A Single Well Chemical Tracer model that accounts for temperature gradients, pH changes and buffering

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ABSTRACT
We present the first ever Single Well Chemical Tracer (SWCT) model that incorporates temperature gradients and pH-driven ethyl acetate hydrolysis rate changes when buffering by either calcite in the oil-bearing formation or by chemical species in the injected brine are accounted for. The model is applied to four generic cases with SWCT test, rock formation and brine composition data based on published values. An analytical model is used to calculate how the brine injection temperature decreases with time and an axially symmetric numerical model is used to simulate the cooling of the oil-bearing formation, chemical reactions and transport of species in the reservoir. The primary oil-water partitioning tracer ethyl acetate hydrolyses into the secondary water tracer ethanol and acetic acid that lowers the pH and changes the hydrolysis rate. The acid driven pH decrease may be significantly reduced by pH buffering mechanisms. We investigate four different buffer models. Model 1 may represent a sandstone with calcite cement. In Model 2, also with calcite cement, the brine has less calcium but more bicarbonate and initially lower pH than Model 1. Model 3 is a clean sandstone without calcite cement and the brine contains no calcium but much bicarbonate. Model 4 has no buffer capacity neither in the brine nor in the target formation. Although we discuss only four models, they are quite different and represent an important subset of the realistic SWCT test parameter space. A temperature gradient develops across the primary tracer bank in all four models and this causes the secondary tracer to be displaced away from the wellbore relative to the primary tracer. We find that most of the ethyl acetate hydrolysis takes place during shut-in. The residual oil saturation ($S_{or}$) is estimated from the synthetic tracer production curves using the simple chromatographic separation equation as well as with the mean residence time correction. The two methods underestimate the true $S_{or}$ value (22%) by 3-5 and 3-11% (saturation points), respectively. These results demonstrate that the ‘handicap’ created by the temperature gradient together with the pH-driven hydrolysis rate changes should be taken into account in $S_{or}$ estimates. We suggest that SWCT tests may be used to evaluate the effective wettability of the target formation at a modest extra cost. Using water tracers with very low quantification limits as primary tracers should reduce or even eliminate the problems caused by temperature gradients and pH-driven hydrolysis rate changes since they will travel well ahead of the temperature gradient and the small amount of acid generated will produce only an insignificant reduction in pH.

1. Introduction

Single Well Chemical Tracer (SWCT) tests are performed in oil producers to estimate the residual oil saturation ($S_{or}$), i.e., the fraction of pore volume occupied by immobile oil after a displacement process. $S_{or}$ is a function of initial saturation, lithology, petrophysical properties, fluid characteristics, recovery methods and production history (Teklu et al., 2013). Reliable estimates of $S_{or}$ are important for reserve assessment, recovery calculations and for increasing our understanding of oil field behavior. One of the most important applications of SWCT tests is to gauge the performance of Enhanced Oil Recovery (EOR) methods. The reduction in $S_{or}$ between SWCT tests conducted before and after an EOR operation has been used to measure the efficiency of hydrocarbon miscible gas floods (Cockin et al., 2000), low salinity water floods (Skrettingland et al., 2010; Khaledialidusti et al., 2015; Al-Shalabi et al., 2017; Kazemi et al., 2019), alkaline-surfactant-polymer (ASP) floods (Carlisle et al., 2014; Fortenberry et al., 2016) just to mention some examples. We estimate that close to a thousand SWCT tests have been...
executed worldwide in all types of reservoirs during the last fifty years. The use of SWCT tests appears to increase annually.

The fundamental mechanism utilized in the SWCT method is the chromatographic separation between an oil-water partitioning tracer and a water tracer when they move towards the producer from a distance of a few meters. Since oil-water partitioning tracers spend some time in the immobile oil, they move more slowly than water tracers that move with the flowing water all the time. The velocity difference depends on $S_{oc}$ and the distribution constant (partitioning coefficient), i.e., the ratio of the oil-water tracer concentration in oil to its concentration in water. The distribution constant can be measured in the laboratory. Together with tracer information gathered by the SWCT test, it is possible to estimate $S_{oc}$. Based on work performed by Exxon Research in East Texas in the late 60’s, Deans (1971) patented the seminal idea to use the oil-water partitioning (primary) tracer itself to generate the (secondary) water tracer in-situ by hydrolysis, i.e., the primary tracer is reactive as well as partitioning.

A prerequisite for the SWCT method to work is that the oil in the target formation is at residual oil saturation. A 98% or higher water-cut is often considered a practical criterion for the oil to be virtually immobile (Deans and Majoros, 1980). If the well has a significant oil-cut, a local water flood is performed before the SWCT test in order to reduce the oil saturation to residual (e.g., Carlisle et al., 2014). The SWCT test proper starts by pumping the primary tracer dissolved in brine from the producer into the oil-bearing target formation where $S_{oc}$ is to be measured (Fig. 1).

