Stability assessment of PITT tracer candidate compounds: the case of benzyl alcohols

Mario Silva[1,2,3,a]; Helge Stray[3]; Tor Bjørnstad[1,3];
[1]The National IOR Centre of Norway, University of Stavanger, 4036 Stavanger, Norway
[2]Department of Energy Resources, University of Stavanger, 4036 Stavanger, Norway
[3]Institute for Energy Technology (IFE), Department of Tracer Technology, Instituttveien 18, 2007 Kjeller, Norway
[a]Corresponding author, mario.silva@ife.no

Abstract

The selection of compounds used as inter-well tracers has traditionally been done taking into consideration the goal of the test and the ease in analyzing the chemicals used. This often led to improper selection of the tracers and insufficient knowledge about their behavior under typical reservoir conditions, resulting in several unsuccessful inter-well tracer tests. One of the critical characteristics of any conservative tracer is its stability under various reservoir conditions. In this document we present the study methodology and the findings from stability experiments carried out on 5 benzyl alcohols investigated as oil/water partitioning tracers for partitioning inter-well tracer tests (PITT). This is the first of three documents reporting such studies on 3 families of chemicals.

A PITT consists of the simultaneous injection of one or more mass-conservative passive and phase-partitioning (one type of active) tracers. PITT is primarily conceived for mature water-flooded oil fields and measures the residual (or even remaining) oil saturation (S_{OR}) in the swept volumes between wells. Knowledge of S_{OR} may be used to identify EOR targets, assess efficiency of EOR operations, and the efficiency of volumetric sweep between wells. This is important information, in particular for the increasing number of mature oil-fields where EOR projects are under consideration and/or development. A thorough knowledge about the static and dynamic properties of the tracers under reservoir conditions is required both to ensure successful field tests, and also to increase accuracy of the data obtained from them.

4-Chlorobenzyl alcohol, 2,6-Dichlorobenzyl alcohol, 4-Methoxybenzyl alcohol, 3,4-Dimethoxybenzyl alcohol, and 4-Hydroxybenzyl alcohol were tested in brine under simulated reservoir conditions with temperatures up to 150 °C during 12 weeks, at different pH values, and in the presence of typical sedimentary basin rock materials, sandstone, carbonate rock (limestone), and clay (kaolinite). 4-Chlorobenzyl alcohol and 2,6-Dichlorobenzyl alcohol were found to be fully stable at all tested conditions. 4-Methoxybenzyl alcohol and 3,4-Dimethoxybenzyl alcohol exhibit thermally induced degradation above 125 °C, but may still be considered for use below this temperature. 4-Hydroxybenzyl alcohol exhibits thermally induced degradation which was found to follow a first order kinetics. The apparent activation energy and pre-exponential constant in the Arrhenius law for the degradation reaction were determined and a kinetic model built. This opens the possibility for use of 4-Hydroxybenzyl alcohol as a non-conservative reservoir tracer to measure temperature or detect thermal fronts.

Keywords: partitioning tracers; inter-well; residual oil saturation; stability; new compounds

1. Introduction

1.1. Partitioning inter-well tracer tests and partitioning tracers

The use of inter-well tracer tests in the oil industry started in the 1960s (Asadi and Shook, 2010; Guan et al., 2005) with molecules successfully applied in hydrology (Ahmad et al., 2003). The future of oil production will increasingly rely on EOR projects to face global demand (IEA, 2016) as the number of mature oil fields increases together with the fact that most of the remaining large unexplored basins rich in hydrocarbons are located in highly environmentally sensitive regions (Muggeridge et al., 2014). Knowledge about residual oil saturation (S_{OR}) in the inter-well region of water flooded reservoirs is a key parameter for the design of EOR operations which can be obtained through a partitioning inter-well tracer test (PITT). PITT in oil reservoirs was introduced by Cooke (Cooke, 1971). The test explores the lag in production experienced by an oil/water partitioning tracer relatively to a passive water tracer. When the partition coefficient ($K=C_{TR,O}/C_{TR,W}$) is known, the delay in production can be directly correlated with the S_{OR} in the flow path. Later studies about PITT focus on interpretation of results to increase the test's accuracy and potential gains from the data (Allison et al., 1991; Carpenter, 2016; Huseby et al., 2015; Shen et al., 2017; Tang, 1995) and in reporting the conception and results of field cases (Al-Murayri et al., 2017; Lichtenberger, 1991; Sanni et al., 2016; Tang and Harker, 1991; Viig et al., 2013; Wood et al., 1990). Tritiated small chain alcohols, detectable in very low concentrations using liquid scintillation counting, were commonly used as partitioning tracers until 1990s when environmental regulations starting imposing severe limitations to the use of such compounds (Serres-Piole et al., 2012). After the 1990s these alcohols were still used in their non-radioactive form, however such use lost interest. Propanol and n-butanol were found to be partially adsorbed in the reservoir (Lichtenberger, 1991) and the methods used for their analysis have high detection limits. These factors increase the error on the interpretation of the tracer production curves and the amount of chemicals required for the test. Promising results were reported for 5 fluorinated benzoic acids (Chatzichristos et al., 2000), phenol (Tang, 2003), and Lichtenberger (Lichtenberger, 1991) also tested methyl-ethyl ketone. Information about requirements for selection and testing of PITT tracer candidates can be found in the available literature (Sanni et al., 2016; Serres-Piole et al., 2012; Silva et al., 2017; Viig et al., 2013). To date, only a small number of partitioning tracers for the inter-well region has been developed (Serres-Piole et al., 2012) and there is a need for such new compounds. As for any other type of conservative reservoir tracer, assessing the stability of the partitioning tracer under harsh oilfield conditions is a critical step for its qualification.

