Mass transfer of H_2O between hydrocarbons and water: Implications for oilfield water sample quality

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ABSTRACT

H_2O mass transfer can occur between water and hydrocarbons during changes in pressure and temperature. This process can result in the dilution or concentration of dissolved ions in the water phase of oilfield hydrocarbon-water samples. In this study we undertook PVT simulations for four hydrocarbon-water systems covering a range of reservoir conditions (80-185°C; 300-1000 bar) and a range of water-hydrocarbon mixtures (volume ratios of 1:1000 to 300:1000) to quantify the extent of H_2O mass transfer as a result of pressure and temperature changes. Conditions were selected to be relevant to different types of oilfield water sample (ie surface, downhole and core samples). The main variables determining the extent of dilution and concentration were found to be (a) reservoir pressure and temperature, (b) pressure and temperature of separation of water and hydrocarbons, (c) hydrocarbon composition and (d) hydrocarbon:water ratio (HWR). The results showed that significant dilution and concentration of water samples could occur, particularly at high HWR. It was not possible to establish simple guidelines for identifying good and poor quality samples due to the interplay of the above variables. Sample quality is best investigated using PVT software of the type used in this study.

INTRODUCTION

Analyses of oilfield water samples have many uses during the life cycle of a field (see Table 1). These samples are often obtained from locations where hydrocarbons and water are in contact. For example, where water and hydrocarbons are co-produced, samples are commonly collected from close to the wellhead or from the separator. Attempts are also being made to obtain samples from the transition zone and hydrocarbon-leg of reservoirs as these data are particularly useful for oil-in-place calculations, reservoir compartmentalisation, and regional palaeohydrogeology studies (eg Thurlow and Coleman, 1997; Mearns and McBride, 1999; McCartney et al., in press).

It is important to understand the quality of the samples before using the analyses in these different applications and where water and hydrocarbons are in contact, one factor that may affect sample quality is the transfer of H_2O between the phases. At oilfield temperatures and pressures, H_2O has significant solubility in hydrocarbons (eg Figure 1) and it has been recognised for a number of years that condensation and evaporation of water during production can artificially raise or lower concentrations of dissolved ions in water samples (eg Kharaka et al, 1977). Several attempts have been made to identify condensation/evaporation affected samples based on gas/water ratios, geochemical anomalies and sampling conditions (eg Kharaka et al. 1977, 1985; Morton and Land, 1987; Hitchon and Brulotte, 1994). Kharaka et al (1977, 1985) used Si geothermometers, steam tables and δ^2H and $\delta^{18}O$ data to provide initial estimates of the effects of condensation and evaporation on water samples. More recently, commercial computer programs have been developed that include PVT modules. These allow more rigorous quantification of H_2O transfer between water, oil and gas during production. For example, Jarinski and Frigo (1997), Jasinski et al. (1997, 1998, 1999) have used such programs to correct for the effects of evaporation and condensation in scaling predictions.

In this paper, we use one of these programs (MultiScale©; Petrotech, 2003) to quantitatively explore the effects of H_2O transfer between water and hydrocarbon phases. Simulation conditions have been selected to match those experienced by oilfield water samples that are either collected in contact with hydrocarbons or are separated from hydrocarbons immediately before collection. The implications of the results with respect to sample quality are discussed.

MultiScale software

MultiScale© is designed to predict mineral precipitation from oil field water in equilibrium with gas and oil phases. The program has an advantage over most prediction models commercially available since it, in addition to an accurate model for aqueous equilibria, 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. For hydrocarbon-water mixtures, it also automatically calculates the H_2O content of hydrocarbons. This facility is important because PVT analyses, required as input data, do not normally include H_2O determinations. Minerals included in MultiScale© are: $BaSO_4$, $CaSO_4$ (Anhydrite, Gypsum and Hemihydrite), $SrSO_4$, $CaCO_3$ (Calcite), $FeCO_3$, FeS and NaCl. An important parameter in MultiScale© is the mass balance. When mass balances are known for all components present at one point in the production system, equilibrium calculations can determine the distribution of all components between the different phases present when thermodynamic data are known for the components in each phase at any point in the system. When the water mass balance is established, for example, at the separator, MultiScale© will calculate the water composition at given temperatures and total pressures, that is at any point in the production system, such that equilibrium is established for water between the water, oil and gas phases. In this calculation both the Pitzer model for aqueous and the PVT model for the hydrocarbon phases are used. This calculation is performed in steps starting with no water in the oil phase (if such a phase is present). Then water is transferred to the oil phase until equilibrium for CO_2, H_2S, CH_4 and H_2O is established between the water, oil and gas phases.

Water samples

There are three general types of sample that are either collected in contact with hydrocarbons or are separated from hydrocarbons immediately before collection: surface samples, downhole samples and core samples.

Where water and hydrocarbons are co-produced at the surface, water phase samples are normally obtained from either the underflow of the main separator or from the underflow of a mini-separator attached at/near the wellhead via an isokinetic sampling probe. Depending on the circumstances, the water may be separated from the hydrocarbons at elevated or atmospheric temperatures and pressures. When collected at elevated pressures and temperature, water samples are flashed and cooled to atmospheric conditions prior to analysis of dissolved ions and other components in the water phase (eg. CO_2). In the flash analysis also the gas/water ratio, GWR, must be determined to obtain the correct mass balance for CO_2. It should also be mentioned at this point that the analysis of CO_2 must also be performed for the oil and gas phases to obtain the total CO_2 mass balance. The oil and the gas must be sampled at the same point as the water, and the production rate of oil, water and gas must be known.

Water samples may be collected downhole using wireline-sampling tools, tubing-conveyed sampling tools or formation samplers. These tools are designed to prevent loss of sample after collection. Typically they are obtained under one of three conditions:

a) Pressure-compensated. These samples are over-pressured immediately after collection to prevent them out-gassing as the samples cool during recovery to the surface.
b) Pressure- and temperature-compensated. These samples are over-pressured as above and heated to maintain the sample temperature close to collection temperature during recovery to the surface.
c) Fixed-volume. Pressure and temperature decline in these samples after collection although pressure is likely to remain elevated above atmospheric pressure.

When downhole sampling tools are deployed to obtain water samples from a well, normally efforts will be made to obtain pure formation water samples from the underlying aquifer and H_2O mass transfer between hydrocarbons and water during sample recovery and transfer need not be considered. However, sometimes only hydrocarbon-water mixtures can be obtained and H_2O mass transfer can occur. In these cases procedures are usually adopted to ensure that only the water phase is removed from the sampling tool and this phase then undergoes a secondary flash to atmospheric pressure and temperature under controlled conditions prior to analysis of dissolved ions.

Water samples can also be obtained from core. They may be directly removed using ultra-centrifugation or heavy liquid displacement. Alternatively, pore fluids and evaporative salts (deposited from pore fluids) can be dissolved from the core in a leachate and formation water compositions can be estimated from leachate analyses, and S_w and porosity data for the core samples (eg $^{87}Sr/^{86}Sr$ Residual Salt Analysis, RSA, Mearns and McBride, 1999; Elemental Residual Salt Analysis, ERSA, McCartney et al., in press). Where information is required on aquifer water compositions, these samples are normally obtained from the water-leg where hydrocarbons may not be present and H_2O mass transfer need not be considered. Where data is required from the reservoir transition zone and hydrocarbon-leg (eg for oil-in-place calculations), H_2O mass transfer can occur during cooling and de-pressurisation of the core as it is recovered and stored prior to sample removal.

The proportions of water to hydrocarbon in these different samples will vary widely. At one extreme, separator water-cuts can exceed 90%. At the other, techniques have been developed to extract 'free' water from oil down to 0.01 weight % (trace water-in-oil analyses; Rosenbaum and Coleman, 1998).