The primary tracer is followed by a slug of tracer free brine. The depth of investigation into the oil-bearing formation (typically a few meters) can be controlled by varying the pump rate and duration of the tracer and brine injections. The primary partitioning tracer is subsequently left to partly hydrolyze into the secondary water tracer. Deans and Majoros (1980) recommended that the shut-in should last sufficiently long for at least 50% of the hydrolysis to take place during shut-in, i.e., when the tracers are stagnant, since a basic assumption in utilizing the chromatographic separation to calculate $S_{oc}$ is that the oil-water and water tracers both start towards the wellbore from the same position, i.e., distance from the wellbore. After shut-in, the tracers are back produced, and their concentrations monitored as functions of produced volume or time. In some cases, $S_{oc}$ can be calculated analytically from the oil-water and water tracer curves like in inter-well tracer tests (Cook, 1971). The inevitable dispersion that occurs when the tracers move through the permeable rock can to some degree be accounted for by using the mean residence times in Cook’s (1971) chromatography formula (Deans and Majoros, 1980; Shook et al., 2009). Doorwar et al. (2020) present an analytical method that in addition to the distribution constant also considers shut-in duration and an ‘average hydrolyses rate’. In most cases, however, computer simulations are required to obtain a good $S_{oc}$ estimate (Deans and Majoros, 1980; Deans and Carlisle, 1986; Jerauld et al., 2010; Mechergui et al., 2012; Kazemi et al., 2019). Deans and Majoros (1980) give a thorough review of the SWCT method and present detailed results from 59 tests. Deans and Carlisle (2007) present an updated discussion of the method and its applications. Khalidialidusti et al. (2014) discuss several unconventional (non-chemical) single well models. To the best of our knowledge, none of these have been tested in the field.

The first SWCT test results were published by Tomich et al. (1973). A SWCT test samples a large rock volume around the well, takes relatively short time (typically 2–3 weeks) and is quite robust to near-well formation damage noise. SWCT tests may yield ‘fair to excellent estimates of $S_{oc}$’ in both sandstone and carbonate reservoirs with large variations in temperature, fluid salinity and rock properties (Chang et al., 1988). An accuracy of about 2–3% is suggested by laboratory results from pressure-core methods under favorable circumstances according to Tomich et al. (1973).

Which primary tracer is found suitable for a particular reservoir depends primarily on the reservoir temperature. Ester acetates are normally employed in high temperature (above about 50 °C) reservoirs whereas formates are preferable at lower temperatures (Deans and Majoros, 1980; Mechergui et al., 2012). The most widely used primary tracer is probably ethyl acetate. Of the 59 tests discussed by Deans and Majoros (1980), 41 (70%) used ethyl acetate as the primary tracer. In a recent paper, Doorwar et al. (2020) discuss 55 published SWCT tests – 44 (80%) of them used ethyl acetate. In this contribution, we focus on ethyl acetate as the primary tracer.

2. Temperature gradients and pH changes

There are two potentially important mechanisms that almost universally are ignored in the planning and interpretation of SWCT tests. The first is that a temperature gradient may develop across the primary tracer bank (Park, 1989). Since the hydrolysis rate of the primary tracer increases exponentially with temperature, such a gradient will cause the secondary tracer to be located further away from the wellbore than the primary tracer is. During the production phase, this ‘handicap’ will reduce the observed time difference between the primary and secondary tracers and this will translate into a too low $S_{oc}$ estimate if the effect isn’t accounted for (Park, 1989; Park et al., 1991; Pedersen, 2018, 2021). Reservoir cooling was discussed by Skrettingland et al. (2010) and Khalidialidusti et al. (2015) on the Snorre field, but then only as an average temperature. They therefore did not consider the $S_{oc}$ error if a temperature gradient can produce. Temperature changes in the target formation will also affect the distribution constant of the partitioning primary tracer and thus the $S_{oc}$ estimates regardless of which method is used in their calculation. To avoid cooling of the oil-bearing formation altogether would seem to require an infinitely low injection rate and thus an infinitely long injection period. However, whether cooling has a significant effect is another question. Park et al. (1991) developed mathematical criteria for when a temperature gradient across the primary tracer bank has a significant bearing on $S_{oc}$ estimates. They provide easy to use graphical solutions that can be used to assess qualitatively whether nonisothermal effects may be important or not. Quantitative results, however, require modelling. Pedersen (2018) demonstrated by computer simulations how hypothetical temperature sensitive fluorescent nanotracers co-injected with the primary tracer might help constrain SWCT temperatures and thus also $S_{oc}$ estimates. Wellington and Richardson (1994a) developed an alternative SWCT method where...
3. Model and data

The temperature model presented in Park (1989) is our starting point. Fluid flow is assumed to be radial from and towards the wellbore during injection and production, respectively. This makes it feasible to have an axially symmetric model centered on the vertical wellbore (Fig. 1). Model parameters and values are given in Table 1.

In this manner, three-dimensional effects are accounted for in a mathematically simple and computationally efficient manner. The wellbore is surrounded by three horizontal rock units. The formation where we estimate \( S_{\text{or}} \), i.e., the target for the SWCT test, is a permeable rock. Two impermeable shales with equal thicknesses are found above and beneath the target formation. We assume, like Park (1989) and Park et al. (1991) that the target formation and the adjacent impermeable layers are at thermal equilibrium (\( T_{\text{or}} = T_{\text{w}} \)) when the calculations commence (Fig. 2). This is realistic due to the small depth interval (typically a few tens of meters) provided the rocks have not been thermally disturbed by for instance a previous SWCT test or a waterflood to reduce oil saturation to residual. All model parameters (except brine composition; see Table 2) and their values are given in Table 1.