In the present work, we report the findings from the stability experiments simulating typical oil reservoir conditions performed on 5 benzyl alcohols. This is the first of 3 documents reporting stability assessment on 3 families of chemicals. Effects of temperature, pH, salinity, and presence of reservoir rock materials were evaluated to obtain a complete description of the behavior and possible use of these chemicals as PITT tracers.

1.2. Benzyl alcohols

Benzyl alcohol is an aromatic hydrocarbon naturally occurring in many plants used as solvent and reaction intermediate in chemical-based industries (Pugh et al., 2015). The chloro-, methoxy- and hydroxyl- substitutes of this compound tested under the scope of the present work exhibit interesting properties for use as PITT tracers, judged from their octanol/water partitioning coefficients (K_{OW}). The relevant properties considered in their selection are presented in Table 1.

It is also important to assess the occurrence of these compounds in oil reservoir fluids or other fluids used in the hydrocarbon recovery process and in the environment, both from natural origin and emitted as pollutants to the hydrosphere from various industries. Large amounts of the studied compounds in the “background” could compromise their use as tracers. Chlorinated, methoxy and hydroxyl benzyl alcohols are not used in large scale industrial operations. Hydroxy, methoxy and chlorobenzyl alcohols are used in small industrial scale as precursors for production of aromatic aldehydes, as model compounds to study the oxidation of substituted benzyl alcohols, and to evaluate the performance of selective catalyzed processes aiming for production of aromatic aldehydes (Esteruelas et al., 2011; Higashimoto et al., 2009; Morad et al., 2017; Scandura et al., 2016). 4-Chlorobenzyl alcohols have also been reported to be used as reagent and to assess catalysts for the Friedel–Crafts alkylation of aromatic hydrocarbons (Mantri et al., 2005). 4-Hydroxybenzyl alcohol is also a natural component of scents and flavours used as flavouring and scenting agent in food industry (Jaiswal and Kuhnert, 2014; Martin et al., 2016; Shyamala et al., 2007), in the pharmaceutical industry as an agent to mitigate some neurological disorders (Luo et al., 2017) and in the production of special application ceramic nano-fibers (Tao et al., 2017). This information suggests that reservoir fluids are unlikely to be contaminated with the benzyl alcohols, however any make-up injection water and engineered fluids used in single-well operations should be screened for the possible presence of these tracer candidates before use.

2. Materials and Methods

2.1. Materials

4-Chlorobenzyl alcohol (99%), 2,6-Dichlorobenzyl alcohol (99%), 4-Methoxybenzyl alcohol (> 98%), 3,4-Dimethoxybenzyl alcohol (99%), 4-Hydroxybenzyl alcohol (> 98%), kaolinite (natural aluminium silicate 125 µm – 250 µm with linear formula $Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$) and limestone powder type “BCR-116” (95.7% $CaCO_3$ + 4.3% $MgCO_3$) were purchased from Sigma-Aldrich (Sigma-Aldrich Norway AS, 0252 Oslo). Berea sandstone powder (125 µm – 250 µm) was obtained by crushing and sieving sandstone cores purchased from Berea Sandstone™ Petroleum Cores (Ohio, USA). The composition of the Berea sandstone indicated by the supplier is as follows: 93.13% silica (SiO_2), 3.86% alumina (Al_2O_3), 0.11% ferric oxide (Fe_2O_3), 0.54% ferrous oxide (FeO), 0.25% magnesium oxide (MgO), and 0.10% calcium oxide (CaO).

2.2. Experimental setup and procedures

2.2.1 Preparation of the test tubes

50 cm long durex glass rods (i.d. 6 mm, o.d. 9 mm) were cut from 1.5 m rods (Schott AG, Mitterteich, Germany). The hollow rods were then thermally sealed on one end. The obtained test tubes were submitted to thermal decontamination/healing at 550 °C during 15 minutes under normal atmosphere.

2.2.2 Preparation of the mixed tracer candidates’ solution

The benzyl alcohols were dissolved in 1L of brine further referred to as “synthetic Gullfaks water”. Table 2 presents the brine’s ionic composition. The solution was then sonicated at room temperature and simultaneously sparged with argon at 5 mL/min during 20 minutes to remove the dissolved air.

2.2.3 Stability test procedures

2 mL of the benzyl alcohols solution (2.2.2), kept under constant sparging with argon at 5 mL/min, were transferred to each tube in four sets of test tubes (2.2.1). One set of test tubes was empty, and the other 3 sets contained 600 mg of Berea sandstone, kaolinite, and limestone, respectively. All test samples were prepared in triplicate. The test tubes containing the samples were then thermally sealed under vacuum. 3 sealed test tubes without any rock material were picked out to determine the exact initial tracer candidates’ concentration.

Every heating cabinet had a rotation mechanism incorporated to ensure smooth agitation during the test. These experiments were performed at three different initial pH values: 5.5, 7.1 and 8.0. The concentration of the benzyl alcohols in the test samples was determined after 1, 3, 6 and 12 weeks of incubation. pH was also measured at the end of the incubation period.

