Oilfield water sample quality: effect of H_2O mass transfer between water and hydrocarbons

R. A. McCartney
GeoScience Limited, Falmouth, United Kingdom

T. Østvold
Norwegian University of Science and Technology, Trondheim, Norway

ABSTRACT: H_2O mass transfer can occur between water and hydrocarbons during changes in pressure and temperature. PVT simulations for gas condensate-water systems covering a range of reservoir conditions (80-125°C; 300-350 bar) and hydrocarbon-water ratios (HWR; 3.3 to 1000 by volume) have been undertaken to quantify the extent of H_2O mass transfer during the collection of surface, downhole and core samples. The results show that significant dilution and concentration of water samples can occur, particularly at high HWR. It is recommended that the quality of formation water analyses derived from water samples obtained from gas condensate fields is assessed using PVT software, of the type used in this study, prior to use.

1 INTRODUCTION

Understanding water-rock reactions in sedimentary systems can benefit hydrocarbon exploration and production. For example, the information can be used to constrain regional palaeo-fluid flow and reservoir quality models, and aid understanding of the sources of detrimental constituents such as CO_2, H_2S, Ba, and Sr. Water-rock reaction studies often utilise analyses of formation waters obtained from locations where hydrocarbons and water are in contact (e.g. in co-produced fluids, downhole sampling tools, and in core samples from the transition zone and hydrocarbon-leg). In these locations, samples are susceptible to transfer of H_2O between hydrocarbons and water giving artificially raised or lowered concentrations of dissolved ions in the water phase (e.g. Kharaka et al. 1977). Previous studies have used empirical or geochemical techniques to identify and quantify these effects to avoid incorrect interpretation of formation water analyses (e.g. Kharaka et al. 1977, 1985; Morton & Land 1987; Hitchon & Brulotte 1994). In this study we used scale prediction software with an integrated PVT model (MultiScale©; Petrotech 2003) to quantitatively explore the effects of H_2O transfer between water and hydrocarbon phases in gas condensate fields during the collection of different types of sample from which formation water analyses are generated. The implications of the results with respect to sample quality are discussed.

2 CALCULATIONS

MultiScale© is designed to predict mineral precipitation from oil field water in equilibrium with gas and oil phases. In addition to the Pitzer model for aqueous equilibria, it contains a complete PVT model, which can calculate bubble points, phase distribution, and distribution of components between phases, especially CO_2, H_2S, CH_4, and H_2O.

We considered medium-temperature (Case 1; 80°C, 300 bar) and high-temperature (Case 2; 125°C, 350 bar) gas condensate-water systems. In both cases, the reservoir hydrocarbon phase is gas, saturated with H_2O, and in equilibrium with reservoir water (Table 1).

For each case, three different types of calculation were undertaken. These simulated H_2O transfer between the water and hydrocarbon phases under conditions associated with the sampling of formation waters (a) at the surface (e.g. wellhead or separator), (b) in downhole tools and (c) from core samples respectively. In all calculations it was assumed that mass transfer occurred under equilibrium conditions (i.e. the hydrocarbon phases were in equilibrium with the water phase and kinetics were not considered). The effect of H_2O transfer was assessed through changes in the Cl^- concentration of the samples relative to the Cl^- concentration of the reservoir water.

Collection of surface samples was simulated by flashing various hydrocarbon-reservoir water mixtures (hydrocarbon-water volume ratios, HWR, between 3.3 and 1000 at reservoir conditions) from

reservoir conditions to typical separator (52°C; 65 bar) or atmospheric (15°C; 1 bar) conditions. These were closed-system calculations.

Table 1. Compositions of reservoir hydrocarbons and formation waters used in the simulations.

Constituent	Case 1 (mol %)	Case 2 (mol %)	Constituent	Case 1* and 2# (mg/kg H_2O)
H_2O	0.49	1.61	Na	7061
N_2	0.74	0.73	K	163
CO_2	3.41	3.37	Mg	25.2
C_1	73.0	72.2	Ca	474
C_2	9.89	9.78	Ba	11.1
C_3	4.82	4.77	Sr	0.3
iC4	1.30	1.28	Cl	11766
nC4	0.73	0.72	Tot. Alk	
iC5	0.50	0.49	(HCO_3)	325
nC5	0.38	0.37	CO_2	2917*, 2806#
C6	0.36	0.35	CH_4	2133*, 1818#
C7	0.37	0.37		
C8	0.38	0.37		
C9	1.21	1.20		
C10+	2.42	2.39		
Total	100.00	100.00		

Collection of pressure-compensated downhole samples was simulated through the closed-system cooling of a hydrocarbon-water mixture (HWR = 25) from reservoir temperatures to 15°C at reservoir pressures. Collection of fixed-volume downhole samples was simulated through closed-system pressure reduction of the same mixture from reservoir pressure to 1 bar at (a) 52°C and (b) 15°C.

