Reactive transport modelling of mud filtrate invasion during drilling and application to mud contamination corrections on formation water analyses

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Abstract

When a well is drilled with water-based mud (WBM), it is not unusual for formation water samples collected from the well to be contaminated with mud filtrate that has invaded the formation during drilling. This can make the composition of these water samples unrepresentative of formation water in the reservoir. Under these circumstances, a common approach is to apply a tracer to the drilling mud during drilling, analyse mud filtrate and the formation water samples, and then attempt to correct the formation water analyses for mud filtrate contamination. Corrections are normally made assuming simple mixing between mud filtrate and formation water. But, reactions can occur between the formation, mud filtrate and formation water during invasion and there is a risk that these might cause the corrections to be erroneous.

A series of mud-contaminated formation water samples have been obtained from wells drilled with potassium chloride (KCl) WBM (with sodium thiocyanate tracer, NaSCN) on Field X. Given the location of the field, these water samples were unusual in that they contained significant concentrations of sulphate and low concentrations of barium and it was suspected that this might be an artefact of mud contamination. To confirm whether simple mixing-type corrections could be applied to the water analyses, a 1-D reactive transport model was used to simulate mud filtrate invasion and its mixing with formation water. This allowed the resulting reactions occurring in the reservoir and their effect on the water samples to be evaluated.

The model results showed that the most significant reaction expected in the reservoir was potassium↔sodium ion exchange between the mud filtrate, mud filtrate/formation water mixtures and clays/micas in the reservoir. Minor calcite and barite precipitation/dissolution were also predicted. The contaminated formation water compositions predicted by the model are consistent with those of the water samples supporting the predictive capability of the model for this field. Based on the model results, it was established that a simple mixing-type correction model could indeed be used to estimate the formation water composition from mud contaminated samples. These mud contamination corrections were subsequently applied.

The model results also showed that if circumstances had been different (i.e. higher clay content of reservoir rock, different mud contamination levels), a simple mixing-type correction model would not have been appropriate for some constituents.

This work has shown how 1-D reactive transport modelling can both reduce and highlight uncertainties in estimated formation water compositions when mud contamination has occurred. In each case, the risks associated with the use of mud-contamination corrected formation water compositions (e.g. for injection water selection, scale management planning, etc) are reduced.

Introduction

A series of reservoir 'formation water' samples have been obtained from appraisal wells for Field X in the North Sea. These were obtained because reliable formation water compositions were required for field development planning. The wells were drilled with KCl WBM containing a tracer (NaSCN or ³H) and the presence of tracer in the samples indicated they were contaminated with varying amounts of mud filtrate. Of particular concern for samples obtained from the earlier appraisal wells were the very high SO₄ concentrations (and hence low concentrations of Ba) in the samples because in this region of the North Sea, Baenriched (SO₄-depleted) formation waters are common. So, was this SO₄-enrichment and Badepletion an artefact of contamination or was it a characteristic of local formation water? An answer was required to this question to allow confident development of scale mitigation strategies, including selection of the injection water for the field.

It was recognised that corrections for mud filtrate contamination would be needed to estimate not only the Ba and SO_4 content of the formation water, but its entire composition. In this respect, it is common industry practice to use Equations 1 and 2 to correct formation water sample analyses for mud filtrate contamination. This requires (a) the use of a stable/inert tracer in the drilling mud whose concentration in the formation water is known (i.e. ideally, the tracer is selected so that the concentration is negligible in the formation water) and (b) full analyses of the mud filtrate and formation water samples.

$$X_{sample} = \frac{T_{sample} - T_{FW}}{T_{MF} - T_{FW}}$$
Eq. 1
$$Z_{FW} = \frac{Z_{sample} - (X \cdot Z_{MF})}{(1-X)}$$
Eq. 2

Where:

Sample = Formation water sample.

FW = Formation water.

MF = Mud filtrate

X = Mud filtrate fraction.

T = Tracer concentration (mg/L, Bq/mL).

Z = Concentration of ion of interest (mg/L).

These equations assume that a mud filtrate contaminated formation water sample is a simple mixture of formation water and mud filtrate. The correction effectively separates these components and is a simple mixing-type correction model (SMCM). But, during mud filtrate invasion reactions can occur between mud filtrate and formation minerals, mud filtrate and formation water, and mixtures of these fluids and formation minerals. Where these reactions significantly affect the composition of mud filtrate or mixtures of mud filtrate and formation water, the above correction method is inappropriate and formation water compositions estimated with it may be erroneous.

To determine whether such reactions were likely to have significantly affected the formation water sample compositions from Field X, a 1-D reactive transport model was developed. This simulates mud filtrate invasion and the subsequent extraction of water samples from the formation. It has been used to predict the effects of contamination and reactions on formation water sample compositions of the type obtained from Field X.

This paper describes the 1-D reactive transport model, the simulations undertaken with it and the predictions obtained. By comparing the predictions with actual formation water sample compositions from one well (well A), it has been possible to demonstrate that SMCM methods, such as that outlined above, can be applied to Field X formation water sample analyses to obtain estimates of the actual formation water composition. It has also highlighted those conditions where such methods may be unreliable. Advice is given regarding how mud-contaminated formation water sample analyses (from wells drilled with KCl mud) can be evaluated to determine how best to estimate formation water compositions from them.