Table 1

| Symbol | Value | Description |
|--------|-------|-------------|
| \( H \) | 12 m | Target formation height |
| \( W \) | 10 m | Model width |
| \( r \) | Radial distance from center of wellbore |
| \( Q_{\text{inj}} \) | 450 bbl/d | Injection rate |
| \( Q_{\text{prod}} \) | 480 bbl/d | Production rate |
| \( C \) | Concentration |
| \( C_0 \) | See Table 2 | Injection concentration |
| \( C_0 \) | See Table 2 | Reservoir concentration |
| \( D_T \) | \( 10^{-6} \) m²/s | Diffusivity |
| \( T \) | Temperature |
| \( T_{\text{inj}} \) | See Fig. 2 | Injection temperature |
| \( T_{\text{shutin}} \) | 6 d | Shut-in period |
| \( T_{\text{prod}} \) | 6 d | Production period |
| \( \phi_0 \) | 23% | Target formation porosity |
| \( \phi_{\text{eff}} \) | 18% | Effective porosity |
| \( \phi_s \) | 29% | Shale porosity |
| \( k \) | See text | Ethyl acetate hydrolysis rate |
| \( S_{\text{or}} \) | 22% | Residual oil saturation |
| \( S_{\text{br}} \) | Estimated \( S_{\text{br}} \) using Eq. (23) |
| \( S_{\text{br}}^{**} \) | Estimated \( S_{\text{br}} \) using Eq. (25) |
| \( S \) | 20 000 ppm | Salinity |
| \( u \) | Eq. (1) | Darcy velocity |
| \( v \) | \( u / \text{effective porosity} \) | Interstitial velocity |
| \( (p_C)_{\text{oil}} \) | \( 1.67 \times 10^3 \) J/m²/K | Oil volumetric heat capacity |
| \( (p_C)_{\text{rock}} \) | \( 4.18 \times 10^3 \) J/m²/K | Rock volumetric heat capacity |
| \( (p_C)_{\text{water}} \) | \( 4.18 \times 10^3 \) J/m²/K | Water volumetric heat capacity |
| \( k_{\text{sandstone}} \) | 3.00 W/m/K | Sandstone matrix thermal conductivity |
| \( k_{\text{shale}} \) | 2.45 W/m/K | Shale matrix thermal conductivity |
| \( k_s \) | 0.12 W/m/K | Oil thermal conductivity |
| \( k_w \) | 0.6 W/m/K | Water thermal conductivity |
| \( A \) | 0.021 K/m | Geothermal gradient |
| \( Z \) | 3000 m | Depth to target formation |
| \( B \) | 10 °C | Earth’s surface temperature |
| \( C_p \) | 4180 J/K/kg | Water specific heat |
| \( r_0 \) | 0.1 m | Well radius |
| \( \alpha \) | \( 1.1 \times 10^{-2} \) m²/s | Thermal diffusivity of the Earth |
| \( \alpha \) | \( 10^{-3} \) m²/s | Radial dispersivity |
| \( \alpha \) | 0.5 m/s | Vertical dispersivity |
| \( U \) | Fluid velocity in wellbore |
3.1. Fluid velocity

The injected brine flows into the permeable layer from the left (Fig. 2). For perfect radial flow of an incompressible fluid, the Darcy velocity \( \vec{u} \), as a function of distance, \( r \), from the center of the wellbore is (e.g., Park, 1989):

\[
\vec{u} = \left( \frac{Q}{2\pi H r} \right) \nonumber
\]

in which \( Q \) is the pumping rate, \( H \) the thickness of the permeable layer and \( r \) is distance from the wellbore center.

3.2. Temperature calculations

The temperature, \( T \), is calculated by solving the heat equation:

\[
(\rho C_p)_\text{eff} \frac{\partial T}{\partial t} + (\rho C_p)_m \vec{u} \cdot \nabla T = \nabla (k_{\text{eff}} \nabla T) 
\]

in which the effective volumetric heat capacity is:

\[
(\rho C_p)_\text{eff} = \varphi (\rho C_p)_w + (1 - \varphi) (\rho C_p)_r 
\]

where the subscripts \( w \) and \( r \) refer to residual oil, water and rock, respectively, \( \varphi \) is rock porosity, and \( S \) is saturation. In a two-phase system, we have that

\[
S_w = 1 - S_o 
\]

(4)

\[
k_{\text{eff},i} \text{ is the effective thermal conductivity:} 
\]

\[
k_{\text{eff},i} = \varphi [k_o S_o + k_w S_w] + (1 - \varphi) k_{wi} 
\]

(5)

in which \( i \) represents the sandstone target formation or the shales above and beneath it, \( k_o \) and \( k_w \) are the thermal conductivity of oil and water, respectively, and \( k_{wi} \) is the matrix thermal conductivity of sandstone or shale. The hydrolysis reaction of ethyl acetate is slightly exothermic, but with the tracer concentrations used in SWCT tests, its effect on temperature can be ignored.