CALCULATIONS

Three different types of calculation were undertaken with MultiScale© to simulate H_2O transfer between the water and hydrocarbon phases under conditions associated with surface, downhole and core samples respectively. With each type of calculation, we considered four different hydrocarbon-water systems (Table 2): medium-temperature gas condensate (Case 1), high-temperature gas condensate (Case 2), high-temperature oil (Case 3) and ultra-high-temperature high-pressure (HTHP) oil (Case 4). Trial calculations demonstrated that at equilibrium under reservoir conditions with S_w less than 0.01, the H_2O content of the reservoir hydrocarbons is within 2% of saturation values for all four cases. Therefore, in all our calculations reservoir hydrocarbon compositions were obtained by (a) recombining separator gas and oil analyses (recombined analyses are shown in Appendix 1) and (b) 'saturating' these with H_2O (Table 3). The amount (by weight percent) of H_2O in the reservoir hydrocarbons is most significant in Cases 2 and 4 (Table 2). The reservoir water compositions were obtained by equilibrating separator water analyses (see Appendix

1) with the H_2O-saturated hydrocarbon phases at reservoir conditions (Table 4). As the recombined hydrocarbon analyses and separator water analyses were identical for Cases 1 and 2 and for Cases 3 and 4 respectively (see Appendix 1), the reservoir hydrocarbon and water compositions for Cases 1 and 2 were similar, as were those for Cases 3 and 4. In all calculations it was assumed that mass transfer occurred under equilibrium conditions (ie 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 content of the samples relative to the Cl content of the reservoir water.

To assess the effects of H_2O mass transfer on surface samples, various hydrocarbon-reservoir water mixtures were flashed from reservoir conditions to either elevated P-T conditions typical of main separators or to atmospheric conditions (see Table 2; atmospheric conditions are 1 bar and 15°C in this paper). These were closed-system calculations with hydrocarbon-water volume ratios, HWR at reservoir conditions, between 3.3 and 1000. Calculations showed that negligible H_2O mass transfer occurs when water samples undergo secondary flashing to atmospheric conditions after separation from the hydrocarbon phase.

The various types of downhole sampling conditions were evaluated by simulating the closed-system cooling of a hydrocarbon-water mixture (HWR = 25) from reservoir temperatures to 15°C at reservoir pressures. At the separator temperature (Table 2) and at 15°C in each case, the effect of closed-system pressure reduction from reservoir pressure to 1 bar was also simulated.

During retrieval of core from the well, and during storage, fluid pressure and temperature decline leading to fluid expansion and loss of fluids prior to extraction of the water phase. This open-system process was simulated by linearly decreasing the pressure and temperature from reservoir to atmospheric conditions for a hydrocarbon-water mixture (HWR = 10). 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 either excess oil and water (in 10:1 volume ratio; where no gas phase was present) or excess gas (where a gas phase was present) were removed from the system.

RESULTS

Surface samples

When the hydrocarbon-water mixtures are flashed at separator and atmospheric conditions, in Cases 1 and 2 oil condenses out of the reservoir gas phase and in Cases 3 and 4 gas is released from the reservoir oil phase. In all cases the water-cut increases and the gas-water ratio (GWR) decreases with decreasing HWR (Figures 2 and 3). GWR increases from Case 1 > Case 2 > Case 3 > Case 4. GWR's are significantly higher under atmospheric conditions compared with separator conditions (Figure 4).

At separator conditions, although there is some transfer of H_2O between hydrocarbon phases, the majority of H_2O transfer is from the reservoir hydrocarbon phase into the water phase causing dilution of reservoir water (eg Figures 5 and 6). Dilution is most significant at low water-cuts (high GWR and HWR) where the proportion of condensing water to reservoir water is highest. Most dilution occurs in Cases 2 and 4 where the reservoir hydrocarbon phases contain most H_2O. For Case 2, the 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, H_2O is transferred from the water phase into the hydrocarbon gas phase in Cases 1 and 2 causing concentration of water sample Cl (eg Figure 5). For Case 2, H_2O transfer is minor. Most concentration is seen in Case 1 where the sample analysis will overestimate the reservoir water composition by 90% and 30% with water-cuts of approximately 3% and 7% respectively. In Cases 3 and 4 H_2O is transferred from the hydrocarbon phase into the water phase causing dilution of water sample Cl (Figure 6).

For the above calculations, as water-cut increases, the effects of dilution and concentration on water sample Cl decrease. In each calculation, at some water-cut the water sample Cl analysis becomes insignificantly different from the reservoir water composition (ie they will be within ±4% of each other being typical analytical uncertainty; see Table 5). At lower water-cuts than those in Table 5, the sample analysis will be in error and at higher water-cuts the sample analysis will be representative of the reservoir water composition. These water-cuts can be significant (>10%) for samples collected under separator conditions in Cases 2 and 4 and under atmospheric conditions in Cases 1 and 4.

Downhole samples

During cooling, the hydrocarbon phase changes from gas to oil in Cases 1 and 2 and remains as oil in Cases 3 and 4. The effects on Cl were similar in all cases (eg Figure 7). Transfer of H_2O from the hydrocarbon to the water phase caused a reduction in Cl content of the water the extent of dilution increasing in the order Case 1 < Case 3 < Case 2 < Case 4. For Case 4, Cl is ~10% less than the reservoir water sample.

At separator and atmospheric temperatures and reservoir pressures, the hydrocarbon phase is oil in all cases. As pressure is reduced, gas is released from the oil causing an increase in GWR and GOR and an initial decrease in water-cut. H_2O is transferred from the water phase to the hydrocarbon gas phase. Most transfer occurs at lower pressures resulting in a decrease in water-cut and increase in Cl content under these conditions. At atmospheric temperature, only in Case 1 does the increase in Cl exceed losses associated with condensation at that temperature (net increase of 6.4% above reservoir water Cl content). At separator temperatures, in all cases significant net increases in Cl occur. The highest net increases occur where the separator temperatures are highest and condensation effects lowest (Case 3; 790%; Figure 7). The lowest net increases occurred with Case 2 (173%). At each temperature, pressures need to fall to relatively low values before the large increases in Cl occur (eg less than ~10 bar at 52^{o}C, Case 2). These 'threshold' pressures are higher at higher temperatures. As demonstrated by the flash calculations, the above changes in Cl content will be exaggerated or minimised for samples with HWR higher than or lower than 25 respectively.

Core samples

In all cases, 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. Only in Case 4 were water and oil expelled (<2% by volume). In Cases 1 and 2, oil initially condenses out of the reservoir gas phase causing the GOR, GWR and water-cut to decrease but this situation is reversed as pressure and temperature fall to atmospheric conditions. In Cases 3 and 4, gas is released from the reservoir oil phase as pressure and temperature are reduced causing GOR, GWR and water-cut to increase. All the cases produce similar effects on water phase Cl content (eg Figure 8). Transfer of H_2O into the water phase from the hydrocarbon phase dominates H_2O mass transfer giving dilution effects of a similar order to those seen in the downhole sample cooling simulations. Only as the pressure declines the last few bars to atmospheric are any effects of H_2O transfer in the opposite direction observed and these are minor compared with concentration effects observed during flashing to atmospheric under closed-system conditions (see Figure 8). Again, these changes in Cl content will be exaggerated or minimised for samples with HWR lower than or higher than 10 respectively.

DISCUSSION

Factors determining changes in sample Cl content

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. The key variables affecting sample Cl content are:

a) Pressure and temperature of the reservoir.
b) Hydrocarbon composition.
c) Pressure and temperature conditions at the point where water is separated from the hydrocarbons.
d) Salinity at reservoir conditions.
e) Hydrocarbon:water ratio (HWR).

Reservoir pressure and temperature determine the amount of H_2O dissolved in the reservoir hydrocarbons and available for transfer. As shown in Figure 1, the dominant factor under oilfield conditions determining H_2O solubility in hydrocarbons is temperature. Highest H_2O in hydrocarbons will occur in high temperature reservoirs. Increasing pressures will partially reduce these levels such that the highest dissolved H_2O is likely to occur in shallower, high temperature reservoirs (eg in areas of high heat flow).