Well A samples: sampling and analysis

The reservoir section of Field X is sandstone. Well A was one of the earliest appraisal wells and was drilled using KCl water-based polymer mud with barite weighting agent and NaSCN tracer. On completion of drilling, three formation water samples were collected via MDT (modular formation dynamics tester) in MPSR (multisample production sample receptacle) bottles from a target zone in the reservoir below the oil-water contact. The objective was to collect samples with low mud contamination and using minimal pressure drawdown during pump-out and sampling. To achieve this, a large diameter probe, in-situ fluid analyser, and QuicksilverTM probe were used together with the low shock sampling technique. Sample 1 was collected after 314L had been pumped out and samples 2 and 3 were collected after an additional 89L had been removed. The initial sampling zone pressure and temperature were 196.7bar and 73.7°C. The maximum drawdown pressure throughout pumping and sampling was 1.85 bar. The samples were overpressured on collection (>580 bar) and then transported to an onshore laboratory where they were decanted for analysis.

Mud samples were also collected during drilling of the reservoir section and one, collected immediately after the sampled zone was drilled, was also sent to the onshore laboratory for analysis after filtration.

Both formation water and mud filtrate samples were analysed using the same standard methods. Density was measured by digital density meter (oscillating U-tube), pH by potentiometry, conductivity by electrometry, cations, anions and organic acids by ion chromatography, and SCN by spectrophotometry (after complexing with ferric ions). The sample compositions are shown in Table 1.

Sample Type/No.	Mud	Sample 1	Sample 2	Sample 3
	filtrate	-	-	-
Na (mg/L)	7497	14800	15385	15678
K (mg/L)	35920	2631	572	630
Mg (mg/L)	20	542	629	583
Ca (mg/L)	466	2671	2872	2905
Ba (mg/L)	<1	2	3	4
Sr (mg/L)	10	132	144	144
Cl (mg/L)	43144	31380	31600	32140
Br (mg/L)	323	152	144	142
SO ₄ (mg/L), Dionex	344	322	339	350
SCN (mg/L)	505	34	5	5
Formate (mg/L)	1260	72	13	19
Acetate (mg/L)	3241	220	77	157
Cation total (meq/L)	1269.78	892.11	882.35	894.43
Anion total (meq/L)	1319.87	899.72	901.94	918.87
Ion balance (%)	-1.93	-0.42	-1.10	-1.35
Calculated TDS (mg/L)	92730.2	52961	51786	52760
Mud filtrate contamination (%)		6.7	1.0	1.0

 TABLE 1
 WELL A: COMPOSITIONS OF MUD FILTRATE AND FORMATION WATER SAMPLES.

Quality of data

The ion balances for all the samples are very good ($\pm 1.93\%$) indicating that no major ionic constituents are present that have not been analysed and the major ion analyses are likely to be accurate (i.e. Cl, Na, Ca and K).

Between the time when the sampled zone was drilled and the time when the samples were collected, rig drilling fluid analyses show that the mud composition (at least for KCl and Cl) was varying by no more than typical sampling/analytical precision suggesting that the mud sample composition is likely to be representative of mud invading the sampled zone.

SCN is believed to be a stable and inert tracer under the conditions of use because it has similar properties to the halides (i.e. low adsorption) and although it can be decomposed by bacteria this is considered unlikely to be significant given the short period between drilling and sampling the tested zone (5 days) (Hutchins and Dovan, 1991; Smith and Brigham, 1965). An evaluation of SCN tracer data for all formation water samples collected from Field

X did not provide any evidence to the contrary. SCN is present in the three formation water samples indicating contamination with mud filtrate. Sample 1 is most contaminated (mud filtrate fraction = 0.067) based on analysed tracer content of the sample and mud filtrate samples) and Samples 2 and 3 least contaminated (mud filtrate fraction = 0.01) as expected given the order of collection.

Between the time of sampling and analysis, the samples were cooled and de-pressurised. To understand how this may have affected the sample compositions, the in-situ compositions of Samples 2 and 3 were estimated using MultiScaleTM 7.1 (Petrotech, 2006) assuming equilibrium with reservoir oil and calcite (present in the reservoir) under reservoir pressure and temperature conditions. This indicated that the samples were oversaturated with respect to barite (SR_{BaSO4} = 1.96 and 2.66 for Samples 2 and 3 respectively). It is considered unlikely that mud filtrate contamination is responsible for this oversaturation because the mud filtrate and MDT samples contain similar SO₄ (see Table 1). A more likely explanation is that the Ba analyses are in error (i.e. if the water samples are saturated with respect to barite in the reservoir, they are too high by ~1.5-2.5 mg/L). Such analytical errors are feasible given the low Ba concentrations (3-4 mg/L) and elevated water salinity.