3.3. Injection temperature

For a wellbore-rock system initially at thermal equilibrium, Ramey (1962) derived an approximate expression for the brine temperature in the wellbore as a function of depth, \( z \), and time, \( t \):

\[
T(z, t) = a z + b - aA + (T_o + aA - b) \exp \left( -\frac{z}{A} \right) 
\]

(6)

in which \( z \) is depth, \( a \) is the geothermal gradient of the Earth, \( b \) is the surface geothermal temperature, and \( T_o \) is the surface temperature of the injected brine. For water injection down casing, we had used an abrupt temperature change like for example Park et al. (1991) did, our simulations show that it would have been difficult to avoid using unrealistically high dispersivity values to stabilize the combined temperature and pH dependent hydrolysis rate numerical calculations. Most important is that such a smooth temperature change would appear to be more realistic. Pedersen (2018) demonstrates how properly designed fluorescent nanoparticles co-injected with the primary tracer can yield information on the real temperature history during a SWCT test.

Parameter values are given in Table 1 and boundary conditions in Fig. 2.

The perhaps most important feature in that figure is that there is a smooth decrease in the temperature of the injection fluid with time. If we had used an abrupt temperature change like for example Park et al. (1991) did, our simulations show that it would have been difficult to avoid using unrealistically high dispersivity values to stabilize the combined temperature and pH dependent hydrolysis rate numerical calculations. Most important is that such a smooth temperature change would appear to be more realistic. Pedersen (2018) demonstrates how properly designed fluorescent nanoparticles co-injected with the primary tracer can yield information on the real temperature history during a SWCT test.

3.4. Chemical reactions and solute transport

Ethyl acetate hydrolyzes to produce ethanol and acetic acid:

\[
\text{Ethyl Acetate} + H_2O \rightarrow \text{Ethanol} + \text{Acetic Acid} 
\]

(8)

In addition, there are several equilibrium reactions:

\[
\text{Acetic Acid} \leftrightarrow H^+ + \text{Acetate Ion}^- 
\]

(9)

Fig. 3. Injection temperature as function of time derived from Eqs, 6–7 with the parameters in Table 1.
with the equilibrium constant, $K_{eq}$ (for concentrations in mole l$^{-1}$ (i.e., M) – in the simulations we use the SI unit m$^{-3}$):

$$K_{eq} = 1.8 \times 10^{-5}$$

and the dissociation of water equilibrium reaction:

$$H_2O \leftrightarrow H^+ + OH^-$$

is described by the equation:

$$K_w = [H^+][OH^-]$$

The ethyl acetate concentration in the injected brine ($C_{eq}$) is 40 mol/m$^3$ (=0.04 M) (cf. Fig. 2).

The buffering due to carbonate species is modeled by three equilibrium reactions (Deans and Ghosh, 1994):

$$H_2CO_3 \leftrightarrow H^+ + HCO_3^-$$

$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$$

$$CaCO_3(s) \leftrightarrow Ca^{2+} + CO_3^{2-}$$

The equilibrium constants for the first two reactions at the reservoir conditions are $10^{3.4}$ and $10^{10.3}$, respectively, and the solubility product of calcite is $10^{-8.3}$ (Plummer and Busenberg, 1982).

The transport of the various chemical species in the target formation is described by the equation:

$$\frac{\partial C_i}{\partial t} + \rho_b \phi \frac{u}{\tau_i} \nabla C_i = \nabla \left[ D_{ij} \frac{\phi}{\tau_i} \nabla C_j \right] + \phi \rho_f k_i$$

Here, $\phi_{eff}$ is the effective porosity equal to $\phi(1-S_w)$, $\rho_b$ is the dry bulk density, $k_i$ is the adsorption isotherm, $C$ is the concentration, $D_{ij}$ is the dispersion, $\tau_i$ is the tortuosity, $D_{ij}$ is the diffusivity, $R_i$ is a reaction term and $i$ refers to solute number $i$. For ethyl acetate $R = -kC_{ethyl acetate}$ whereas for ethanol and acetic acid, $R = kC_{ethyl acetate}$. The adsorption isotherm is

$$k_i = \frac{S_w \phi K}{\rho_f(1-\phi)}$$

for ethyl acetate and zero for the other solutes. $K$ is the distribution constant (partitioning coefficient), $\rho_f$ is rock density and the other terms have been defined earlier. We use the following expression for $K$ (Deans and Majoros, 1980):

$$K = \left\{ 2.4 + \left( 1.0 + \frac{S_w}{24.000} \right)(0.018T - 5.197) \right\}$$

where $S_w$ is salinity

$$\text{pKw as a function of temperature. Based on Bandura and Lvov (2006).}$$

Fig. 4.

where we have neglected K’s dependency on the tracer concentration because this effect is small (Deans and Majoros, 1980). $S_w$ is salinity measured in ppm while temperature is measured in Kelvin. The boundary conditions for the solute transport calculations are given in Fig. 2.