The pressure and temperature at which the water phase is separated from the hydrocarbon phase(s) determines the amount of transfer between the phases between the reservoir and the separation point. During cooling, reduction in solubility of H_2O in the hydrocarbon phase causes condensation of H_2O into the water phase to be the dominant process. The larger the temperature reduction between the reservoir and separation point, the greater the condensation and dilution of Cl in the water phase. During pressure reduction, H_2O evaporates from the water phase into the gas phase. At atmospheric temperatures, this process only becomes important as pressures are reduced close to atmospheric pressures. At higher temperatures significant evaporation can occur with less pressure reduction.

H_2O is more soluble in lighter hydrocarbons than heavier hydrocarbons. Therefore, at given reservoir pressures and temperatures, lighter hydrocarbons hold more H_2O than heavier hydrocarbons. Also, during temperature and pressure reductions, more H_2O is condensed from and evaporated into lighter hydrocarbons where conditions allow (see above) compared with heavier hydrocarbons. As shown in Figure 1, this factor becomes more important at higher temperatures where differences in H_2O solubility are greatest.

Where H_2O mass transfer into and out of the water phase occurs, for a given amount of transfer the absolute change in Cl content of the water sample will be greatest where the Cl content at reservoir conditions is high and vice-versa. However, the percentage change in Cl content will not be dependent on the Cl content at reservoir conditions. The absolute and percentage change in Cl content will be dependent on the HWR. Highest absolute and percentage changes will occur at high ratios (eg high water-cut or high GWR) and vice-versa.

Sample quality

Surface samples. As discussed below, due to the interplay of these different variables it is not possible to quantitatively assess the quality of water samples derived from hydrocarbon-water mixtures without undertaking calculations of the type described in this paper. However, our calculations have shown under what conditions better or poorer quality samples might be obtained. For example, better quality wellhead and separator samples are likely to be collected where:

a) The samples have low HWR.
b) The reservoir contains heavier hydrocarbons.
c) The reservoir temperature is low.
d) Samples are collected at elevated temperature and moderate pressure.

Poorer quality samples significantly diluted by condensation or concentrated by evaporation are likely to be collected where:

i) The samples have high HWR.
ii) The reservoir contains lighter hydrocarbons.
iii) The reservoir temperature is high.
iv) Samples are collected at elevated temperature and low pressure (maximum evaporation potential).
v) Samples are collected at low temperature and moderate pressure (maximum condensation potential).

For these poorer quality samples, our calculations suggest that evaporation effects under the conditions identified in (iv) are much more significant than condensation effects under those conditions in (v), all other factors being equal.

Downhole samples. As neither pressure nor temperature decline with P-T compensated tools, water sample Cl analyses will be representative of the Cl content of water in the reservoir. If pressure compensated tools are allowed to 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 and HTHP oil reservoirs.

Fixed-volume samples 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 content 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.

Efforts are often made to heat and pressurise the samples back up to reservoir temperatures and pressures once at the surface, but 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, arguably in some circumstances (eg Case 2) more representative analyses will be obtained where the tools have been allowed to cool and de-pressurise to atmospheric conditions before sample transfer.

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. As pressures decline to atmospheric, negligible evaporation occurs because of the low volume of hydrocarbon gas remaining in contact with the water phase. Where water phase in the 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 or HTHP oil reservoirs. The same conclusions can be drawn where the core is to be used for ERSA. For RSA core samples, the analyses will be unaffected by dilution because only isotopic ratios ($^{87}Sr/^{86}Sr$) are of interest.

High hydrocarbon:water ratio samples

The poorer quality surface, downhole and core samples are those that have high HWR. For example, samples collected from low- rather than high-water-cut producing wells. Recently, a technique has been developed to extract very low levels of free water (down to 0.01 weight %) from oil samples for analysis (trace water-in-oil analysis; Rosenbaum and Coleman, 1998). Table 6 shows the water-cut that can be generated by condensation from 'dry' hydrocarbon samples (0% water-cut under reservoir conditions) flashed to separator or atmospheric conditions. The water-cut is largest for gas condensate samples collected under separator conditions and generally small for samples collected under atmospheric conditions. In all but two cases, the water-cut exceeds the lower limit of application of the technique. Coleman

(1999) recently reported analyses from trace water-in-oil samples for seven fields where the trace water-in-oil salinity was lower than the salinity of water in the underlying aquifer. Although there may be natural explanations for these results (eg Coleman, 1999), the above results suggest that the potential for condensation contamination should also be investigated.

Relevance of empirical sample quality guidelines

Several authors had attempted to provide empirical guidelines with respect to water sample quality as a result of H_2O mass transfer. Kharaka et al. (1977) noted that condensation was most likely to occur with wells producing GWR > 30,000 m^3/m^3. Morton and Land (1987) suggested condensation was most likely to occur with wells producing < 2.4 bbl water/day or GWR > 17800 m^3/m^3. Hitchon and Brulotte (1994) rejected all DST samples where HWR < 10% and all separator samples where separator water production was less than 1200 l/day. Our study has shown that it is very difficult to provide simple and clear guidelines to identify good or poor quality samples. For example, with Case 2, and flashing at atmospheric conditions, even with a GWR of 253,000 m^3/m^3 and 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, GWR is 622 m^3/m^3, water-cut is 4%, and the water sample Cl is 45% lower than at reservoir conditions. The differences between our results and the guidelines proposed by earlier workers may reflect constraints on some of the important variables in their cases. For example, their samples may have been obtained from fields with a restricted range of reservoir and separator temperatures and pressures. Where this is not the case, however, the relative importance of the variables discussed earlier will change with reservoir and sampling conditions. It is evident in these circumstances 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.

Implications for other analyses

Our calculations have only assessed the effects of H_2O mass transfer on Cl. Evidently these results can also be applied to other dissolved ionic constituents if H_2O mass transfer does not induce reactions in the water phase. For example, mineral deposition might occur prior to analysis if the sample is affected by evaporation. Some applications (eg water source identification) make use of ratios of dissolved ions. Mass transfer of H_2O should not affect these ratios directly but induced reactions in the sample would affect them.

Quality of H_2O mass transfer simulations

The validity of our results is dependent both on the accuracy of our simulations and on our assumption of equilibrium conditions. In MultiScale©, the water mass transfer is calculated by first obtaining the water fugacity above the water phase. Then water is transferred to the oil phase until water fugacity in each of the 3 phases; water, gas and oil is equal and equilibrium is established. The vapour pressure of pure water is fitted to data in the range 0-370°C taken from Lide (1999) using the equation:

$$P_{H_2O} = \exp\left(\frac{a_1}{T/^o K} + a_2 + a_3 \cdot \ln\left(T/^o K\right) + a_4 \cdot T/^o K \right)$$

where $a_1 = -7862.5$, $a_2 = 86.707$, $a_3 = -11.754$ $a_4 = 0.010672$. This gives the vapour pressure in atmospheres at 1 atm total pressure up to 100°C. At higher temperatures the total pressure equals the vapour pressure. It is corrected for pressure by the Poynting correction, which can be approximated by:

$$P_{H_2O} = P_{H_2O,1atm} \cdot \exp\left(V_{molar} \frac{P - P_{H_2O,1atm}}{R(T/^o K)} \right)$$

The partial molar volume of water does not change much with pressure and composition for most oil field waters, and is therefore approximated by the molar volume of water, V_{molar}, which is calculated from the density given by:

$$\rho = \frac{\left(\rho_0 + a_1 \cdot (T/^o C) + a_2 \cdot (T/^o C)^2 + a_3 \cdot (T/^o C)^3 + a_4 \cdot (T/^o C)^4 + a_5 \cdot (T/^o C)^5\right)}{1 + a_6 \cdot (T/^o C)}$$

The a_j parameters are given by Kaasa (1998; page 97) and ρ_o is the density of water in kg/m^3 at 0°C. This is the vapour pressure of pure water as function of pressure and temperature. In salt solutions, the water fugacity is given by:

$$f_{H_2O} = a_{H_2O} \cdot P_{H_2O}$$

The activity of water is calculated from the Pitzer model as the osmotic coefficient (Kaasa 1998; page 46 and Table 4.9). The equation involves all interactions between all species in the solution, ie. an error in the Pitzer coefficients will cause an error in the osmotic coefficient. However, in most formation waters and seawater, NaCl contributes to typically 80-95% of the salts. As long as the NaCl parameters are correct, the result will be accurate. Kaasa (1998; pages 259-266) gives the different Pitzer interaction parameters at least up to 200°C. Pitzer parameters, for the most important species (Na-Cl-Mg-Ca-K), are available to high temperatures. In our opinion therefore, the calculated fugacity of water used in the model is very accurate.