MultiScaleTM was used to simulate the effects of decreasing the temperature and pressure from those of the reservoir to laboratory conditions (1 bar, 20°C, equilibrium with air) for Sample 2. These calculations showed that at most, 1.24 mg/L Ba, 0.86 mg/L SO₄ and 17.7 mg/L Ca could have been lost from the sample as precipitated BaSO₄ and CaCO₃ before analysis. Therefore, it would be expected that measured Ba would be between 0.31 and 1.55 mg/L depending on whether Ba was lost from the sample through BaSO₄ precipitation after sampling or not. This emphasises that the actual Ba content of the samples is likely to be lower than measured, as is the Ba content of the formation water. Also, precipitation of BaSO₄ and CaCO₃ would not significantly affect the concentration of Ca and SO₄ of the MDT samples or estimates of the formation water composition (the above losses are well within sampling/analytical uncertainty).

In summary, the formation water sample analyses appear to be reasonably representative of the water produced from the reservoir, at least with respect to cation and anion concentrations.

Reactive transport model

The 1-D reactive transport model was set up using X1t which is part of the Geochemist's Workbench (GWB) software suite (Version 9.0.1) (Bethke and Yeakel, 2011). This simulated (see Figure 1):

- Invasion of drilling mud filtrate into the near-wellbore formation and mixing of it and formation water adjacent to well A in the reservoir.
- Reactions occurring between these fluids, and between these fluids and the formation.
- Subsequent extraction of mud filtrate, mixtures of mud filtrate and formation water (decreasing mud filtrate fraction over time) and finally formation water.



Figure 1 Schematic diagram showing mud filtrate contamination of formation water and collection of MDT samples (mud filtrate = blue, formation water = red).

The model was supported by an in-house thermodynamic database that adopts the Pitzer approach to calculate ion activity coefficients. This was developed to provide similar results to those obtained by MultiScaleTM 7.1 for calcite and sulphate mineral saturation ratios and precipitated scale masses under the reservoir temperature and pressure conditions for well A when mud filtrate and formation water are mixed.

Table 2 summarises the model conditions used in this study. It was not possible to accurately set up a model to portray the mud filtrate invasion and sampling environment because (a) the model is only one dimensional, (b) the sampled zone has not been fully characterised with respect to porosity and permeability variations and (c) fluid extraction details for the guard and sampling lines were not available. Therefore, the model was initially set up to broadly mirror reservoir conditions close to the well where mud filtration invasion would have occurred. Trial calculations were then undertaken to determine how model conditions may affect the results and to help select final model parameters.

The simulations were undertaken with an arbitrary domain size and node (block) size of 20m and 5cm respectively. The domain size is considered to be that over which mud filtrate contamination might occur. The node size was selected so as to minimise numerical dispersion effects (a minimum of 50 nodes was required). Over such distances dispersivity is estimated to be ~0.4m (Mahadevan et al., 2003). Numerical dispersion is estimated to be 0.05m (Lantz, 1970) so to give a total dispersivity of 0.4m, dispersivity was entered as 0.375m. The maximum length (in terms of reaction progress, which varies from zero to one over the course of the simulation) of the reaction step was set to 0.0001, again to avoid the effects of numerical dispersion.

Parameter	Value
Temperature, Pressure	73.7°C, 196.7 bar
Domain size	20m x 1cm x 1cm
Dispersivity	0.4m
Node size	5cm x 1cm x 1cm
No. nodes along path	400
Maximum length of reaction step	0.0001
Porosity	28%
Permeability	10D
Invasion and extraction flow rate	+0.24 cm ³ /cm ² /s and -0.24 cm ³ /cm ² /s
Invasion/extraction duration	10 minutes invasion, 110 minutes extraction
Reservoir rock	Calcite (1% vol), Clays (ion exchange surfaces)
CEC of ion exchange surfaces	1×10^{-7} to 1.41 x 10^{-4} eq/g rock
Ion exchange selectivity coefficients	Average values from Appelo and Postma (1999)
Reaction rates	Instantaneous equilibrium
Formation water composition	See Table 3
Mud filtrate composition	See Table 3
Reservoir reactions	Multi-component ion exchange (Na, K, Mg, Ca, Sr, Ba)
	Dissolution/precipitation of sulphate and carbonate minerals

 Table 2 1-D reactive transport model conditions.

The sandstone permeability and fractional porosity adopted (10D and 0.28 respectively) are estimates for the reservoir. Mud filtrate invasion and extraction flow rates and times were set to ensure that mud filtrate contamination did not extend to the domain boundary and that the mud filtrate was fully extracted. This ensured that the composition of the extracted water at the well varied across a full range of mud filtrate fractions during the simulation (i.e. from 0 to 1).

A number of studies of reservoir reactions have been undertaken to date on producing fields into which injection is occurring (Tjomsland et al., 2012; McCartney et al., 2010a; McCartney et al., 2010b; Østvold et al., 2010; McCartney et al., 2007). These indicate that on the timescale of production, reactions involving dissolution/precipitation of silicates and aluminosilicates (quartz, feldspars, clays, etc; 'slow' reactions) do not significantly affect produced water compositions. The latter are, however, affected by the faster reactions: dissolution/precipitation of carbonates and sulphates, and ion exchange reactions. These studies can be used as analogues for mud filtrate invasion processes in that over the shorter timescales of this process, only the faster reactions are likely to occur and so these reactions were included in the model. The ion exchange reactions were multi-component reactions involving Na, K, Ca, Mg, Ba, and Sr.