The overall reaction rate for the hydrolysis of ethyl acetate to ethanol, $k$, depends on $[H^+]$ and $[OH^-]$ (International Critical Tables first edition, 1930):

$$k = k_n [H^+] + k_b [OH^-]$$

in which $k_n$ and $k_b$ are the acid and base catalysis factors, respectively.

The much used pH independent expression for the hydrolysis rate of ethyl acetate per day, $k_h$, published by Deans and Majoros (1980), reads:

$$\log_{10}(k_h) = 8.6 - \frac{3469}{T}$$

where $T$ is in K is used for comparison.

We calculate the tortuosity in the target formation from the Millington and Quirk (1961) formula $\tau = \phi^{1/3}$. For the porosity in Table 1, this yields 1.6. Dispersion is calculated from the expressions (Bear, 1979):

$$D_{lh} = \alpha \frac{u^2}{\eta}$$

and

$$D_{lv} = (\alpha_r - \alpha_v) \frac{u^2}{\eta}$$

where $\alpha_r$ and $\alpha_v$ are the radial and vertical dispersivities, respectively. See Table 1 for parameter values.

The set of equations above are solved using the commercial finite element PDE software COMSOL Multiphysics (2018). The mesh consists of triangular elements with higher resolution near the wellbore because that is where most of the variations take place. Time stepping is performed by a second order implicit backward differentiation formula (BDF). It takes typically between five and 10 min to solve a model on a 64 bit computer with two processors and 128 GB RAM memory.

The most important difference between our chemistry model and the models published by Khaledialidusti and Kleppe (2018) is probably that we have a realistic 3D description of the temperature changes during a SWCT test whereas their models are isothermal. That the assumption of
3.5. Test, brine and formation rock data

As in Pedersen (2021), we define a generic or representative (approximate arithmetic averages) SWCT test and rock data set (Table 1) based on Tables 5-1 in Deans and Majoros (1980). Their table contains data from 59 SWCT tests mostly in sandstones although a few limestone cases are included as well. We only consider the common ethyl acetate primary tracer.

We define four simulation models (Table 2). They are based on Ghosh (1994) but slightly modified to be consistent with the model parameters in Table 1.

Model 1 may represent a sandstone with calcite cement. In Model 2, also with calcite cement, the brine has less calcium but more bicarbonate and lower pH than Model 1. Model 3 is a clean sandstone without calcite cement and the brine contains no calcium but much bicarbonate. Model 4 has no buffer capacity neither in the brine nor in the target formation. Although we discuss only four models, they are quite different and represent an important subset of the realistic SWCT test parameter space. Future work should investigate also other buffer models.

3.6. Sor estimates

Sor is estimated from the synthetic tracer concentration curves using two methods. The first is the direct application of Cook’s (1971) chromatography formula:

\[
S_{or} = \frac{[\text{Ethyl Acetate} - \text{Ethanol}]}{[\text{Ethyl Acetate} + \text{Ethanol}](K - 1)} \tag{23}
\]

where Etyl Acetate or Ethanol is estimated from the synthetic tracer concentration curves using two methods. The first is the direct application of Cook’s (1971) chromatography formula:

\[
S_{or} = \frac{[\text{Ethyl Acetate} - \text{Ethanol}]}{[\text{Ethyl Acetate} + \text{Ethanol}](K - 1)} \tag{23}
\]

in which \( t \) is the time when the concentrations of ethyl acetate or ethanol are at their maximum and K is again the distribution constant.

One of the assumptions in Eq. (23) is that dispersion of the tracers is negligible. In a real SWCT test, there will be dispersion. Deans and Majoros (1980) suggested to use the ratio between the first and zero statistical moments (i.e., the mean residence time) defined as

\[
T = \frac{\int_{0}^{\infty} r C, dr}{\int_{0}^{\infty} C, dr} \tag{24}
\]

to account for dispersion in SWCT tests; \( i \) stands for ethyl acetate or ethanol. The estimated value of \( S_{or}^* \) is obtained by inserting the times from Eq. (24) into Eq. (23), i.e.,

Table 2

| Model | \( C_0 \) | \( C_a^{++} \) | \( CO_2^{++} \) | \( HCO_3^- \) | \( H_2CO_3 \) | pH |
|-------|------------|----------------|----------------|-------------|-------------|-----|
| 1     | 40         | 1500           | 3.34 \( 10^4 \) | 0.0035      | 4.62 \( 10^{-4} \) | 7.3 |
| 2     | 40         | 3.74           | 0.00134        | 7.49        | 5.26        | 6.55|
| 3     | 40         | 0              | 0.18           | 206.8       | 29.79       | 7.24|
| 4     | 40         | 0              | 0              | 0           | 0           | 6.34|

4. Results

Fig. 6 illustrates how pH and k change with time in a vial (small glass, plastic vessel or bottle) due to hydrolyses of ethyl acetate with the compositions in Table 2.