In general, classical cubic equations of state (eg Soave-Redlich-Kwong, SRK; Peng-Robinson) are not very accurate in calculating properties of polar components, such as water, in hydrocarbons. In MultiScale© to improve the calculations, water fugacity of the hydrocarbon phases is calculated using an SRK equation of state, Huron-Vidal non-classical mixing rules and temperature dependent interaction parameters (Pedersen et al., 2001). An example is shown in Figure 9. For the CH_4 – H_2O system at 50°C with varying pressures up to 200 bar. Very good agreement between measurements (Baard Kaasa, STATOIL, private communication) and MultiScale© calculations can be observed. Pedersen et al. (op. cited) presented calculated and experimental data at 35, 120 and 200°C and pressures of 700 and 1000 bar. In their calculations the SRK equation was also used to obtain the water fugacity above the water phase. The calculated water compositions in the hydrocarbon phases were accurate within ± 9% of the actual water content in the oil.

In summary, for our simulations we believe that the model for the water fugacity in the aqueous phase is very accurate, and the water fugacity in gas/oil probably has accuracy better than ±9%. Therefore, where equilibrium conditions exist, our simulation results should be representative of actual sample conditions.

We have assumed that equilibrium does exist during sampling and that kinetics of water transfer can be ignored in the different sampling environments. This may be the case in the reservoir where water and hydrocarbons are likely to have been in contact for perhaps many Ma, or in the separator where mixing is vigorous. It is less certain that equilibrium will have been achieved between water and hydrocarbons in sampling tools and core as temperature and pressure change. Laboratory studies are required to determine rates of H_2O mass transfer for these sampling conditions.

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. The effect of these processes on dissolved ions in the water phase of a hydrocarbon-water mixture is dependent on the reservoir pressure and temperature, the pressure and temperature at which the water phase is separated from the hydrocarbon, the hydrocarbon:water ratio (HWR) and the hydrocarbon composition. Dilution effects are likely to be most significant where (a) reservoir temperature is high, (b) separation occurs at low temperature and moderate pressures, (c) HWR is high and (d) the reservoir hydrocarbons are lighter. Concentration effects are likely to be most significant where (a) separation occurs at higher temperature and low pressures, (b) HWR is high and (c) the reservoir hydrocarbons are lighter.

Due to the interplay of the above variables it is difficult to provide simple but quantitative guidelines (eg using values of HWR, GWR, and water production rate) to determine to what extent a sample has been affected by H_2O mass transfer. PVT simulations, such as those undertaken in this study, are required if the effects of H_2O mass transfer on sample quality are to be quantified. However, in general terms, where HWR is low, dilution or concentration effects on surface, downhole and core sample will be negligible. As HWR increases, the possibility that H_2O mass transfer will affect the sample will increase and most types of sample are at risk. Techniques involving the separation of very low levels of water from oil for analysis (eg trace water-in-oil analyses) are likely to be particularly susceptible to the effects of H_2O mass transfer. Only pressure- and temperature-compensated downhole samples are sure to be of good quality at higher HWR, but only if the pure water phase can be removed from the tool at reservoir pressures and temperatures. Finally, there is a need to undertake laboratory studies to determine rates of H_2O mass transfer for different sampling conditions to determine whether the kinetics of this process may affect the conclusions drawn in this study.

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TABLES

Table 1 Uses of oilfield water analyses

Exploration

- Regional palaeohydrodynamics studies
- Proximity-to-pay assessments
- Seismic processing
- Understanding the distribution of detrimental species (eg H_2S, Ba, etc).

Appraisal/development

- Oil-in-place calculations
- Reservoir characterisation
    - Compartmentalisation studies
    - Reservoir quality studies
    - Identification of hydrocarbon-water contacts
- Development planning
    - Scale, corrosion, emulsion, H_2S treatment
    - Produced water injection
    - Produced water discharge
    - Drilling/completion fluid selection

Production

- Identification of the source of produced water
- Produced water allocation (eg waterflood breakthrough assessments)
- Understanding the production of detrimental species (eg H_2S, Ba, etc).
- Operational production monitoring (eg scale control, environmental regulations, etc)

Table 2 Hydrocarbon-water systems simulated

Parameter	Case 1	Case 2	Case 3	Case 4
Reservoir hydrocarbon type	Gas condensate	Gas condensate	Oil	Oil
Reservoir T	Medium-temperature (80°C)	High-temperature (125°C)	High-temperature (125°C)	Ultra-high temperature (185°C)
Reservoir P	300 bar	350 bar	350 bar	1000 bar
Separator P, T	65 bar; 52°C	65 bar; 52°C	82.1 bar; 73.4°C	82.1 bar; 73.4°C
Atmospheric P, T	1 bar, 15°C	1 bar, 15°C	1 bar; 15°C	1 bar; 15°C
Reservoir water Cl	11,766 mg/kg H_2O	11,766 mg/kg H_2O	21,652 mg/kg H_2O	21,652 mg/kg H_2O

Table 3 Compositions of reservoir hydrocarbons*

Component	Case 1 (mol %)	Case 2 (mol %)	Case 3 (mol %)	Case 4 (mol %)
H_2O	0.49	1.61	1.40	2.61
N2	0.74	0.73	0.22	0.21
CO_2	3.41	3.37	3.73	3.69
C1	73.0	72.2	53.5	52.9
C2	9.89	9.78	8.18	8.07
C3	4.82	4.77	5.26	5.19
iC_4	1.30	1.28	0.96	0.95
nC_4	0.73	0.72	2.37	2.34
iC_5	0.50	0.49	0.99	0.97
nC_5	0.38	0.37	1.20	1.18
C_6	0.36	0.35	1.62	1.60
C_7	0.37	0.37	2.47	2.44
C_8	0.38	0.37	2.63	2.59
C_9	1.21	1.20	1.70	1.68
C_{10+}	2.42	2.39	13.77	13.58
Total	100.00	100.00	100.00	100.00
	Wt %	**Wt %**	**Wt %**	**Wt %**
H_2O	0.32	1.06	0.4	0.75

* At reservoir conditions after H_2O saturation (HWR = 25)

Table 4 Compositions of reservoir waters*

Parameter	Cases 1 and 2	Cases 3 and 4
Na (mg/kg H_2O)	7061	12637
K (mg/kg H_2O)	163	142
Mg (mg/kg H_2O)	25.2	354
Ca (mg/kg H_2O)	474	768
Ba (mg/kg H_2O)	11.1	15.2
Sr (mg/kg H_2O)	0.3	25.3
Cl (mg/kg H_2O)	11766	21652
Total alkalinity (as HCO_3) (mg/kg H_2O)	325	657
Total organic acids (as CH_3COOH) (mg/kg H_2O)	0	17.2
CO_2 (mg/kg H_2O)	2917, 2806$^{\#}$	3766, 6450$^{\wedge}$
CH_4 (mg/kg H_2O)**	2133, 1818$^{\#}$	3766, 5275$^{\wedge}$