The cation exchange capacity (CEC) was varied between 1×10^{-7} eq/g (low clay) and 1.41 x 10^{-4} eq/g (very high clay) based on XRD analyses for the reservoir and typical CEC for clay and mica minerals (Appelo and Postma, 1999). Calcite cement is also present in the reservoir and so was included in the rock phase of the model (1% by volume). Although dolomite is present in the reservoir (~1.5%) trial calculations showed that it did not influence the extracted water compositions so it was not included in the final model.

It was assumed that the reactions occurring in the reservoir will be instantaneous and so kinetic effects were ignored. This is reasonable given (a) the time between drilling the sampled zone and sample collection (5 days), (b) the importance of ion exchange reactions which proceed to equilibrium in minutes to hours.

The mud filtrate composition was based on that given in Table 1 but equilibrated with barite (Ba adjusted to 2.1 mg/L) and calcite (total alkalinity adjusted to 12.1 mg/L) at reservoir temperature and pressure (Table 3). The organic components (formate and acetate) were ignored to simplify the calculations (these did not participate in the reactions) and SCN was not included because it is not present in the Pitzer data set used by X1t. A minor amount of Fe was added (~1 mg/L) as a non-reactive tracer from which the SCN content of mud filtrate-formation water mixtures was later calculated.

The formation water composition (Table 3) was estimated by applying Equations 1 and 2 to the composition of Sample 2. Ba, pH and alkalinity were then adjusted assuming equilibrium with barite, calcite and petroleum CO_2 and CH_4 at reservoir pressure and temperature. Again, the organic components were ignored and SCN was not included but minor Fe was added as a tracer.

Initial calculations demonstrated that the most important reactions affecting the extracted water compositions were ion exchange reactions and two of the more important parameters that might affect the impact of these reactions on the compositions are (a) invasion time (and hence the distance of penetration of the mud filtrate into the formation) and (b) dispersivity. But further calculations showed that predicted extracted water compositions were relatively insensitive to these two parameters. So despite the generality of the model, the results obtained from the model should provide a reasonable indication of how extracted water compositions would be expected to vary with mud filtrate fraction under different CEC conditions.

Simulations undertaken

To assess the impact of reactions (particularly the ion exchange reactions) on the extracted water composition as the mud filtrate fraction declines from 1 to 0, five simulations were undertaken. Simulation 1 modelled the effects of simple mixing of mud filtrate and

formation water (no reaction). In simulations 2 to 5 the CEC was increased from 1 x 10^{-7} eq/g (low clay value) to 2.46 x 10^{-6} eq/g (average clay) to 1.25 x 10^{-5} eq/g (high clay) and to 1.41 x 10^{-4} eq/g (very high clay value) respectively.

Constituent	Formation water	Mud Filtrate		
	mg/L	mg/L		
Ba ²⁺	1.54	2.10		
Br	142	323		
CH _{4(aq)}	576	18.4		
CO _{2(aq)}	42.69	0.03		
CO_{3}^{2}	0.16	0.59		
Total Ca ²⁺	2889	471		
CaCO ₃	1.07	1.06		
Cl	31410	43144		
Fe ²⁺	5.48E-05	1.08		
H^+	9.25E-04	8.79E-06		
HCO ₃ ⁻	114	6.32		
HSO ₄ ⁻	9.31E-03	1.08E-04		
K ⁺	217	35850		
Mg^{2+}	633	21.2		
Na ⁺	16589	6845		
OH	0.01	0.93		
Total SO ₄ ²⁻	338	344		
Sr ²⁺	145	10.3		
Total alkalinity	116	12.1		

 Table 3 Formation water and mud filtrate compositions used in the simulations.

Simulation results

Figure 2 shows the SCN results for the domain from Simulation 1, from which the extent of invasion of the formation by mud filtrate over time and its subsequent extraction/sampling can be tracked. It can be seen that under the model conditions, the maximum extent of mud filtrate saturated rock is ~0.85m but due to dispersion the extent of invasion of the mud filtrate is much further (~12.6m). Figure 3 shows the SCN results for the same simulation at node 0 (immediately adjacent to the well). It can be seen that during extraction, initially pure mud filtrate is produced (for 45 secs), but, again due to dispersion, mud filtrate/formation water mixtures with declining mud filtrate fraction are produced for much longer (for 41 minutes). Finally pure formation water is produced although as shown below, ion exchange reactions may affect the composition of the formation water for some time after apparently (from the SCN tracer) pure formation water starts to be produced.



Figure 2 Simulation 1: Variation of SCN in water in the formation over time during mud filtrate invasion and subsequent extraction/sampling.

Reactions occurring in the formation

The dominant reactions occurring during mud filtrate invasion and extraction are ion exchange reactions. Figure 4 shows the variation of the composition of ion exchange sites at node 0 (immediately adjacent to the well) during mud filtrate invasion (up to 10 minutes) and subsequent extraction for Simulations 2 (low clay) and 5 (very high clay). During extraction, mud filtrate is produced over the exchange sites first, followed by mixtures of mud filtrate and formation water (decreasing mud filtrate fraction) and finally formation water.