The vial is kept at a constant temperature of 73 °C, i.e., the reservoir temperature, TR, and there is no oil in it. Such models are useful for understanding the chemistry of a SWCT test but ignore any interaction (temperature, partitioning, dispersion) between the injected fluids and the rocks surrounding the wellbore except from the calcite ‘cement’ in Models 1 and 2. We observe in Fig. 6.1 (Model 1) that after less than one day, the pH has dropped below 6 and the hydrolysis rate is reduced by a factor of about 25. In Model 2 (Fig. 6.2), there is only a small fall in pH and the hydrolysis rate is reduced by about 50% after six days. In Fig. 6.3 (Model 3, i.e., the model without calcite ‘cement’ but very high in bicarbonate), there is again only a minor reduction in pH and k is only decreased by approximately 50%. Finally, Fig. 6.4 (Model 4, i.e., the ‘no-buffer’ case with no buffer capacity in either the injected brine nor in the rock), demonstrates a very rapid pH reduction beyond the hydrolysis rate minimum point in Fig. 5, after which the hydrolysis rate increases and eventually surpasses its initial value. These simple vial simulations indicate that when we now include interactions between injected brines and the rocks surrounding the wellbore, a quite complex picture may be expected.

The vial model results in Fig. 6 ignore the effects of injecting the various brines into the porous target formation surrounding the wellbore and leaving them there to hydrolyze, as well as the cooling caused by the relatively cold brine.

Fig. 7 illustrates pH and temperature as functions of distance from the well bore center, r, at the end of shut-in for the SWCT model in Fig. 1. The pH minima are close to those seen in Fig. 6. This suggests that at least in some cases, the minimum pH may be estimated by a simple vial model. The temperature curves are all the same because the thermal properties of the brine do not change due to the small variations in brine composition or tracer concentrations. Far from the wellbore, i.e., r larger than approximately 5 m, the temperature equals the initial reservoir temperature; TR. Approaching the wellbore, the temperature tapers off until it reaches the wellbore temperature shown in Fig. 3. The pH reductions observed in Fig. 7.1 and 7.4 are not only much larger than in Fig. 7.2 and 7.3, but also much wider and will thus affect the ethyl acetate hydrolysis more substantially.

The hydrolysis rate, k (cf., Fig. 5), and the commonly used pH independent rate, \( kh \) (Deans and Majoros, 1980), are presented in Fig. 8 for the pH and temperature data in Fig. 7. For the latter, we use the reservoir temperature since that is the only temperature that is available without temperature calculations. In Fig. 8.1, we see a dramatic reduction in k since a pH value of about 5.5 (Fig. 7.1) yields the minimum hydrolysis rate (Fig. 5). The rate is also much lower than the much used pH independent rate, kh. Designing SWCT tests using the kh may thus underestimate the time required to obtain a certain degree of hydrolyses in rocks with calcite, or other carbonates, with the Model 1 brine composition. Also, in Models 2 and 3 (Fig. 8.2 and 8.3, respectively) we note that k is lower than kh, but the difference is much smaller than for Model 1. In Fig. 8.4 (Model 4) we observe a more complicated k constant temperature during a SWCT test is almost universally used in the literature on SWCT tests does not make it any more realistic. Because temperature governs the hydrolysis rate of ethyl acetate and other esters, induced pH changes and distribution constants, a sound model of temperature changes during a SWCT test is important. The ‘handicap’ (horizontal separation between the ethyl acetate and ethanol tracer curves when production commences) identified already by Park and co-workers around 1990 cannot be studied in isothermal models. Furthermore, our model has a radial velocity field representative for most SWCT tests while Khaledialidusti and Kleppe (2018) use a 1D transport equation. We also consider diffusivity and dispersion. These effects were ignored by Khaledialidusti and Kleppe (2018).

\[
S_{or}^* = \frac{[\text{Ethyl Acetate} - \text{Ethanol}]}{[\text{Ethyl Acetate} + \text{Ethanol}](K - 1)} \tag{25}
\]

We use the distribution constant (Eq. (18)) with the reservoir temperature TR in Eqs. (23) and (25). That is the only temperature value available without performing temperature calculations. Pedersen (2021) demonstrated that in some SWCT synthetic tests the simple Eq. (23) may yield better estimates than Eq. (25). We do not mean to suggest that Eqs. (23) and (25) are the best ways to obtain good \( S_{or} \) estimates. However, they are much used – perhaps more than any others.
This is because with the pH values in Fig. 7.4, the hydrolysis rate passes through its minimum (Fig. 5) and then increases as pH continues to fall.

Fig. 9 shows the calculated ethyl acetate and ethanol concentrations at end of shut-in for the four models in Table 2. In all four displays, we note that the ethanol curves are slightly displaced to the right relative to the ethyl acetate curves. This is the ‘handicap’ discovered by Park (1989) and Park et al. (1991). For Model 1, only a small fraction of the ethyl acetate has been converted into ethanol. This is because with Model 1 the hydrolysis rate is close to its minimum (Fig. 5). For Model 2,
the rate is higher and consequently more ethanol has been generated. With Model 3, we note that more than 50% of the ethyl acetate has been hydrolyzed. Finally, Model 4 yields a degree of hydrolysis between Models 2 and 3, congruent with the hydrolysis rates in Fig. 8.