During retrieval of core from a well and subsequent storage, fluid pressure and temperature decline leading to fluid expansion and loss prior to extraction of the water phase. This open-system process was simulated by linearly decreasing the pressure and temperature of a hydrocarbon-water mixture (HWR = 10) from reservoir to atmospheric conditions. Total fluid volume (gas + oil + water) was calculated at each simulation point. Where the total fluid volume exceeded the reservoir pore volume, at each step excess gas was removed from the system.

3 RESULTS

3.1 *Surface samples*

When the hydrocarbon-water mixtures are flashed at separator and atmospheric conditions, oil condenses out of the reservoir gas phase. However, the gas-oil ratio is higher at atmospheric conditions compared with separator conditions. The water-cut increases with decreasing HWR (e.g. Fig. 1). H_2O mass transfer is predominantly from the hydrocarbon phase into the water phase as temperature declines (condensation) and from the water phase into the hydrocarbon phase as pressures approach atmospheric conditions (evaporation). The effect of these competing processes on Cl^- concentration of the water phase are shown in Figure 2.

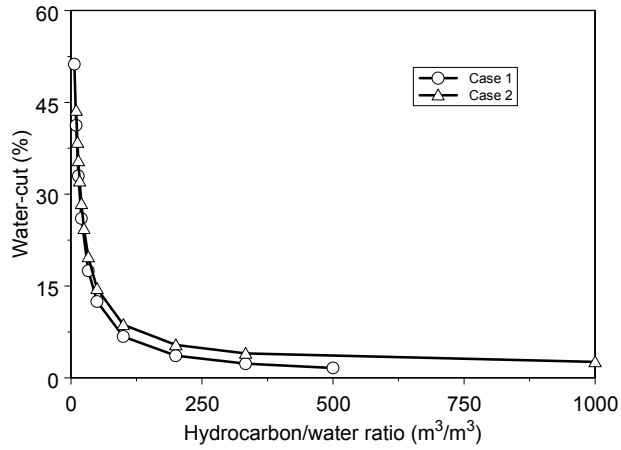

Figure 1. Variation of water-cut at the separator with hydrocarbon/water volume ratio under reservoir conditions.

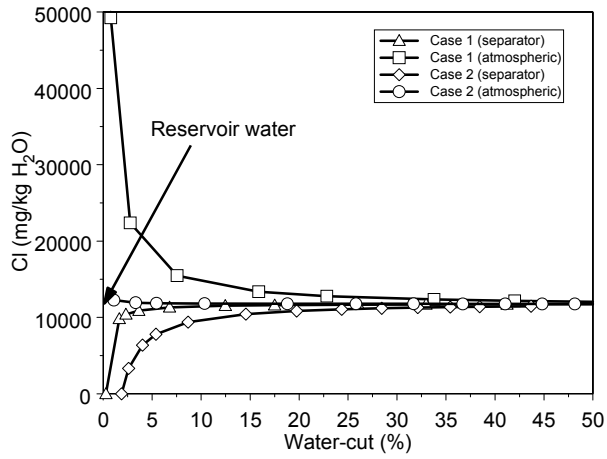

Figure 2. Variation of water phase Cl^- concentration with water-cut at separator (52°C, 65 bar) and atmospheric (15°C, 1 bar) flash conditions.