It can be seen that in the presence of formation water the order of dominance on the ion exchange sites is Na > Ca > K,Mg > Sr > Ba. During mud filtrate invasion, K displaces a significant proportion of all the other ions from the sites although the primary reaction is K_{mud} filtrate $\leftrightarrow Na_{clay/mica}$. Following invasion, the order of dominance becomes K > Na > Ca > Mg > Sr > Ba. Subsequently, during extraction, the reactions are reversed so that all the other ions displace K from the exchange sites. The amount of clays/micas in the simulations do not affect the predominance of ions on the ion exchange sites nor the nature of the ion exchange reactions, but they do affect the influence of ion exchange reactions on the extracted water compositions with the most significant effects occurring with sampling zones containing higher clay/mica fractions. As a result, for high clay/mica formations, formation water has to be extracted for a greater period of time before the ion exchange sites and the formation water have equilibrated. Most notably, K continues to be released to the formation water long after apparently (based on the tracer content) pure formation water is being produced.



Figure 3 Simulation 1: Variation of SCN in water at node 0 (immediately adjacent to the well) over time during mud filtrate invasion and subsequent extraction/sampling.

Minor calcite and barite precipitation/dissolution also occur during mud filtrate invasion as a result of mixing of the mud filtrate and formation water, coupled with release of Ca and Ba from clays/micas during invasion and uptake of these constituents on the same minerals during extraction. But, the reactions have negligible effects on the Ca and SO_4 concentrations of the produced waters and only minor effects on Ba.

Effect on extracted water compositions

Ion exchange reactions have the most significant effect on extracted water compositions. These effects increase with the CEC of the formation (e.g. see Figures 5-10). Where the CEC is low, ion exchange effects are negligible and the extracted water compositions essentially coincide with simple mixtures of mud filtrate and formation water. Extracted water compositions with average, high and very high CEC show increasing deviations from those of simple mixtures and this reflects the increasing influence of ion exchange reactions. At higher mud filtrate fractions (>0.2; >~200 mg/L SCN), K is depleted (relative to the K content of simple mixtures), whilst Na, Ca, Mg and Sr are enriched reflecting exchange of K from the mud filtrate for the other ions on ion exchange sites during mud filtrate invasion.



Figure 4 Composition of ion exchange sites at node 0 (Model 2 = solid line, Model 5= dashed line).

But, during extraction, as the mud filtrate fraction decreases, K is released from ion exchange sites causing it to be enriched where mud filtrate fractions are <0.2 whilst Na, Ca, Mg and Sr show the opposite behaviour reflecting their uptake on clays/micas. As indicated above, where the formation has higher clay/mica content these ion exchange reactions continue to affect the extracted formation water even after the mud filtrate fraction has declined to 0 such that Na, Mg, Ca and Sr are still increasing and K is still decreasing, only to reach their natural concentrations of the formation water after a period of production of zero mud fraction water.

Although Ba participates in ion exchange reactions in the same way as, for example, Sr, its concentration on the ion exchange sites is low and its concentration in the extracted water is also regulated by minor barite precipitation/dissolution. As a result, the variation with mud filtrate fraction is approximately linear (Figure 11). Reactions involving calcite have negligible effects on the Ca concentrations of the extracted water (Figure 9). As SO₄ is only affected by the minor barite precipitation/dissolution that occurs in the formation, the SO₄ concentrations of the extracted water also coincide with the compositions of simple mixtures (Figure 12). Produced water Br and Cl concentrations are not affected by reactions and so all the model results coincide with simple mixtures (e.g. Figure 13).



Figure 5 Variation of K and SCN concentrations in extracted water from simulations 1-5 and comparison with mud filtrate and formation water sample analyses.



Figure 6 Variation of K and SCN concentrations in extracted water from simulations 1-5 and comparison with mud filtrate and formation water sample analyses (at low mud filtrate fractions only).



Figure 7 Variation of Na and SCN concentrations in extracted water from simulations 1-5 and comparison with mud filtrate and formation water sample analyses.



Figure 8 Variation of Mg and SCN concentrations in extracted water from simulations 1-5 and comparison with mud filtrate and formation water sample analyses.



Figure 9 Variation of Ca and SCN concentrations in extracted water from simulations 1-5 and comparison with mud filtrate and formation water sample analyses.



Figure 10 Variation of Sr and SCN concentrations in extracted water from simulations 1-5 and comparison with mud filtrate and formation water sample analyses.



Figure 11 Variation of Ba and SCN concentrations in extracted water from simulations 1-5 and comparison with mud filtrate and formation water sample analyses.



Figure 12 Variation of SO₄ and SCN concentrations in extracted water from simulations 1-5 and comparison with mud filtrate and formation water sample analyses.



Figure 13 Variation of Cl and SCN concentrations in extracted water from simulations 1-5 and comparison with mud filtrate and formation water sample analyses.