2.2.4 Quantification of the benzyl alcohols

The benzyl alcohols were analysed by ultra-performance liquid chromatography (UPLC) with UV detection at 222 nm and 254 nm. Both the samples used to determine the initial concentration of the solution and the test samples were filtered through a “Chromacol 30mm Syringe Filter 0.45 µm PTFE” (Thermo Fisher Scientific, Waltham, Massachusetts, United States). 10 µL of the filtered test samples were directly injected on an “Agilent Technologies 1290 Infinity II” UPLC (Agilent Technologies, Santa Clara, California, USA) equipped with a Waters “Acquity UPLC BEH” reversed-phase C18 1.7 µm packed column (Waters Corporation, Milford, Massachusetts, USA). The mobile phase consisted of buffer solution of 5 mM NH_4HCO_2 (A), methanol (B) and acetonitrile (C) at a constant flow of 0.5 mL/min. Gradient elution was used for separation of the analytes: initially 98% A and 1% B. The amount of B increased to 20% after 4 minutes and was kept at this value during 1.5 minutes. Fraction of B was then increased until 70% at minute 8 and kept at this value during 0.5 min. Gradient conditions were then reset to the initial ones at minute 9 and held during 1 minute. The amount of eluent C was constant at 1% during the 10 minute chromatographic run.

2.3. Degradation Kinetics

Treatment and analysis of the experimental data for one of the tracer candidates was performed in order to investigate the possibility of its use as a non-conservative reservoir tracer. The method of time, based on the integrated rate law, was applied to the analysis of the degradation kinetics of 4-Hydroxybenzyl alcohol. The mass balance of a given compound A in a closed system can be written as (Fogler, 2006):

$$K'C_A^n = -\frac{dC_A}{dt} \qquad (1)$$

where C_A is the concentration of compound A, K’ is the apparent degradation rate constant and n the order of the reaction. The data used was obtained from experiments performed in brine, thus the use of the designation “apparent rate constant”. The salinity of the experimental aqueous medium could influence the rate of the reaction. By integrating equation 1 supposing the reaction follows a first-order kinetics:

$$\ln\left(\frac{C_A}{C_{A0}}\right) = -K't \qquad (2)$$

where C_{A0} is the initial concentration of compound A. K’ is temperature dependent. Through linear regression analysis of the results at the different tested temperatures, K’ (T) can be obtained. The apparent activation energy of the reaction and the pre-exponential factor of the rate constant can be obtained from the linearized Arrhenius equation:

$$\ln K(T) = \ln A - \frac{E_a}{R}\frac{1}{T} \qquad (3)$$

where A is the pre-exponential factor, E_a the apparent activation energy, R the gas constant, and T the temperature in Kelvin (K).

3. Results and Discussion

3.1. Influence of pH

Fakhru'l-Razi et al. (2009) present extensive data on physicochemical characteristics of produced waters from oil reservoirs. The initial pH values in the stability experiments were intended to cover a pH range representative of real conditions. The pH value remained stable until the end of the experimental thermal incubation period. The largest measured variations were a decrease of 0.3 units in the experiments with kaolinite as substrate after 12 weeks at initial pH 7.1, increase of 0.2 units in the experiments with Berea sandstone as substrate after 12 weeks at initial pH 5.0, and an increase of 0.4 units in the experiments with limestone as substrate after 12 weeks at initial pH 5.0. No significant variation on the pH of the stability experiments carried out without rock substrate was observed. Results suggest that pH has no impact on the stability of the benzyl alcohols. The concentration of the tracer candidates in samples from experiments with the same time and temperature of incubation does not vary at all tested pH values. Complete results may be found in figures A1 – A4 and B1 – B4 in the "supplementary materials" section to this document.

3.2. Influence of temperature and time

The remaining fraction of the tracer candidates (RF) is defined as the concentration as a function of temperature and time of incubation of the compounds divided by their initial concentration. For a fully stable tracer candidate, a RF equal to 1, considering the uncertainty of the analytical method used for its quantification, should be observed under all experimental conditions. The results allowed organizing the tracer candidates in 3 groups: fully stable, partially stable and unstable with other potential applications.

4-Chlorobenzyl alcohol (4-Cl-BZA) and 2,6-Dichlorobenzyl alcohol (2,6-DiCl-BZA) exhibit no decrease in concentration after the total incubation period at every tested temperature. Figure 1 presents RF values for 4-Cl-BZA and 2,6-DiCl-BZA as a function of time of incubation at all tested temperatures in the experiments at initial pH of 7.1. Both the compounds possess the required stability for use as active conservative tracers in oil reservoirs. Results for 4-Methoxybenzyl alcohol (4-MET-BZA) and 3,4-Dimethoxybenzyl alcohol (3,4-DiMET-BZA) are shown in Figure 2.

Both these compounds exhibit a very high stability within temperatures up to 125 °C during the total period of testing. Loss in RF is observed at 150 °C both for 4-MET-BZA and 3,4-DiMET-BZA during the whole period of incubation. A trend is observable as function of time at this temperature; the amount lost increases as the time of incubation increases. Considering that such behaviour was not observed at all other temperatures, the observed decrease of RF at 150 °C is most likely reflecting a purely temperature dependent mechanism: the energy of the system reaches the necessary value to trigger degradation and/or reaction of the compounds above 125 °C.

Attempts to identify degradation products which would allow proposing a reaction mechanism to validate these assumptions have proven unsuccessful.