For separator samples, condensation dominates due to cooling of the sample whilst elevated pressures are maintained. Most dilution occurs in Case 2 where the reservoir hydrocarbon phase contains most H_2O. In this case, the separator sample analysis will underestimate the reservoir water composition by 10 and 50% with water-cuts of approximately 17% and 4%, respectively. For samples collected under atmospheric conditions, the effects of evaporation are superimposed on condensation effects resulting in net concentration of Cl^- in the sample. For Case 2, net H_2O transfer is minor because the magnitudes of the condensation and evaporation effects are similar. Most concentration is seen in Case 1 where the effects of condensation are less. Here the sample analysis will overestimate the reservoir water composition by 90% and 30% with water-cuts of approximately 3% and 7% respectively. For the above calculations, as water-cut increases, the effects of dilution and concentration on water sample

Cl^- decrease. For Case 1, water-cuts of at least approximately 7% (separator conditions) and 40% (atmospheric conditions) are required before water sample Cl^- analysis becomes insignificantly different (±4%) from the reservoir water composition. For Case 2 the figures are 32% and 1%.

3.2 *Downhole samples*

Condensation effects are dominant during cooling at reservoir pressures causing a reduction in water sample Cl^- concentration (e.g. Fig. 3). However, with HWR = 25, in both cases dilution is less than 7% (Table 2). As pressure declines at both separator and atmospheric temperatures, evaporation occurs. This dominates condensation effects in Case 1 at both temperatures and in Case 2 at the separator temperature. The largest net increase in Cl^- occurs at the separator temperature in Case 1 where the condensation effects associated with cooling are lowest (Table 2). At each temperature, pressures need to fall to relatively low values before the large increases in Cl^- occur (eg less than ~5 bar at 52°C, Case 1). These 'threshold' pressures are higher at higher temperatures.

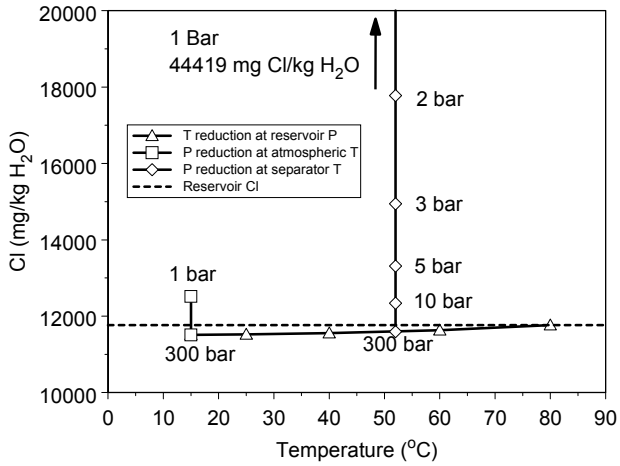

Figure 3. Case 1. Variation of water phase Cl^- concentration with changes in (a) temperature at reservoir pressure, (b) pressure at separator temperature and (c) pressure at atmospheric temperature.

Table 2. Net change in water sample Cl^- concentration (%) relative to reservoir water Cl concentration for downhole sample simulations.

Simulation conditions	Case 1	Case 2
Cooling (at reservoir P, 300 bar) to:		
(a) Separator T (52°C)	-1.4%	-6.4%
(b) Atmospheric T (15°C)	-2.2%	-7.0%
Pressure reduction from 300 to 1 atm at:		
(a) Separator T (52°C)	+277.5%	+173.4%
(b) Atmospheric T (15°C)	+6.4%	+0.1%

As demonstrated by the surface sample calculations, the above changes in Cl^- concentration will be exaggerated or minimized for samples with HWR higher or lower than 25, respectively.

3.3 *Core samples*

Under the open-system conditions of the core samples, cooling induced condensation is the dominant H_2O transfer process causing dilution of Cl^- in the water phase of a similar order to those seen in the downhole sample cooling simulations (Fig. 4). Significant amounts of gas were expelled from the samples as pressure and temperature declined. For example, in Case 2, 80% by mass of the reservoir hydrocarbons were lost as gas. As pressures decline to atmospheric, negligible evaporation occurs because of the low volume of hydrocarbon gas remaining in contact with the water phase.

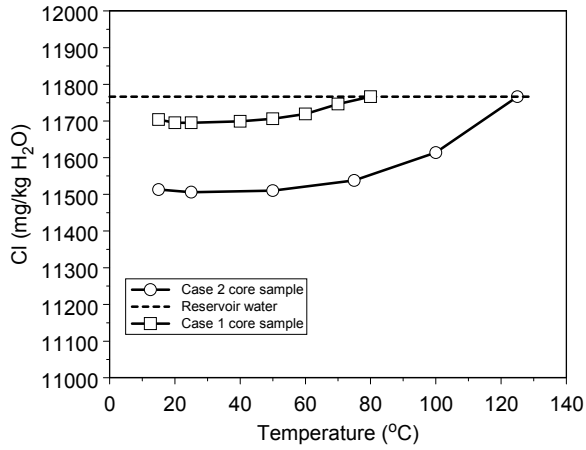

Figure 4. Variation of water phase Cl^- concentration in core samples during pressure and temperature reduction from reservoir to atmospheric conditions.

