; it deserves attention from a scientific perspective.

Effects of geochemical processes on wellbore stability

Wellbore instability can be caused by corrosion of wellbore (casing and cement) and near-wellbore rock. Injection of CO_2, other acid gas, or waste waters for geological storage or EOR can significantly acidify the near-wellbore region and lead to corrosion.

In the case of CO_2 injection, a dryout zone can form at the near-wellbore region as long as the CO_2 under injection is dry, as discussed above. Theoretically, a dryout zone around the wellbore can prevent the acid fluid from reaching the wellbore, protecting it from corrosion. However, in reality, the dryout zone barrier cannot be as effective as expected because: (1) residual brine is present in pore spaces after the "dry" CO_2 equilibrates the chemical potential of water with the water chemical potential (i.e., water activity) in the residual brine; and (2) low-permeable layers hold water much longer because of their high capillarity. Even if the adjacent high-permeable layer is dried out, CO_2 from the adjacent 'dryout' layers acidify the low-permeable layers. In particular, the top and bottom seals that are contacting the wellbore always stay wet (see right plot on Figure 3), resulting in a high risk of corrosion. Wellbore cement can be quickly corroded at the contacts of low-permeable layers.

Strong dissolution of near wellbore formation rock can lead to a cavity loosing up the wellbore. This type of incident has in the past taken place in carbonate reservoirs, especially when CO_2 or other acid gases are injected.

RTM is useful in predicting corrosion of the wellbore and dissolution of near-wellbore rock. In addition to the challenge of high-T, high-P and high salinity, RTM must account for cement-concrete. An RTM that incorporates formation rock and wellbore cement will be an ideal model. Successful examples of such models have not been reported for the oil and gas industry, although some RTM development holds promise in this regard (Huet et al., 2010).

A water-alternate-gas (WAG) injection in a carbonate (chalk) reservoir as an EOR scheme was modeled using TOUGHREACT-Pitzer (Figure 5). The WAG involves injection cycles of seawater and CO_2, alternatively, starting with a 15-year injection of seawater, followed by a 2-year injection of CO_2 and then a 2-year injection of seawater. Alternate injection of seawater (again for 2 years) and CO_2 (again for 2 years) continues until the end of field life.

During the 15-year injection of seawater, the seawater displaces 30–40% of the oil at the near-wellbore (injector) region (a zone extending from the injector wellbore to ~100 m away from the injector, top part of Figure 5), especially, within the high-permeable layers. The subsequent 2-year CO_2 injection acidifies the previously injected seawater, leading to calcite dissolution. The dissolution is strongly enhanced when the subsequent 2-year seawater injection is followed, because (1) more water is available and (2) dissolved carbonates are transported away from the near-wellbore region. The largest dissolution of calcite takes place during the 2-year seawater injection following the 2-year CO_2 injection, leading to increased porosity in the near-wellbore zone of about 4 units (i.e., 4% of the total rock volume).

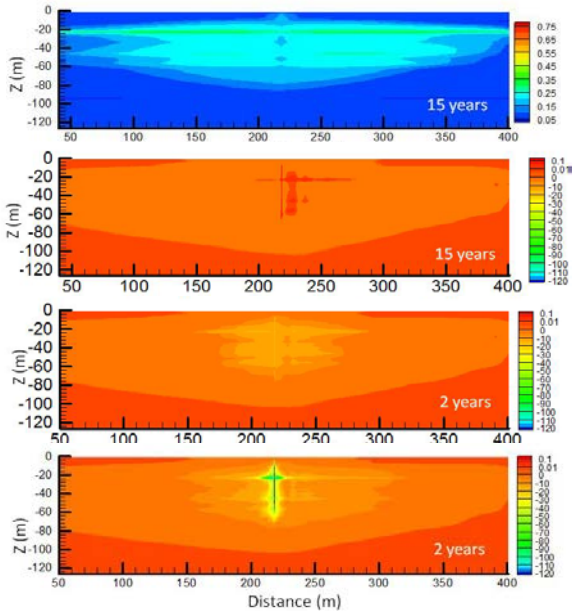

Figure 5. TOUGHREACT RTM predicted swap efficiency (shown as water occupied porosity in the top figure) and change of calcite abundance on the second figure from the top (in mol/m^3 of rock, positive for precipitation) at the end of a 15-year seawater injection, and the change in calcite abundance after the subsequent 2-year CO_2 injection (third) and after the following 2-year seawater injection (bottom), respectively. Injector is located in the middle, producer is at the right, and the left boundary is open.

CONCLUDING REMARKS

Geochemical RTM can contribute significantly to the understanding of HC systems, from exploration to production. Challenges for RTM application in the oil and gas industry are mainly from high-T, high-P and high-salinity conditions, and involvement of HC as both fluid phases and chemical components. Dedicated experimental work and improvement of numerical simulators are needed. Currently available simulators and thermodynamic data should be used with caution, and model calibration is strongly recommended.

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