Many oilfields have temperatures below 125 °C, therefore 4-MET-BZA and 3,4-DiMET-BZA may still be considered for use as active conservative reservoir tracers. The onset of degradation may even be exploited to detect thermal fronts in the swept volumes of the reservoirs. Results indicate that if a significant loss of 4-MET-BZA or 3,4-DiMET-BZA is observed in a real field test, it will most likely be caused by a thermal effect. At 150 °C, a loss of about 25% was observed just after 1 week. The velocities of fluids inside a reservoir are low (typically around 1 foot/day), which lead to significant contact periods between the tracers and existing thermal fronts. This would result in a considerable loss of the original tracer compound, thus allowing detection of the temperature variation. Such information is important, particularly if EOR methods are under consideration or use, as they are likely to be temperature dependant.

4-Hydroxybenzyl alcohol (4-HYD-BZA) exhibits high stability during 12 weeks at the lowest tested temperatures (25 °C and 50 °C). This compound degrades at temperatures ≥ 75 °C. These results also suggest a thermally driven phenomenon where increasing temperature leads to the available energy of the system to rise above the activation energy barrier of the degradation reaction. Figure 3 presents 4-HYD-BZA's RF as a function of time and temperature in the experiments at initial pH of 7.1 without any rock substrate.

The rate of degradation of 4-HYD-BZA is clearly temperature dependant, increasing with the increase of T (lowest values for RF are achieved faster as T increases). The decrease in the RF is not linear at any tested temperature which suggests that the degradation kinetics is concentration dependant. A linear decrease in the RF of the compound should be expected if the order of reaction was zero relatively to the concentration of 4-HYD-BZA. Further treatment of the experimental data relative to this compound was performed to assess the possibility of its use as a non-conservative active reservoir tracer to retrieve information about temperature in flooded areas of an oil reservoir.

3.3. Influence of rock substrate

For a compound to be used as a conservative tracer in an oil reservoir it is crucial that it has no significant interaction with the rocks that form the porous medium, which could affect both its stability and dynamic properties. Conventional sedimentary oil basins are primarily constituted by sandstones and/or carbonates which present a significant variation in geochemistry from reservoir to reservoir and even within the same formation (Carroll et al., 2016; Morad et al., 2010). Thus selecting a rock substrate completely representative of every possible formation encountered to test the interaction of the tracer candidates with it is an impossible task. Clays are also present in the rock formations with kaolinite being one of the most occurring (Jiang, 2012). Kaolinite has been reported to be a good adsorbent both for ions (Bhattacharyya and Gupta, 2008) and organic compounds (Yu et al., 2013). Often ion exchange is the proposed adsorption mechanism. Berea sandstone, limestone and kaolinite were selected as “model” reservoir rock substrates to assess the behaviour of the tracer candidates when in contact with sedimentary oil basins.

The RF (t, T) for each benzyl alcohol obtained from the stability experiments using each of the 3 rock substrates were compared with the respective RF (t, T) in the stability experiments without any rock substrate. Figure 4 presents the maximum absolute difference encountered between the RFs for each compound and rock substrate. Differences are presented together with 2 times the standard deviation associated with the determination of the RF value from the tests performed in triplicate. No significant difference was observed between RF at a given time and temperature of incubation in the experiments with rock substrate and the corresponding experiments without rock substrate. Even the highest differences encountered fall inside the uncertainty in the determination of the compounds’ concentration. No systematic trend is also observable regarding the benzyl alcohols or the rock substrates. Results suggest that RF values obtained in the presence of the model reservoir rocks are randomly higher or lower than the ones in experiments without any rock material. This apparent lack of interaction between the benzyl alcohols and typical reservoir rocks meets one of the requirements for their use as tracers in oil reservoirs.

3.4. Kinetics of degradation of 4-hydroxybenzyl alcohol

A study on the degradation of 4-HYD-BZA was performed to assess its use as a tracer to measure temperature in the flooded areas (preferably short sections) of an oil reservoir, or to detect thermal fronts which may be present in lower temperature fields. Such use requires knowledge of the reaction of degradation's activation energy and the pre-exponential factor of the Arrhenius equation. These parameters can be obtained from the treatment of the data from the stability experiments. A first order reaction was assumed for data treatment. Experimental data at 75 °C, 100 °C, 125 °C, and 150 °C were used. Values of C_A/C_{A0} (RF) at time 0 (when C_A/C_{A0} = RF = 1 in every used temperature) were included to increase the number of points in the linear regression analysis. Figure 5 presents the natural logarithm of RF as a function of time (equation 2) at the considered temperatures. The slopes in the linear regressions directly supply the rate constant of the reaction (K) (weeks^{-1}) for each temperature.

The ln (K (T)) values were then plotted against 1/T (K) and a linear regression analysis was performed. Figure 6 presents the plot. From the linearized form of the Arrhenius equation (eq. 3) follows that the slope equals E_a/R and ln (A) is the y-intercept. E_a has a value 58,8 kJ/mol and A = 2,30E+07 weeks^{-1}. Equation 2 can be rewritten as follows with the Arrhenius parameters:

$$\ln\left(\frac{C_A}{C_{A0}}\right) = -\,2{,}30\times10^{07}\,e^{\frac{-58{,}8\times10^{03}}{RT}}\cdot t \qquad \text{(eq. 4)}$$

Equation 4 is the model which describes RF of 4-HYD-BZA as a function of temperature and time, which can be used to obtain information about temperature in a reservoir.

The values of the RF of 4-HYD-BZA predicted by equation 4 were compared with the experimental ones to assess the accuracy of the model. 2 additional tests (2.2.3) were performed where RF values were determined after 2 and 4 weeks. Figure 7 presents the experimental RF values, ± 2 σ in the determination of each one, vs the RF values predicted by equation 4 for 4-HYD-BZA, between 75 and 150 °C.