* At reservoir conditions in equilibrium with H_2O-saturated hydrocarbons (see Table 3; HWR = 25)

** Added to get sum of gas partial pressures equal to total pressure

$^{\#}$ Case 1, Case 2

$^{\wedge}$ Case 3, Case 4

Table 5 Minimum water-cut required for sample analyses (Cl) to be representative of reservoir water composition

Case/conditions	**Water-cut (%)**
Case 1; separator	6.8
Case 1; atmospheric	~40
Case 2; separator	32
Case 2; atmospheric	1
Case 3; separator	6
Case 3; atmospheric	0.6
Case 4; separator	13
Case 4; atmospheric	10.5

Table 6 Water-cut derived from 'dry' hydrocarbon

Case/conditions	**Water-cut (%)**
Case 1; separator	0.28
Case 1; atmospheric	0
Case 2; separator	1.88
Case 2; atmospheric	0
Case 3; separator	0.21
Case 3; atmospheric	0.03
Case 4; separator	0.54
Case 4; atmospheric	0.44

FIGURES

Fig. 1 Solubility of H_2O in gas condensate and oil (see Appendix 1 for compositions) between 85 and 185°C and at 1000 and 350 bar (calculated using MultiScale©).

Fig. 2 Variation of water-cut at the separator with hydrocarbon/water volume ratio under reservoir conditions.

Fig. 3 Variation of gas/water ratio at the separator with hydrocarbon/water volume ratio under reservoir conditions.

Fig. 4 Case 4. Variation of gas/water ratio at atmospheric (1 bar, 15°C) and separator (82.1 bar, 73.4°C) flash conditions with hydrocarbon/water volume ratio under reservoir conditions (1000 bar, 185°C).

Fig. 5 Case 1. Variation of water phase Cl content with water-cut at separator (65 bar, 52°C) and atmospheric (1 bar, 15°C) flash conditions.

Fig. 6 Case 4. Variation of water phase Cl content with water-cut at separator (82.1 bar, 73.4°C) and atmospheric (1 bar, 15°C) flash conditions.

Fig. 7 Case 3. Variation of water phase Cl content with changes in (a) temperature at reservoir pressure (350 bar; open triangles), (b) pressure at separator temperatures (73.4°C; open circles), and (c) pressure at 15°C (open squares). Reservoir water composition shown with dotted line. HWR = 25.

Fig. 8 Case 2. Variation of water phase Cl content in a core sample (HWR = 10) during pressure and temperature reduction from reservoir (350 bar, 125°C) to atmospheric conditions (1 bar, 15°C). Reservoir water flashed at separator (82.1 bar, 73.4°C) and atmospheric conditions (1 bar, 15°C) are shown for comparison.

Fig. 9 Measured mole fractions of CH_4 in H_2O and H_2O in CH_4 for the CH_4-H_2O system versus total pressure at 50°C compared with MultiScale© calculations. The calculation was performed with $CH_4(g)$ in equilibrium with $H_2O(l)$.

Fig 1

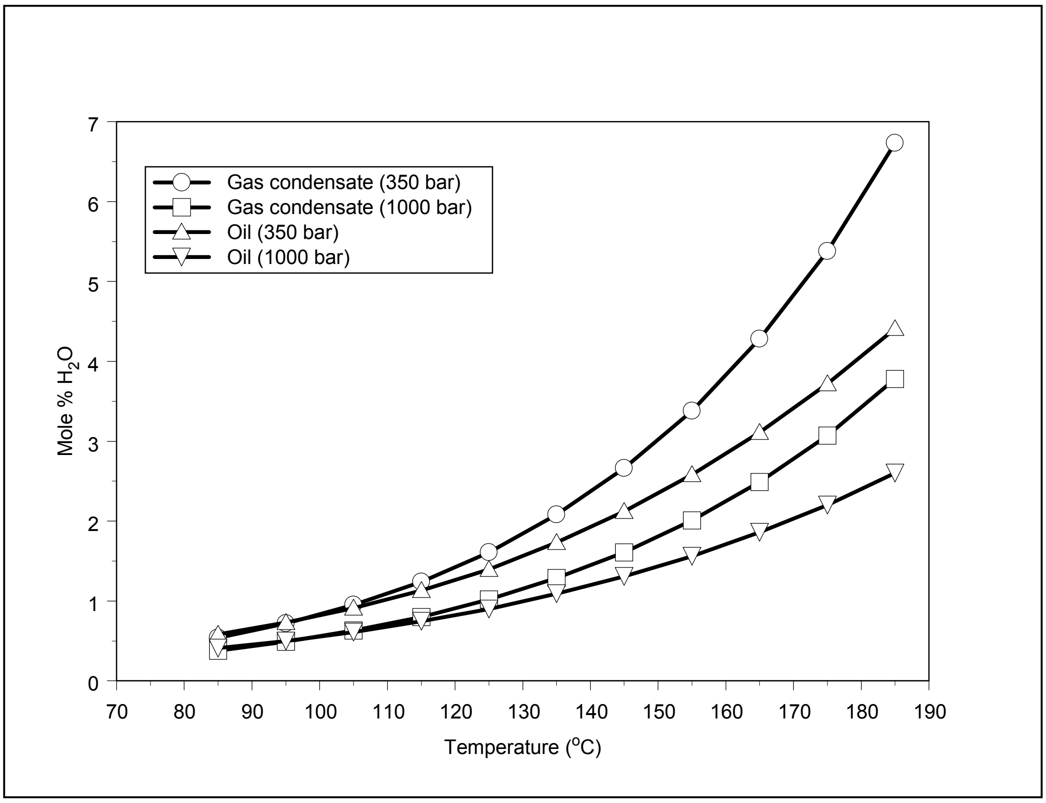

Gas condensate (350 bar)
Gas condensate (1000 bar)
Oil (350 bar)
Oil (1000 bar)
Mole % H_2O
0
1
2
3
4
5
6
7
70
80
90
100
110
120
130
140
150
160
170
180
190
Temperature (°C)