Fig. 8. $k$ (solid) and $kh$ (dashed) as function of distance at the end of shut-in for Models 1 to 4.

Fig. 9. Ethyl acetate (solid) and ethanol (dashed) concentrations as functions of position at the end of shut-in (9.3 d) for Models 1 to 4.

The ethyl acetate and ethanol production curves are illustrated in Fig. 10 together with the Sor* and Sor** estimates (Eqs. (23) and (25)). We see that $S_{op}*$ and $S_{op}**$ underestimate the true $S_{op}$ (22%) value by 3–5% and 3–11% (saturation units), respectively.

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would thus argue that this also pertains to many real SWCT tests. Hydrolysis rate variations should be included already in the planning phase of the test. Using Eq. (19) or other T-pH models is quite straightforward, and there is not much reason in our opinion to use some sophisticated T-pH models. Wellington and Richardson (1994b) use the hydrolysis rate parameters for injection, shut-in and production. Although they include expressions requires, however, solving for temperature as well as pH.

5. Discussion

Judging from Figs. 6–8, it is difficult to define a meaningful ‘average’ rate of hydrolysis in any of the four models discussed in this contribution since the rate changes considerably in space as well as with time. Our four models span a relatively large SWCT test parameter space and we would thus argue that this also pertains to many real SWCT tests. Hydrolysis rate variations should be included already in the planning phase of the test. Using Eq. (19) or other T-pH models is quite straightforward, and there is not much reason in our opinion to use some ‘average’ rate of hydrolysis. To fully exploit such more realistic rate expressions requires, however, solving for temperature as well as pH changes during the SWCT test. Overestimating the time required for sufficient hydrolysis to take place costs money. It may also lead to there being not sufficient primary tracer left to observe. A too short shut-in may lead to poor Sor estimates because of an insufficient secondary tracer concentration.

Fig. 10. Produced ethyl acetate (solid) and ethanol (dashed) concentration curves. Sor* and Sor** are the Sor estimates with Eqs. (23) and (25), respectively.

Fig. 11.1 illustrates the relative percentages of ethyl acetate converted into ethanol for the pre-, syn- and post-shut-in periods for Models 1–4. We find that in all four models, the fraction of ethyl acetate that hydrolyzes during shut-in is higher than the minimum 50% recommended by Deans and Majoros (1980). In other words, we do not observe that the generation of ethanol during transit (i.e., injection + production) overshadows the generation during shut-in as did Wellington and Richardson (1994b) in their SWCT model of a carbonate cemented California turbidite and a Gulf Cost sandstone. We believe that the principal reason for this difference is the difference in modelling methodology. Whereas we solve the conservation laws for energy (temperature; Eq. (2)) and mass (transport of dilute chemical species; Eq. (16)) and use the calculated temperature and pH to define the rate of hydrolysis by Eq. (19), Wellington and Richardson (1994b) use the observed pH values (in the produced fluid) to estimate average hydrolysis rates for injection, shut-in and production. Although they include ethyl acetate hydrolysis also in the tubing during production (which we do not), this probably cannot explain the difference because once the ethyl acetate enters the tubing, it will start to cool on its way towards the surface and quite rapidly hydrolysis should become very slow. In addition, Wellington and Richardson (1994b) do not consider the temperature gradient across the primary tracer bank. Further work would be required to investigate this matter more deeply.

That Sor** may yield poorer residual saturation estimates than Sor* was also discovered by Pedersen (2021) in a study of SWCT tests without buffering in neither the formation rock nor the injected brine. We suggest the following explanation for this phenomenon. Wellington and Richardson (1994b) proposed that the distorted shape of the secondary tracer (ethanol) curve in a California turbidite SWCT test was a consequence of most ethanol being generated during transit. Our study does not support this explanation since most of the secondary tracer (63%) in Model 3 was produced during shut-in (Fig. 11a). Anyway, since all the secondary tracer has been produced under such conditions, whereas the rest primary tracer is what remains of a more ideal shape. In Fig. 11.2, we again see the production curves for Model 3 as well as the Sor* and Sor** estimates. Also illustrated are the elapsed times relative to start of production (9.3 d) for the ethyl acetate (p for primary) and ethanol (s for secondary) tracers. The times are given for the Sor* estimate (**, i.e., time is defined by the top of the concentration curves) as well as the Sor** estimate (**, time is defined by Eq. (23)). We note that the effect of applying Eq. (24) is greater for the secondary tracer (0.21 d) than for the primary tracer (0.18 d), and this reduces Sor** relative to Sor*. There does not seem to be much point in pursuing the topic of the relative merits of the Sor* and Sor** estimates, since a straightforward, more transparent and mathematically sounder way forward is simply to use models like the model applied in this paper. Such models can also be refined to include more physical and chemical processes as well as more complicated rock geometries and properties like dual porosity, fracture and faults, coarsening, diagenetic effects, and so on and so forth.
Fig. 11.1 Relative percentage of ethyl acetate converted to ethanol during pre- (dark grey), syn- (black) and post-shut-in (light grey). 2. Concentration of produced ethyl acetate (solid) and ethanol (dashed) as functions of time. Included are also the times since production started for ethyl acetate ('p') and ethanol ('s') with times defined by top of peak concentration ('p*', Eq. (23)) and mean residence time ('s**'; Eq. (25)). 3. Ethyl acetate and ethanol concentrations as functions of time for an isothermal model with temperature equal to the reservoir temperature, TR. Also shown are the Sor* and Sor** estimates of Sor. 4. Ethyl acetate and ethanol concentrations as functions of time for the kh hydrolysis rate model (Eq. (20)).