Good agreement is encountered between experimental and predicted data. Predicted values are always included in the confidence interval accounting for the variance in the experimental determinations. This suggests the assumption made of a first order kinetics of degradation is a sufficiently accurate description of the phenomena, and that no other chemical species present in the bulk is taking part in the reaction.

The use of non-conservative tracers in an oil reservoir is not common, but can provide useful information if the tracer's degradation process is understood and/or modellable. Chemical EOR processes such as conformity control with micro-emulsions, permeability modification with gels, or wettability modification with surfactants, for example, depend strongly on temperature. Thus previous up-front knowledge of this in-situ parameter can be valuable to increase recovery rates and decrease operational cost.

4. Conclusions

The stability of five benzyl alcohols was investigated in batch experiments under typical conditions encountered in oil reservoirs as part of their qualification process for use as partitioning tracers (one type of active tracers). Experiments were performed in a synthetic brine to account for the effect of elevated salinity (ion strength and ionic composition). The influence of temperature, time, and pH on the stability of the compounds was evaluated. Interaction with typical reservoir rock (kaolinite, sandstone and limestone) was also studied. The pH was found to have no significant impact on the stability of all tested compounds in the studied range (5,5 – 8,0). No difference outside the analytical uncertainty was encountered between experiments at different pH values. 4-Chlorobenzyl alcohol and 2,6-Dichlorobenzyl alcohol were found to be fully stable up to 150 °C during 12 weeks. No significant interaction between these 2 compounds and the rock materials was observed. 4-Methoxybenzyl alcohol and 3,4-Dimethoxybenzyl alcohol are also insensitive to the presence of rock substrates. These compounds were found to exhibit limited thermal stability. Both are fully stable up to 125 °C and 12 weeks, and an onset of degradation is observable at 150 °C even after 1 week of incubation. 4-Methoxybenzyl alcohol and 3,4-Dimethoxybenzyl alcohol may still be used as partitioning tracers, as most oil reservoirs have temperatures below 125 °C. The degradation they exhibit above 125 °C may also be exploited to retrieve information about the existence of thermal fronts in the swept volumes of oil fields. 4-Hydroxybenzyl alcohol is stable during the 12 weeks of testing at 25 and 50 °C exhibiting degradation at temperatures above this threshold. The degradation of this compound increases both with temperature and time of incubation, and is not affected by the presence of rock materials. Results agree with a first order degradation kinetic purely thermally driven without influence of any other chemical species. The apparent activation energy and the pre-exponential factor of the Arrhenius equation were determined and a kinetic model for the degradation was developed, thus opening the possibility for using this compound as a non-conservative active (temperature sensitive) tracer.

5. Acknowledgements

The authors acknowledge the Research Council of Norway and the industry partners; ConocoPhillips Skandinavia AS, Aker BP ASA, Eni Norge AS, Maersk Oil Norway AS, Statoil Petroleum AS, ENGIE E&P Norge AS, Lundin

Norway AS, Halliburton AS, Schlumberger Norge AS, Wintershall Norge AS, DEA Norge AS of The National IOR Centre of Norway for support.

6. References

Ahmad, M. et al., 2003. Interwell tracing by environmental isotopes at Fimkassar Oilfield, Pakistan. Applied radiation and isotopes : including data, instrumentation and methods for use in agriculture, industry and medicine, 58(5): 611-9.

Al-Murayri, M.T., Al-Qenae, A., AlRukaibi, D., Chatterjee, M. and Hewitt, P., 2017. Design of a Partitioning Interwell Tracer Test for a Chemical EOR Pilot Targeting the Sabriyah Mauddud Carbonate Reservoir in Kuwait. Society of Petroleum Engineers.

Allison, S.B., Pope, G.A. and Sepehrnoori, K., 1991. Analysis of field tracers for reservoir description. Journal of Petroleum Science and Engineering, 5(2): 173-186.

Asadi, M. and Shook, G.M., 2010. Application of Chemical Tracers in IOR: A Case History. Society of Petroleum Engineers.

Bhattacharyya, K.G. and Gupta, S.S., 2008. Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite: A review. Advances in Colloid and Interface Science, 140(2): 114-131.

Carpenter, C., 2016. Use of Partitioning Tracers To Estimate Oil-Saturation Distribution. Journal of Petroleum Technology, 68(09): 72-73.

Carroll, S. et al., 2016. Review: Role of chemistry, mechanics, and transport on well integrity in CO2 storage environments. International Journal of Greenhouse Gas Control, 49: 149-160.

Chatzichristos, C., Dugstad, Ø., Haugan, A., Sagen, J. and Muller, J., 2000. Application of Partitioning Tracers for Remaining Oil Saturation Estimation: An Experimental and Numerical Study. Society of Petroleum Engineers.

Cooke, C.E.J., 1971. “Method of determining fluid saturations in reservoirs”. Esso Production Research Company, USA.

Esteruelas, M.A., García-Obregón, T., Herrero, J. and Oliván, M., 2011. Osmium-Catalyzed Oxidation of Primary Alcohols with Molecular Oxygen. Organometallics, 30(23): 6402-6407.

Fakhru’l-Razi, A. et al., 2009. Review of technologies for oil and gas produced water treatment. Journal of Hazardous Materials, 170(2): 530-551.