Fig 2

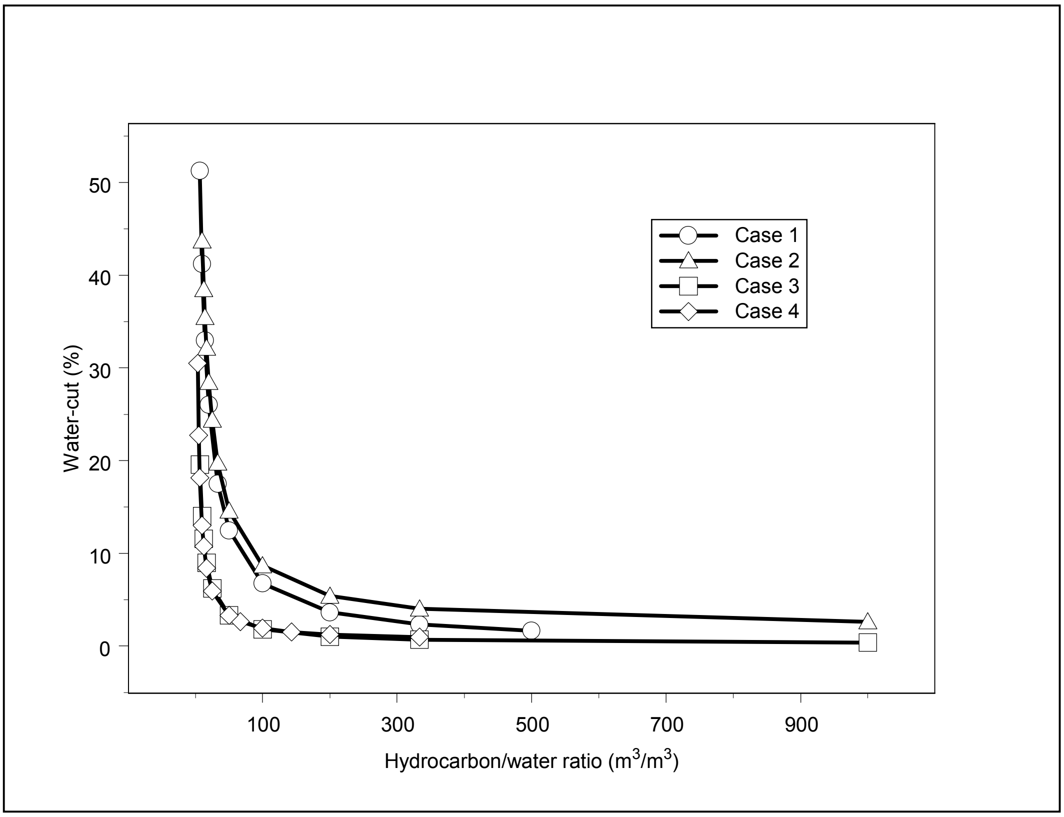

Case 1
Case 2
Case 3
Case 4
Water-cut (%)
0
10
20
30
40
50
100
300
500
700
900
Hydrocarbon/water ratio (m^3/m^3)

Fig 3

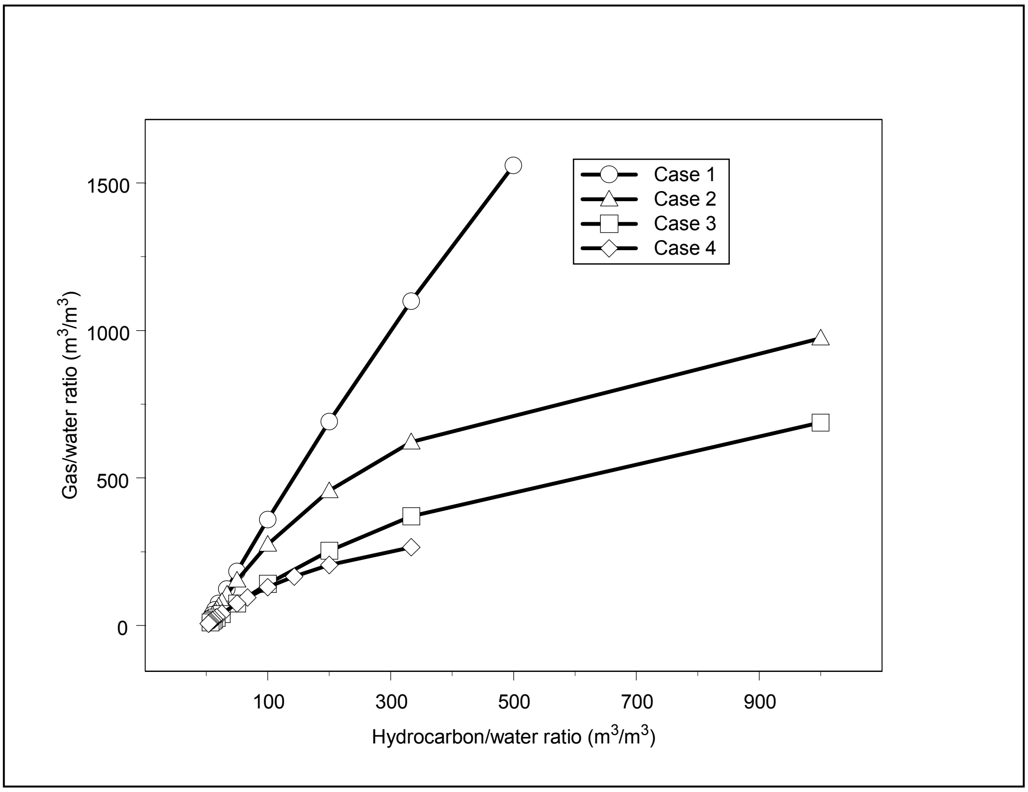

Case 1
Case 2
Case 3
Case 4
Gas/water ratio (m3/m3)
0
500
1000
1500
100
300
500
700
900
Hydrocarbon/water ratio (m3/m3)

Fig 4

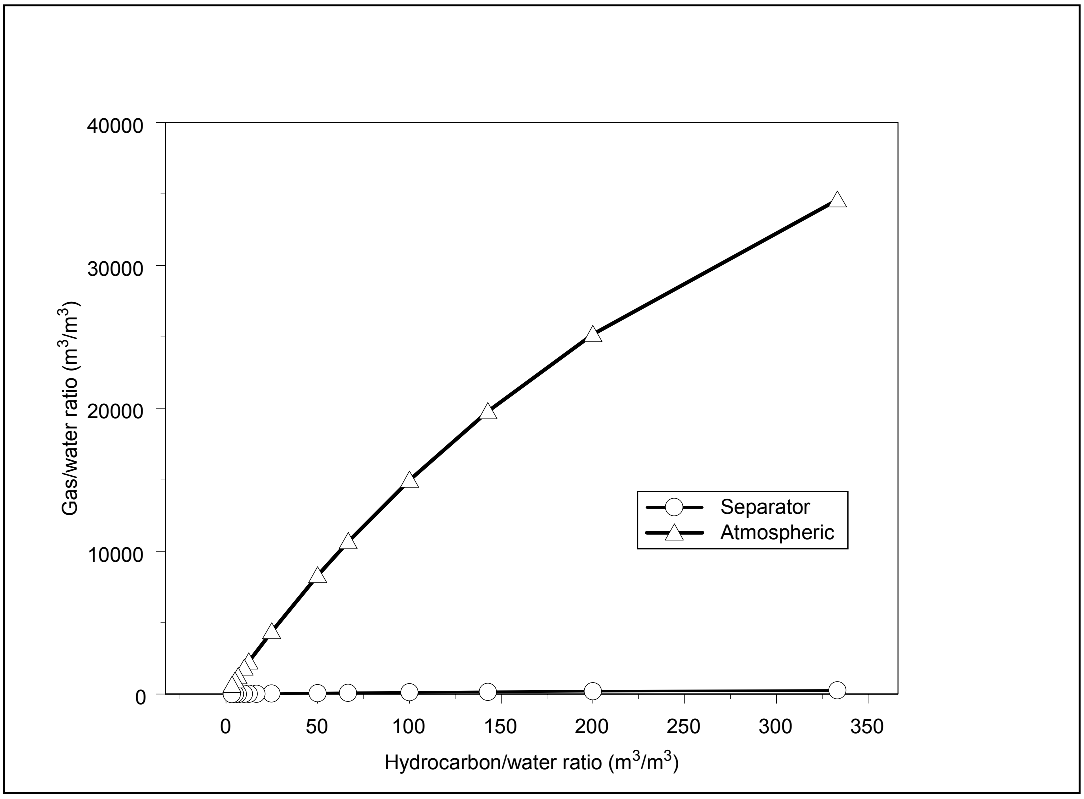

Separator
Atmospheric
Gas/water ratio (m3/m3)
0
10000
20000
30000
40000
0
50
100
150
200
250
300
350
Hydrocarbon/water ratio (m3/m3)