4 DISCUSSION

The above results have demonstrated that where water samples are collected in contact with hydrocarbons, mass transfer of H_2O between the phases can occur during cooling and pressure reduction.

Based on the above results, the key variables affecting sample Cl^- concentration are:

- Pressure and temperature of the reservoir.
- Pressure and temperature conditions at the point where water is separated from the hydrocarbons.
- Hydrocarbon:water ratio (HWR).

There are individual conditions that should result in the collection of better quality wellhead and separator samples from gas condensate fields. For example, where:

- The samples have low HWR.
- The reservoir temperature is low.
- The samples are collected at elevated temperature and moderate pressure.

However, when considering these variables collectively, it is difficult to provide simple and reliable

guidance on the conditions required for good quality samples. For example, in Case 2, flashing to atmospheric conditions, with a water-cut of only 1.1%, the water sample Cl^- is only 4% higher than at reservoir conditions. Similarly, in the same case and flashing at separator conditions, water-cut is 4%, and the water sample Cl^- is 45% lower than at reservoir conditions. It is evident that the effects of H_2O mass transfer on the quality of water samples is best investigated using computer programs similar to that used in this study. Such programs can also be used to design sampling and sample transfer procedures to obtain better quality samples and to correct for the effects of condensation and evaporation where poorer quality samples are collected.

Recently, a technique has been developed to extract very low levels of free formation water (down to 0.01 wt %) from oil samples for analysis (trace water-in-oil analysis; Rosenbaum & Coleman 1998). The above results suggest that when applying the technique on gas condensate fields the potential for condensation and evaporation contamination of the free water should be investigated for high HWR samples.

When samples are collected in pressure and temperature compensated tools, water sample Cl^- analyses will be representative of the Cl^- concentration of water in the reservoir. If sampling tools are only pressure compensated and the samples cool prior to removal of the water phase, condensation of H_2O into the sample water can occur resulting in an underestimate of reservoir water Cl^-. This will be most significant where the samples are cooled to atmospheric temperatures, where HWR of the sample is high, and where the samples have been obtained from high temperature gas condensate reservoirs. Samples collected in fixed-volume tools will also be affected by H_2O condensation from the hydrocarbon phase into the water phase but this will be offset in part or completely by transfer of H_2O from the water phase into the hydrocarbon phase as sample pressure declines prior to transfer. Errors in water sample Cl^- concentration will be greatest where pressure is allowed to decline significantly (eg below ~20 bar) and temperature remains elevated, and where the HWR of the sample is high.

Although efforts are often made to heat and pressurize downhole tool samples back up to reservoir temperatures and pressures once at the surface, it is uncertain at what rate H_2O will be redistributed between the phases to match the distribution at reservoir conditions. Although counter-intuitive, when using pressure-compensated or fixed-volume tools and major ion concentrations are of interest, in some circumstances (e.g. Case 2) more representative analyses may be obtained where the tools have been allowed to cool and de-pressurize to atmospheric conditions before sample transfer.

Where the water phase in core is to be removed by heavy-liquid displacement or ultra-centrifugation, dilution of the water phase Cl^- will be greatest for low S_w core samples derived from high-temperature gas condensate reservoirs. The same conclusions can be drawn where the core is to be used for residual salt analysis where absolute concentrations are of interest.

5 CONCLUSIONS

This study has shown that, under equilibrium conditions, mass transfer of H_2O into and out of water in contact with hydrocarbons can cause significant dilution and concentration of dissolved ionic constituents in the water phase, particularly where reservoir temperature and HWR are high. Dilution effects are likely to dominate where the water phase is separated from the hydrocarbon phase at low temperature and moderate pressures. Concentration effects are likely to be most significant where separation occurs at higher temperature and low pressures. When utilizing formation water analyses from gas condensate fields, it is recommended that PVT simulations, such as those undertaken in this study, are performed to quantify the effects of H_2O mass transfer on the samples.

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