Implications

Selection of methods for estimating well A formation water composition

Figures 5-13 also include the formation water and mud filtrate sample analyses which are displayed with estimates of their sampling/analytical uncertainty ($\pm 2\sigma$). Because the formation water composition used in the simulations was estimated using a SMCM, as expected, in most cases the mixing line passes through the analyses. This is not the case for Ba where the formation water concentration was estimated assuming equilibrium with BaSO₄ (see above). Also, the match to the Na analyses is slightly offset because the formation water Na concentration used in the simulations was estimated via ion balance.

It can be seen in these figures that where the CEC is average or low, relative to the uncertainty on the analyses, reactions have little effect on the extracted water compositions. So, where these conditions can be demonstrated to exist it can be expected that a SMCM method will provide reasonable estimates of formation water Na, K, Ca, Mg and Sr concentrations. But, where the CEC is high or very high, there is a risk that use of the simple mixing model will give erroneous results for these constituents.

Figure 14 shows an example of how ion exchange effects can result in erroneous results when the CEC is high and a SMCM method is used to estimate formation water Ca concentrations. It can be seen that for a sample with 260 mg/L SCN (0.51 mud filtrate fraction), the estimated formation water Ca concentration could be as high as 3400 mg/L compared with the actual

value of 2887 mg/L (i.e. ~20% too high) whilst for a sample with 20 mg/L SCN (0.04 mud filtrate fraction), the estimated formation water Ca concentration could be as low as 2700 mg/L (i.e. ~7% too low).



Figure 14 Schematic diagram showing how using a SMCM method under high CEC conditions can generate erroneous estimates of the formation water composition.

As discussed above, CEC can be estimated from XRD analyses but such analyses were not available for the sampled zone. However, XRD analyses were available at locations 2.1m and 4.1m away respectively and the CEC of these locations was found to be high suggesting that the mixing model should not be used for well A. But these CEC values may not be representative of those in the sampled zone.

In this case (i.e. because KCl mud was used), K is a sensitive discriminator of the CEC of the sampled zone because the effects of ion exchange on the K concentration of the water samples are expected to be significantly greater than the sampling/analytical uncertainty (see Figure 6). In Figure 6 it can be seen that sample 1 lies on the line of simulation 1 between the mud filtrate composition and the compositions of samples 2 and 3. The fact that sample 1 lies along this line suggests that the CEC of the sampled zone is average or low. If the CEC were high, the samples would be unlikely to lie on the same line.

The likelihood that the CEC of the sampled zone is average or low is also supported by the estimated formation water K concentration obtained via linear regression (i.e. a SMCM method) of the data in Figure 5 (242 ± 36 mg/L K; ± 2 x standard error). Figure 15 shows K

and Cl analyses for North Sea formation waters. It can be seen that the likely K content of the formation water from well A given its Cl content is between ~120 and ~560 mg/L. There are three samples with higher K concentrations at approximately this salinity but the possibility that these are formation water samples collected from wells drilled with KCl mud cannot be discounted. The fact that the estimated formation water K concentration, obtained via a SMCM method, is within this range also suggests that the CEC of the sampled zone is average or lower.



Figure 15 Schematic diagram showing how applying a simple mixing model under high CEC conditions can generate erroneous estimates of the formation water composition.

In summary, there is sufficient evidence to suggest that the CEC of the sampled zone is low enough for a SMCM method to be used to estimate formation water Na, K, Ca, Mg, and Sr concentrations. Therefore, for these constituents the formation water composition was estimated by applying linear regression to the water and mud filtrate sample analyses (see Table 4). This method also generated uncertainties on the estimates (± 2 standard errors).

Linear regression was also used to estimate concentrations of Cl, Br, acetate and formate because these constituents would not be expected to be reactive in the reservoir, and to estimate the concentration of SO_4 because the simulations had shown that this was hardly affected by reactions in the reservoir. Although the estimated concentration of formate was -1.7mg/L, this was within the uncertainty of the regression (±12 mg/L).

Due to the uncertainties in the Ba analyses, the formation water Ba content (and its uncertainty) was estimated using MultiScaleTM assuming equilibrium with BaSO₄. MultiScaleTM was also used to estimate the pH and total alkalinity of the formation water by assuming equilibrium with calcite and petroleum CO₂. The ion balance for the estimated composition is -0.93% suggesting estimates for the major ions at least (i.e. Na, Ca and Cl) are likely to be reasonable.

Sample Type/No.	Corrected	2xStd Error	Method
Initial reservoir P (bar)	196.7		
Initial reservoir T (°C)	73.7		
рН	6.20		Equilibrium with CO ₂
Na (mg/L)	15525	254	Linear regression
K (mg/L)	242	36	Linear regression
Mg (mg/L)	602	34	Linear regression
Ca (mg/L)	2887	54	Linear regression
Ba (mg/L)	1.6	0.05	Equilibrium with BaSO ₄
Sr (mg/L)	144	3	Linear regression
Cl (mg/L)	31382	862	Linear regression
Br (mg/L)	141	1.6	Linear regression
SO ₄ (mg/L), Dionex	337	18	Linear regression
Total alkalinity (mg/L)	172		Equilibrium with calcite
Formate (mg/L)	0*	12	Linear regression
Acetate (mg/L)	60	72	Linear regression
Cation total (meq/L)	878.53		
Anion total (meq/L)	895.04		
Ion balance (%)	-0.93		

Table 4 Estimated formation water composition for well A	Table 4	Estimated	formation	water	composition	for	well	A.
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* Note: Estimated concentration of formate was -1.7mg/L.