Fig 5

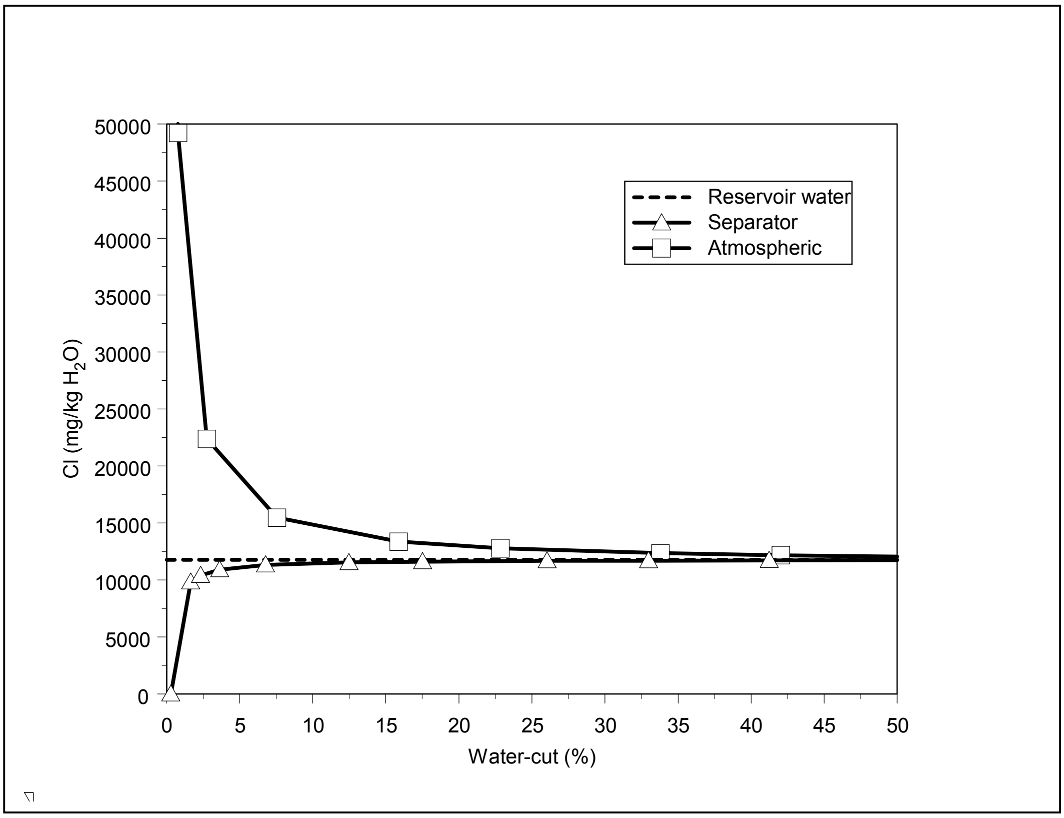

50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
Cl (mg/kg H2O)
0
5
10
15
20
25
30
35
40
45
50
Water-cut (%)
Reservoir water
Separator
Atmospheric

Fig 6

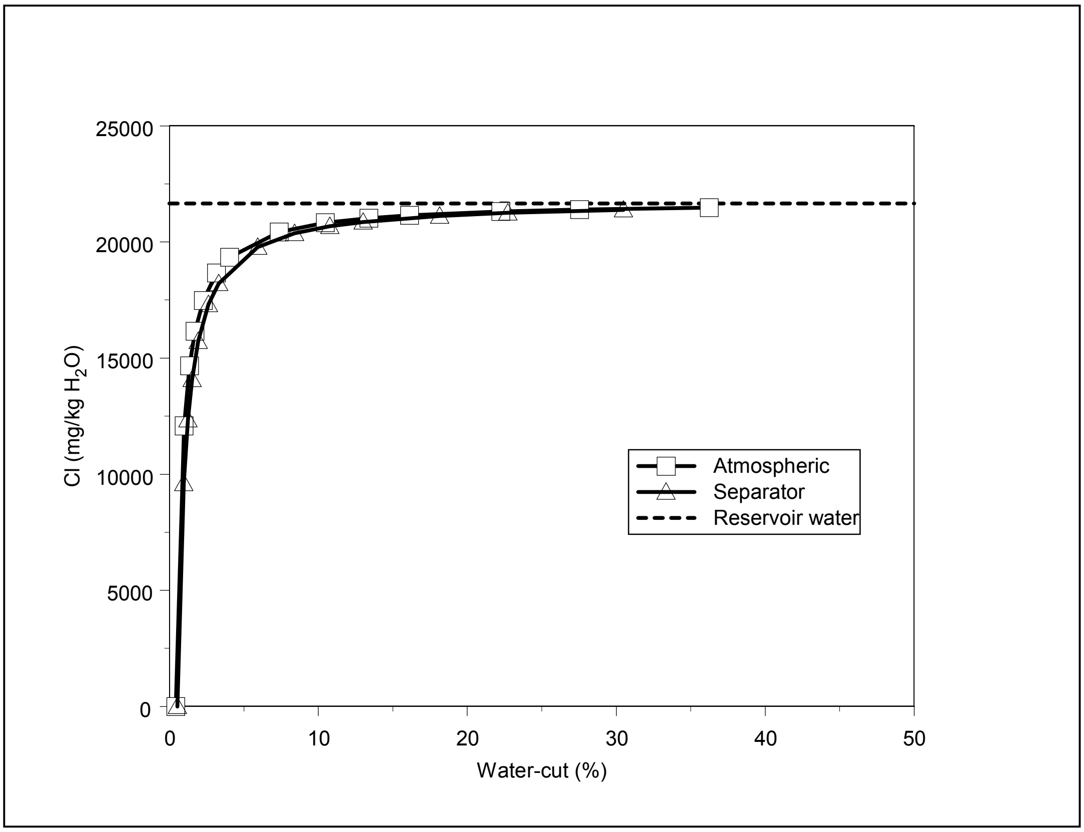

25000
20000
15000
10000
5000
0
Cl (mg/kg H2O)
0
10
20
30
40
50
Water-cut (%)
Atmospheric
Separator
Reservoir water

Fig 7

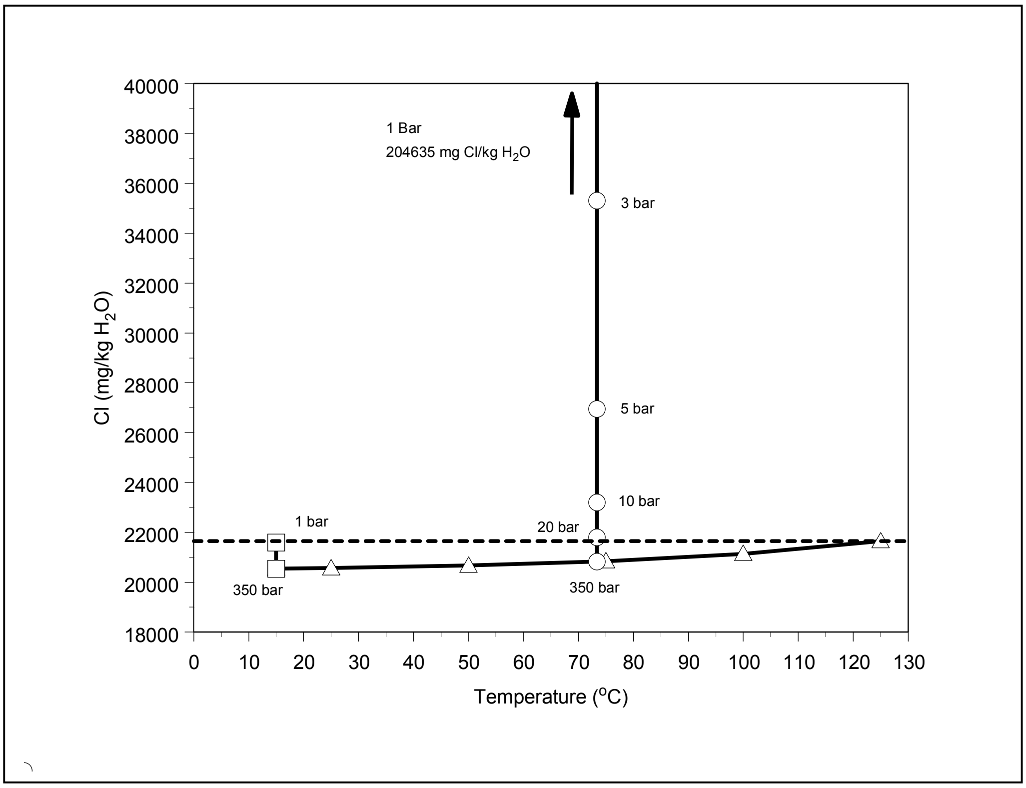

1 Bar
204635 mg Cl/kg H2O
3 bar
5 bar
10 bar
20 bar
1 bar
350 bar
350 bar
Cl (mg/kg H2O)
40000
38000
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
0
10
20
30
40
50
60
70
80
90
100
110
120
130
Temperature (°C)