Fogler, H.S., 2006. Elements of Chemical Reaction Engineering. Prentice Hall PTR, New Jersey.

Guan, L., Du, Y., Johnson, S.G. and Choudhary, M.K., 2005. Advances of Interwell Tracer Analysis in the Petroleum Industry.

Higashimoto, S. et al., 2009. Selective photocatalytic oxidation of benzyl alcohol and its derivatives into corresponding aldehydes by molecular oxygen on titanium dioxide under visible light irradiation. Journal of Catalysis, 266(2): 279-285.

Huseby, O., Hartvig, S.K., Jevanord, K. and Dugstad, Ø., 2015. Assessing EOR Potential from Partitioning Tracer Data, SPE Middle East Oil & Gas Show and Conference. Society of Petroleum Engineers, Manama, Bahrain.

IEA, 2016. Key World Energy Statistics 2016. IEA, Paris, 80 pp.

Jaiswal, R. and Kuhnert, N., 2014. Identification and Characterization of the Phenolic Glycosides of Lagenaria siceraria Stand. (Bottle Gourd) Fruit by Liquid Chromatography-Tandem Mass Spectrometry. J. Agric. Food Chem., 62(6): 1261-1271.

Jiang, S., 2012. Clay Minerals from the Perspective of Oil and Gas Exploration. In: M. Valaškova and G.S. Martynkova (Editors), Clay Minerals in Nature - Their Characterization, Modification and Application. InTech, Rijeka, pp. Ch. 2.

Lichtenberger, G.J., 1991. Field Applications of Interwell Tracers for Reservoir Characterization of Enhanced Oil Recovery Pilot Areas, SPE Production Operations Symposium. Society of Petroleum Engineers, Oklahoma City, Oklahoma.

Luo, L. et al., 2017. Anti-oxidative effects of 4-hydroxybenzyl alcohol in astrocytes confer protective effects in autocrine and paracrine manners. PLoS One, 12(5): e0177322.

Mantri, K., Komura, K., Kubota, Y. and Sugi, Y., 2005. Friedel–Crafts alkylation of aromatics with benzyl alcohols catalyzed by rare earth metal triflates supported on MCM-41 mesoporous silica. Journal of Molecular Catalysis A: Chemical, 236(1): 168-175.

Martin, V. et al., 2016. De Novo Synthesis of Benzenoid Compounds by the Yeast Hanseniaspora vineae Increases the Flavor Diversity of Wines. J. Agric. Food Chem., 64(22): 4574-4583.

Morad, M. et al., 2017. Multifunctional supported bimetallic catalysts for a cascade reaction with hydrogen auto transfer: synthesis of 4-phenylbutan-2-ones from 4-methoxybenzyl alcohols. Catal. Sci. Technol., 7(9): 1928-1936.

Morad, S., Al-Ramadan, K., Ketzer, J.M. and De Ros, L.F., 2010. The impact of diagenesis on the heterogeneity of sandstone reservoirs: A review of the role of depositional facies and sequence stratigraphy. AAPG Bull., 94(8): 1267-1309.

Muggeridge, A. et al., 2014. Recovery rates, enhanced oil recovery and technological limits. Philosophical transactions. Series A, Mathematical, physical, and engineering sciences, 372(2006): 20120320.

Pugh, S., McKenna, R., Halloum, I. and Nielsen, D.R., 2015. Engineering Escherichia coli for renewable benzyl alcohol production. Metabolic Engineering Communications, 2: 39-45.

Sanni, M. et al., 2016. Pushing the Envelope of Residual Oil Measurement: A Field Case Study of a New Class of Inter-Well Chemical Tracers. Society of Petroleum Engineers.

Scandura, G. et al., 2016. Selective photooxidation of ortho-substituted benzyl alcohols and the catalytic role of ortho-methoxybenzaldehyde. Journal of Photochemistry and Photobiology A: Chemistry, 328: 122-128.

Serres-Piole, C. et al., 2012. Water tracers in oilfield applications: Guidelines. Journal of Petroleum Science and Engineering, 98-99(Supplement C): 22-39.

Shen, T., Moghanloo, R.G. and Tian, W., 2017. Interpretation of Interwell Chemical Tracer Tests in Layered Heterogeneous Reservoirs with Crossflow. Society of Petroleum Engineers.

Shyamala, B.N., Naidu, M.M., Sulochanamma, G. and Srinivas, P., 2007. Studies on the antioxidant activities of natural vanilla extract and its constituent compounds through in vitro models. J Agric Food Chem, 55(19): 7738-43.

Silva, M., Stray, H. and Bjørnstad, T., 2017. Studies on New Chemical Tracers for Determination of Residual Oil Saturation in the Inter-Well Region. Society of Petroleum Engineers.

Tang, J.S., 1995. Partitioning Tracers and In-Situ Fluid Saturation Measurements. SPE Formation Evaluation, 10(01): 33 - 39.

Tang, J.S., 2003. Propagation of phenol in aquifer with reversible adsorption, Proceedings of the Go-Expo Gas and Oil Exposition and the 4 Annual Canadian International Petroleum Conference and the 54 Annual Technical Meeting of the Petroleum Society of CIM : Global Challenges and Technology Integration. Petroleum Society of CIM, Canada.

Tang, J.S. and Harker, B., 1991. Interwell Tracer Test To Determine Residual Oil Saturation In A Gas-Saturated Reservoir. Part II: Field Applications. Journal of Canadian Petroleum Technology, 30(04): 34 - 42.