Implications for Field X

The 1-D reactive transport modelling was undertaken in association with the well A formation water analyses because these were the first available for the field. In this example, the estimated compositions of samples 2 and 3 (least contaminated) are not too different from the estimated formation water compositions, with the exception of K. Although this indicates that the corrections applied were not necessary for most constituents of interest, it is only by undertaking such work that this can be demonstrated and so uncertainties in the use of the sample 2 and 3 compositions, or the estimated compositions, are significantly reduced. In

this case, it was most important to be able to confirm that well A formation water is indeed, SO₄-rich and Ba-depleted.

The results of the reactive transport modelling have also been a useful reference data set when evaluating the formation water sample analyses from later appraisal wells for the field These evaluations showed that they too were obtained from average to low CEC zones, so the formation water compositions could also be estimated using the methods outlined above for well A. More importantly, for four of these wells, the lowest mud filtrate fraction of the samples was between 0.28 and 0.50 so the corrected formation water compositions in these cases were significantly different to the formation water sample analyses.

For one well, no tracer was applied to the drilling fluid and yet water samples were opportunistically collected. In this case, the water sample and mud filtrate sample Cl and K analyses lay on a linear trend, consistent with the CEC of the sampled zone being average or lower. This allowed K to be used as the mud filtrate tracer when applying the methods outlined above. Using this approach, it was assumed that the K concentration of the formation water was 0 mg/L; this simplification introduced negligible error in the estimated formation water composition.

Given the potential for using K as the mud filtrate tracer on Field A, it might be questioned why an additional tracer was also used. Other than the latter well, an objective of selected appraisal wells was to obtain formation water samples. Where collection of formation water samples is a well objective, relying on K as a mud tracer is a risk. For example, if it can subsequently be shown that significant ion exchange has occurred or if it is not possible to confirm that ion exchange is negligible, reliable formation water compositions cannot then be estimated because the mud fractions calculated from the K analyses will be, or could be, erroneous. Evidently, this information is not available until after sample collection and analysis. To avoid this uncertainty, and where collection of formation water samples was a well objective, the recommendation was to use an inert/stable tracer as standard practice.

Where obtaining formation water samples was not an objective of a new well, a tracer was not required. The above example does show, however, that even under these circumstances, if there was an opportunity to collect formation water samples and this would be useful, then samples were collected because there was a possibility that formation water compositions could be reliably estimated.

By applying the above methodology, the results also showed that the formation water across the major portion of the field is SO_4 -rich and Ba-depleted. Subsequently, this apparently unusual characteristic was explained the presence of anhydrite-bearing evaporites located under the reservoir which is likely to have been contacted by the reservoir formation waters in the past. The variation of formation water compositions across the field and the origin of these compositions will be the subject of a future publication.

In one isolated area of the field, not underlain be anhydrite-bearing evaporites, it was found that the formation water is enriched in Ba. In this case, because SO_4 was low in the mud filtrate it was again possible to estimate Ba by linear regression because it was shown that

mixing of formation water and mud filtrate was again little affected by $BaSO_4$ precipitation. In this particular example, there was potential for significant precipitation of $BaSO_4$ due to cooling, de-pressurisation and storage of the sample before analysis. Potential for loss of Ba from the sample by this mechanism was accounted for when the formation water Ba concentration was estimated (i.e. the estimated Ba concentration was an upper limit assuming that $BaSO_4$ had precipitated from the sample to equilibrium at ambient conditions).

The process of evaluating the quality of the formation water sample analyses, undertaking the reactive transport simulations and calculating the estimated formation water composition with associated uncertainties has provided confidence in (a) the use of the chosen correction methods and (b) the estimated compositions. This confidence has reduced uncertainties when using the formation water compositions for developing scale mitigation strategies, including selection of the injection water for the field and handling of Ba-rich and SO₄-rich produced formation water on the platform.

Evaluating formation water sample analyses from wells drilled with KCl mud

This study has shown that there is a risk that formation water compositions estimated using SMCM methods could be erroneous without the quality of the formation water sample analyses being evaluated and the potential effects of reactions being assessed. This risk is greatest where minerals with ion exchange sites (e.g. clays and micas) are present in the reservoir, where the mud filtrate and formation water are incompatible (e.g. mixing of Barich formation water and SO₄-rich mud filtrate), and where the mud filtrate fraction of the samples is high.

Before correcting for mud contamination, it is important to ensure that the water and mud filtrate analyses are reliable, and any post-sampling effects are understood. If these have only occurred after sampling (e.g. due to cooling, de-pressurisation, bacterial degradation), these effects need to be corrected for before applying mud contamination corrections. Ideally, sampling and analysis procedures should be adopted to provide reliable analyses and prevent changes in composition after sampling, but this is not always possible.