Fig. 11.3 depicts synthetic production in the case that the reservoir temperature is constant. In this scenario, there will be no temperature gradient ‘handicap’, and the Sor* estimate is wrong with only 1%. If we employ the pH independent hydrolyses model, kh (Eq. (17)), (Fig. 11.4), we arrive at a Sor* estimate equal to 18% and a Sor** estimate of 15%. These relatively large errors are produced by the temperature gradient that is present also when the kh rate is used.

If pH is included in SWCT models implies that there will be one more type of observations available to constrain Sor. Fig. 12 depicts pH and ethanol concentration in the produced brine as functions of time for Models 1–4. We note that the pH curve can be utilized as a control of the timing of the peak in the ethanol curve because of their quasi-mirror shapes. Minimizing the weighted difference (least-squares or other measure) between the calculated pH (and potentially other chemical information), primary and secondary tracer concentrations and the observed values using inversion methods (e.g., Aster et al., 2005) should yield improved Sor estimates and error estimates. Better test design (e.g., Khaledialidusti and Kleppe, 2017) could be combined with such efforts to bring the SWCT technique forward.

Pedersen (2021) studied temperature gradient and pH effects on Sor estimates from SWCT tests assuming no buffer capacity neither in the injected brine nor in the oil-bearing formation. Such a scenario is realistic if the brine contains no significant amounts of chemical species that may buffer the produced acid, and the oil-bearing formation matrix does not contain minerals like calcite that may get in contact with the produced acid and dissolve. Since sandstones almost universally are calcite cemented, the rock type where this ‘no buffer’ scenario may be most realistic is perhaps in carbonate reservoirs since most of them are oil-wet (Høgnesen et al., 2005) and a veneer of oil may protect the rock from the acid. We propose that this mechanism might be used to obtain not only Sor from a SWCT test, but also the effective wettability of the oil-bearing rock surrounding the well. The small figure inside Fig. 12.1 illustrates pH and the ethanol concentration for Model 1 if the calcite in the matrix is shielded from the acid by a veneer of oil. We see that there is a large difference in both pH and ethanol concentration. So if pH (and concentrations of other chemical species as well) was monitored in the produced brine, it should be possible to distinguish between a water-wet and an oil-wet rock. Presumably, a mixed-wettability rock would yield pH and ethanol results somewhere between the curves in Fig. 12.1. Further work is required to investigate this idea.

Al-Abbad et al. (2016) developed a new set of hydrolyzing partitioning primary tracers with much lower quantification limits than the conventional SWCT ester tracers. The primary tracer volumes may thus be reduced by several orders of magnitude. Although not much detail is provided on the new tracers, we anticipate that they should produce only small volumes of acid and give no significant pH reduction. Consequently, the pH-driven hydrolysis rate mechanism should not come into play to any significant degree. Finally, we note that using a water tracer as primary tracer to generate a partitioning secondary tracer (Wellington and Richardson, 1994a), the ‘reverse’ approach so to speak, avoids or reduces several of the problems discussed in this contribution. In particular, in this scenario there is no temperature gradient across the tracer bank since the water tracer moves well ahead of the temperature gradient (Wellington and Richardson, 199b). Perhaps it would be an idea to develop new primary water tracers with another secondary tracer than CO2. As discussed above, if the new tracers had been water tracers, the ‘temperature gradient problem’ should be eliminated or at least much reduced as well.

6. Conclusions

Numerical models that include realistic temperature calculations and
pH-driven primary tracer hydrolysis rate changes are important in the design of SWCT tests and for interpretation of the results.

Simple isothermal vial models provide useful semi-quantitative insight into the chemistry of SWCT tests, but simulation of temperature and chemical species transport in porous media are required for a deeper understanding.

In all four models discussed in this paper, more than 50% of the ethyl acetate hydrolysis occurs during shut-in. Notwithstanding, the ‘handicap’ caused by the temperature gradient across the primary tracer bank, combined with pH-driven hydrolysis rate changes, violates one of the basic tenants in the conventional Sor estimates; that the primary and secondary tracers start form the same position when production commences.

$S_{or}$ was estimated from the synthetic tracer production curves using the standard chromatographic separation equation as well as with the mean residence time correction. The methods underestimate the true $S_{or}$ value (22%) by 3–5% and 3–11% (saturation units), respectively.

SWCT tests might be used to also estimate the effective wettability at only a moderate extra cost.

New primary hydrolyzing water tracers with very low quantification limits might reduce or even circumvent both the temperature gradient and pH-driven hydrolysis rate changes discussed in this contribution.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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