Tao, X. et al., 2017. Fabrication of continuous ZrB2 nanofibers derived from boron-containing polymeric precursors. Journal of Alloys and Compounds, 697: 318-325.

Viig, S.O. et al., 2013. Application of a New Class of Chemical Tracers To Measure Oil Saturation in Partitioning Interwell Tracer Tests, SPE International Symposium on Oilfield Chemistry. Society of Petroleum Engineers, The Woodlands, Texas, USA.

Wood, K.N., Tang, S. and Luckasavitch, R.J., 1990. Interwell Residual Oil Saturation at Leduc Miscible Pilot, SPE Annual Technical Conference and Exhibition. Society of Petroleum Engineers, New Orleans, Louisiana.

Yu, W.H. et al., 2013. Adsorption of proteins and nucleic acids on clay minerals and their interactions: A review. Applied Clay Science, 80-81: 443-452.

Table 1. Selected benzyl alcohols partitioning tracer candidates and respective melting point, boiling point, pKa, and octanol/water partitioning coefficient

Compound	Melting point (°C)	Boiling point (°C)	K_{OW}	pKa
4-Hydroxybenzyl alcohol	114	251	1,8	9,82
4-Chlorobenzyl alcohol	71	232	4,2	13,9
2,6-Dichlorobenzyl alcohol	98	268	7,0	13,5
4-Methoxybenzyl alcohol	23	259	5,1	13,6
3,4-Dimethoxybenzyl alcohol	22	297	4,2	13,3

Data Source: NIST chemistry WebBook

Table 2. Composition of the brine (synthetic Gullfaks water) used in the experiments

NaCl (g/L)	KCl (g/L)	$CaCl_2.2H_2O$ (g/L)	$MgCl_2.6H_2O$ (g/L)	$BaCl_2.2H_2O$ (g/L)	$SrCl_2.6H_2O$ (g/L)	$NaHCO_3$ (g/L) *	Na_2SO_4 (g/L)
36,855	0,629	3,814	2,550	0,088	0,437	0,157	0,046

* $NaHCO_3$ was used as pH buffer in varying amounts (0,157 g/L for initial pH of 7,1; 0.280 g/L for initial pH of 8,0; no $NaHCO_3$ for initial pH of 5,5).

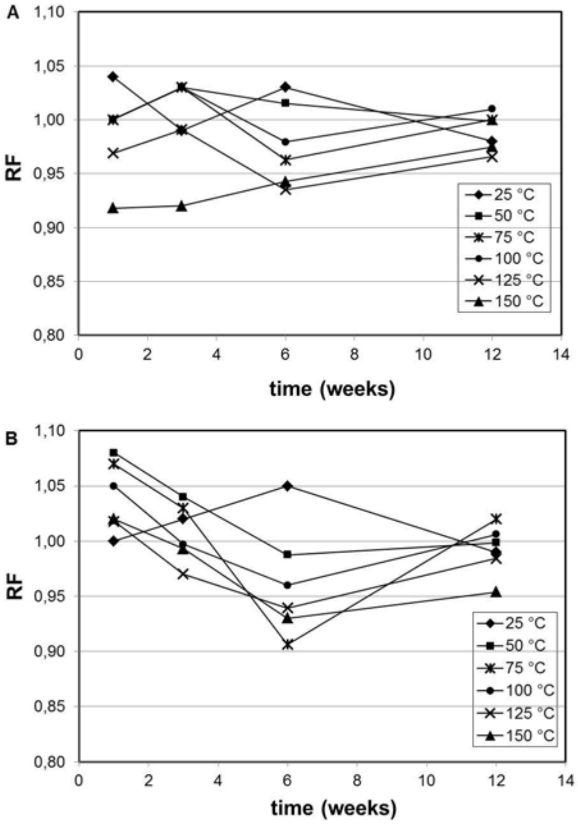

Fig. 1. RF of 4-Chlorobenzyl alcohol and 2,6-Dichlorobenzyl alcohol as function of time and temperature of incubation. (A) 4-Chlorobenzyl alcohol, (B) 2,6-Dichlorobenzyl alcohol. Initial experimental pH 7.1, no rock substrate).

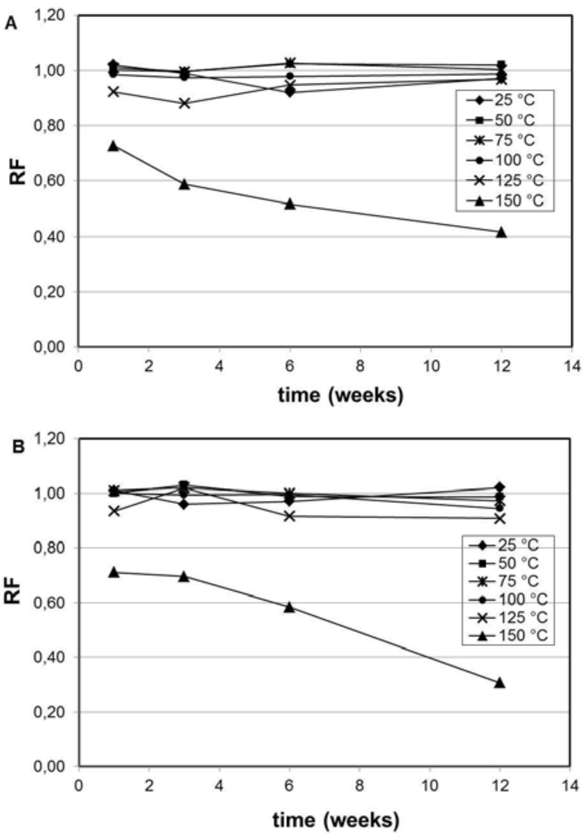

Fig. 2. RF of 4-Methoxybenzyl alcohol and 3,4-Dimethoxybenzyl alcohol as function of time and temperature of incubation. (A) 4-Methoxybenzyl alcohol, (B) 3,4-Dimethoxybenzyl alcohol. Initial experimental pH 7.1, no rock substrate).