Fig 8

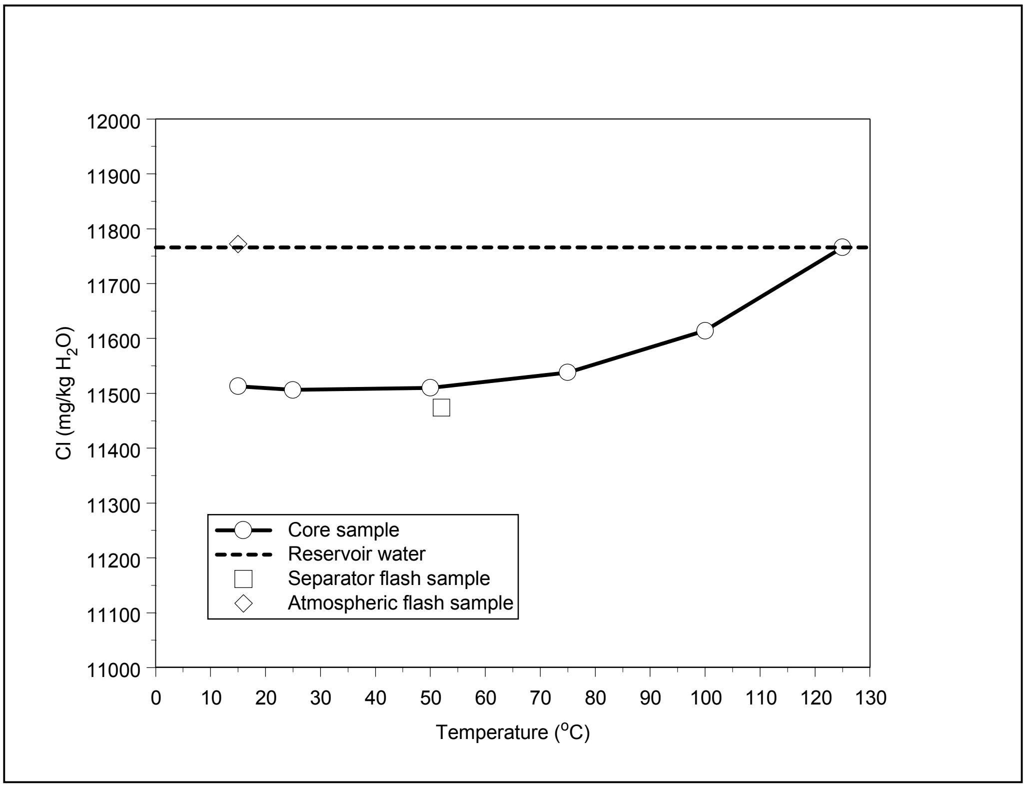
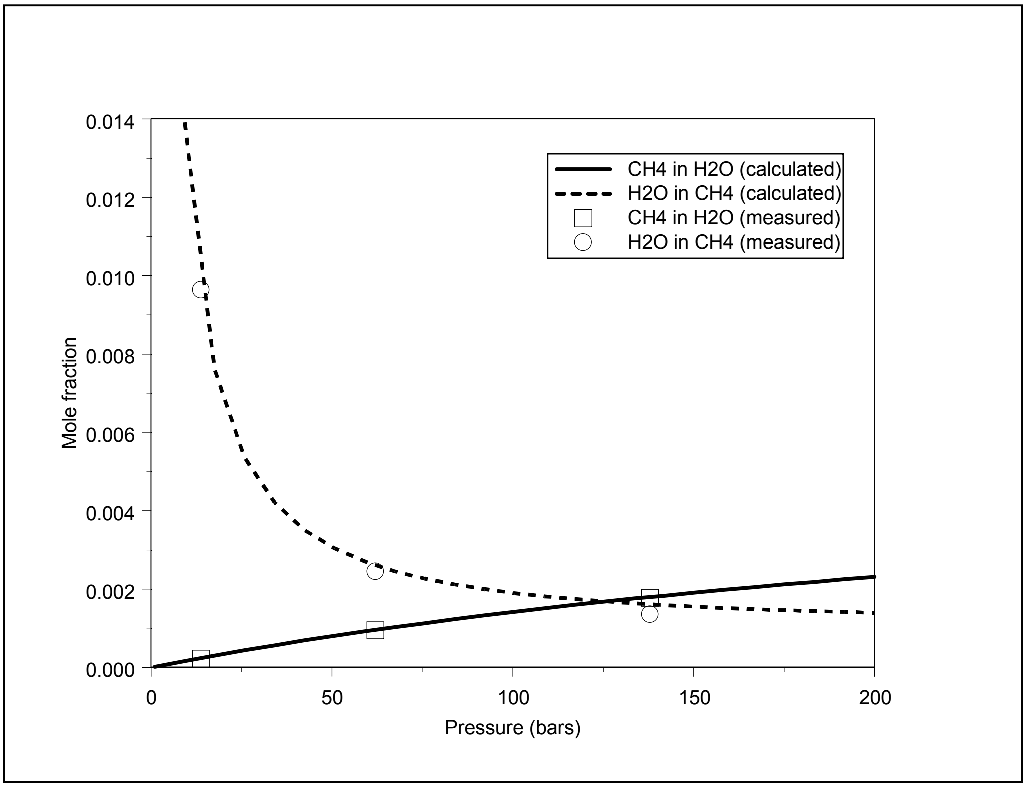

Cl (mg/kg H2O)
12000
11900
11800
11700
11600
11500
11400
11300
11200
11100
11000
Core sample
Reservoir water
Separator flash sample
Atmospheric flash sample
0
10
20
30
40
50
60
70
80
90
100
110
120
130
Temperature (°C)

Fig. 9


0.014
0.012
0.010
0.008
0.006
0.004
0.002
0.000
Mole fraction
0
50
100
150
200
Pressure (bars)
CH4 in H2O (calculated)
H2O in CH4 (calculated)
CH4 in H2O (measured)
H2O in CH4 (measured)

APPENDIX 1

Table 1.1 Recombined compositions of hydrocarbons*

Component	**Gas condensate (Cases 1 and 2)**	**Oil (Cases 3 and 4)**
N_2	0.74	0.22
CO_2	3.43	3.79
C_1	73.35	54.26
C_2	9.94	8.29
C_3	4.85	5.34
iC_4	1.30	0.98
nC_4	0.73	2.41
iC_5	0.50	1.00
nC_5	0.38	1.21
C_6	0.36	1.65
C_7	0.38	2.50
C_8	0.38	2.66
C_9	1.22	1.72
C_{10+}	2.45	13.96
Total	100.00	100.00

* From separator hydrocarbon liquid and gas analyses

Table 1.2 Separator water analyses

Parameter	Cases 1 and 2	Cases 3 and 4
Na (mg/l)	7000	12500
K (mg/l)	162	140
Mg (mg/l)	25	350
Ca (mg/l)	470	760
Ba (mg/l)	11	15
Sr (mg/l)	0.3	25
Cl (mg/l)	11664	21417
Total alkalinity (as HCO_3) (mg/l)	322	650
Total organic acids (as CH_3COOH) (mg/l)	0	17
Flashed gas* CO_2 (mol %)	3.43	3.79
Flashed gas* CH_4 (mol %)**	96.57	96.21

* At reservoir conditions

** Added to get sum of partial pressures equal to total pressure