It is also important to ensure that the mud tracer is stable and has not been affected by reactions in the reservoir and that the mud filtrate analyses are representative of the mud invading the sampled zone. Mud in the well at any time between drilling of the sampled zone and the start of the pump-out phase could have contaminated the formation water samples. In this respect, it is recommended that mud samples be collected regularly during drilling and that after the rig analyses have been evaluated, relevant mud samples are sent for analysis so that any variation in the compositions of these samples can be fully characterised for all constituents of interest.

Where it can be demonstrated that constituents of interest are unlikely to have been affected by reactions in the reservoir, the SMCM method can be used to estimate their concentrations in the formation water. For example, in Field X, these included Cl, Br, formate and acetate. The SMCM method should not be used where sample compositions have been significantly affected by reactions in the reservoir. One method of assessing whether significant reaction effects have occurred is to check the linearity of water and mud filtrate analyses on X vs tracer plots (where X is the constituent of interest). Where the data lie on a single linear trend, and where the samples contain variable amounts of mud contamination, this indicates that reaction effects are not significant and that the simple mixing correction method can be used. Where they do not, this indicates that the reaction effects are significant and if used, the method is likely to give erroneous results.

Often, this check cannot be made because several samples will be collected in succession at the end of pump-out with each having a similar composition. Although it is common for a 'safety' sample to be collected early in pump-out (in case of subsequent failure to obtain end of pump-out samples), this is often discarded if samples are successfully collected at the end of pump-out. But, this will usually have a high mud filtrate fraction and would be very useful for assessing linearity as indicated above. It is recommended that safety samples are collected and subsequently analysed with the end of pump-out samples and the mud filtrate samples.

A method which can be used to assess the impact of ion exchange reactions is to use the SMCM method to estimate the formation water K concentration and to determine whether this value is reasonable by comparing it with analogue formation water compositions. If it is, ion exchange effects are unlikely to be important. The SMCM method can then be used to estimate Na, K, Ca, Mg, Sr and Ba in the formation water (assuming no other reactions have affected these constituents; see below). If the estimated K concentration is much higher or lower (e.g. negative values) than the analogue formation waters, this suggests that if used, the method is likely to give erroneous results.

An alternative method which can be used to assess the impact of ion exchange reactions is to evaluate XRD analyses to estimate the CEC of the sampled zone and then to undertake 1-D reactive transport modelling of the type presented above to see whether ion exchange could have adversely affected the water sample compositions. If not, the SMCM method can be used. But, if significant ion exchange effects are likely use of this method is not advised.

Where the above methods have shown that ion exchange is likely to have significantly affected the formation water sample compositions, the 1-D model results can be used to provide an indication of the magnitude of this effect and so can be used to constrain the formation water compositions. This method will be the subject of a future publication.

An alternative method for assessing the impact of mineral dissolution or precipitation is to undertake mud filtrate and formation water mixing calculations to assess the potential magnitude of reaction. The mixing calculations can be undertaken using a 1-D reactive transport model as in this study but for evaluating precipitation of common scale minerals (e.g. BaSO₄, SrSO₄, etc) scale prediction software such as MultiScaleTM can also be used. Where dissolution/precipitation effects are significant, the results of the mixing calculations

can be used to correct for these effects so that the formation water composition can then be estimated using the SMCM method.

Where none of the above methods or tools can be used to confirm the validity of the simple mixing correction model, 1-D reactive transport modelling results can still be useful for demonstrating the uncertainties in formation water compositions estimated from it. For example, for Field X these showed that with high mud fraction samples (>0.2) the model may overestimate Na, Ca, Mg, and Sr concentrations and underestimate K concentrations, and vice-versa for low mud fraction samples (<0.2). The degree of error will increase with higher mud fractions and higher CEC. Although samples with very low mud fractions may approximate formation water compositions (as did samples 2 and 3 in this study) this might not always be the case. For example, where the mud filtrate and formation water are SO₄-rich and Ba-rich respectively, minor mud contamination (e.g. 0.02) can result in significant stripping of Ba from the sample (e.g. ~80 mg/L where the mud is seawater-based). For this reason, when formation water samples are to be obtained and water-based mud is to be used, it is recommended that the mud make-up water be SO₄-depleted.

Conclusions

A 1-D reactive transport model has been developed to simulate mud filtrate invasion, the subsequent extraction of water samples from the formation, and reactions occurring therein.

This has been used to help understand the potential effects of reactions on mud-contaminated formation water sample analyses obtained from well A on Field X, and particularly whether a simple mixing correction model can be used to estimate formation water compositions from these analyses.

Comparison of the model results and formation water sample analyses has shown that this is a valid model to use not only on samples from well A, but on samples from all appraisal wells on Field X. The results confirmed that both Ba-rich and SO₄-rich formation waters are present in different areas of the field.

The study has provided confidence in (a) the use of the chosen correction methods and (b) the estimated compositions. This confidence has reduced uncertainties when using the formation water compositions for developing scale mitigation strategies, including selection of the injection water for the field and handling of Ba-rich and SO₄-rich produced formation water on the platform.

Based on the results of this study, recommendations have been made for acquiring data for, using and checking the validity of the simple mixing correction model to estimate formation water compositions from mud contaminated samples.

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