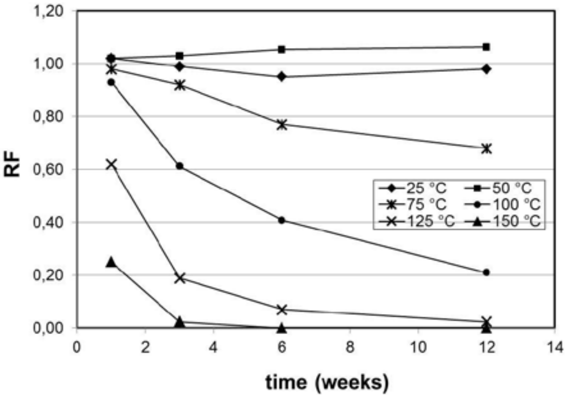

Fig. 3. RF of 4-Hydroxybenzyl alcohol as function of time and temperature of incubation. Initial experimental pH 7.1, no rock substrate.

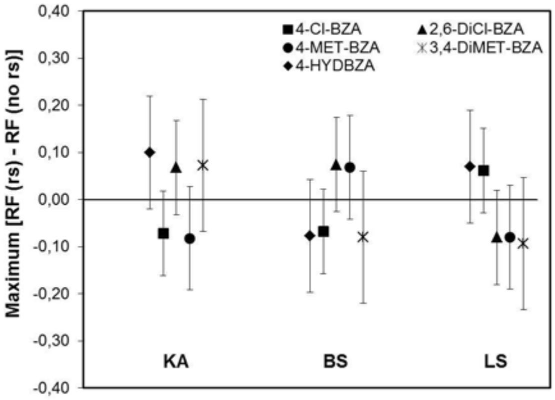

Fig. 4. Maximum differences encountered in RF values between experiments with rock substrate (rs) and experiments without rock substrate ± 2 x σ in RF (t, T). (KA) kaolinite, (BS) Berea sandstone, (LS) limestone.

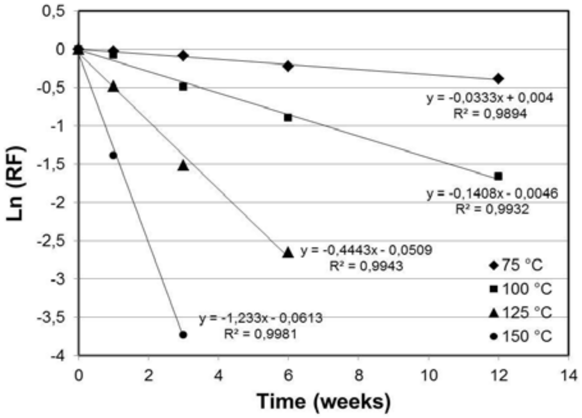

Fig. 5. Ln (RF) of 4-hydroxybenzyl alcohol as a function of time and linear regressions at each temperature. Initial experimental pH 7.1, no rock substrate.

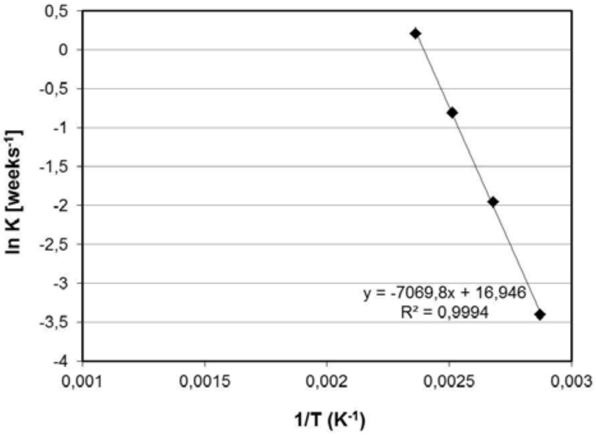

Fig. 6. Arrhenius plot for the degradation of 4-HYD-BZA between 75 and 150 °C.

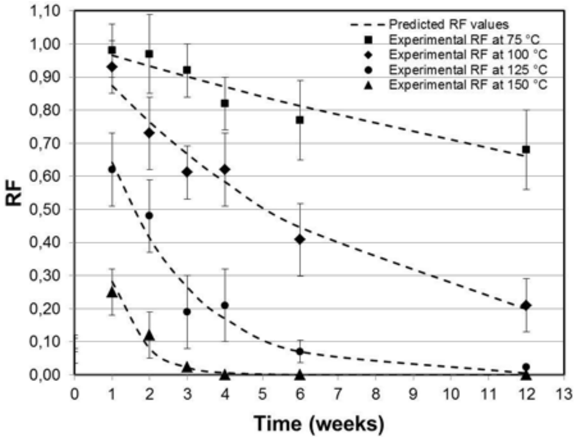

Fig. 7. Experimental vs predicted RF values of 4-HYD-BZA between 75 and 150 °C. Uncertainty is not depicted for values under the lower analytical threshold (RF = 0,05).