Laboratory Investigation of the Elemental Residual Salt Analysis (ERSA) Technique and Implications for Scale Management

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ABSTRACT

Elemental Residual Salt Analysis (ERSA) involves completely extracting remnant formation water and the precipitated salt-residues of evaporated formation water from core material with de-ionised water leachate and then using analyses of the leachate to estimate the formation water composition. Although potentially useful for scale management, there are several reported uncertainties associated with the data. In this study, core has been flooded with synthetic formation water and then ERSA has been applied to obtain estimates of the formation water composition. Comparison of these estimates with the known composition of the formation water has shown that ERSA can provide reasonable estimates of formation water Cl concentrations in the water-leg where water saturation (S_W) and porosity data for core can be obtained. However, under the conditions used in this study, the estimated concentrations of other ions are biased as a result of reactions occurring during the ERSA leaching step and attempts to correct for these were unsuccessful. In the absence of additional laboratory results, geochemical modelling has proved a useful tool for predicting, at least qualitatively, effects of leaching step reactions on ERSA-derived formation water compositions. Modelling results suggest that if good quality, preserved core samples can be obtained from the water-leg, reaction effects might not be significant if the core is either clay-free or if the formation water salinity is high (>~200,000 mg/l TDS) and the clay content is low (<~5%). Therefore, reasonable estimates of formation water composition might be obtained via ERSA in these cases. Under all other conditions, correction for reaction effects is likely to be required. Published correction methods may be successful where the formation water salinity has mNa/mCl close to, but less than, 1, clay contents are moderate to high (>10-15%) and salinity is low to moderate (<~50,000 mg/l). For other conditions, new correction methods need to be developed if ERSA-derived formation water compositions are to be more widely used. Although ERSA can be used to estimate formation water compositions from oil-leg core samples, these results may be particularly prone to uncertainty where small errors in S_W or porosity occur.

INTRODUCTION

Elemental Residual Salt Analysis (ERSA) is a method for estimating the composition of formation water in a core sample. It involves completely extracting remnant formation water and the precipitated salt-residues of evaporated formation water from core material with de-ionised water (the leaching step). The leachate is then analysed by standard methods for constituents of interest (e.g. Na, K, Ca, Mg, Ba, Sr, Cl, SO_4). The concentrations in the original formation water are then estimated via a mass balance method using these analyses, the core volume, and water saturation and porosity data for the core sample. ERSA has been used in the oil industry since the early 1970s to obtain estimates of formation water composition and has attracted interest because where core is available:

1. It is a low-cost and low-risk method compared with conventional methods of obtaining water samples (e.g. DST, formation sampler).

2. It can be used to obtain an estimate of formation water composition where it has not been possible to obtain water samples by conventional methods.

3. It provides an opportunity to understand lateral and depth-related variations in formation water compositions in a reservoir, as well as those occurring between the water-leg and oil-leg. The latter is of particular interest because it may not be possible to obtain water samples from the oil-leg.

ERSA has been used to study water salinity variations in reservoirs (Chilingar and Rieke, 1975; McCoy et al., 1994; Schmidt, 1973), and to evaluate regional compartmentalisation (McCartney et al., 2004). ERSA also has significant potential to aid scale management on both new and existing developments (e.g. Webb and Kuhn, 2004). For example, where formation water compositions across a field are better understood, a more detailed and accurate view of scaling potential across a field can be identified during development planning. Equally, retrospective determination of formation water compositions along a well using ERSA on core samples may help explain unexpected scale occurrence in existing production wells.

Despite being used for over 30 years however, ERSA results can be of questionable quality and the method has been under continuous development (McCartney et al., 2004). For example, some studies have shown that ERSA-derived formation water Cl concentrations obtained from water-leg core samples can be reliable (McCoy et al., 1994; Pearson et al., 2003; Woulé Ebongué et al., 2005) but others have demonstrated that the concentrations of other constituents can be biased, primarily through oxidation and drying of core during storage, and reactions occurring between core and distilled water during the leaching step (Pearson et al., 2003). ERSA procedures also vary in their detail from study to study (e.g. leaching time, solid-liquid ratios, etc). To what extent some of these biasing effects may be attributed to procedural variations is not known. Recognising the limitations of ERSA results, Bradbury and Baeyens (1998) have proposed a method to correct for reaction effects occurring during the ERSA leaching step which, when applied to preserved core, appears to provide reasonable estimates of formation water compositions for many constituents in certain cases. Their method involves undertaking both ERSA and Exchangeable Ion Displacement (EID) tests on core samples. The latter are essentially ERSA but using Ni-etheylenediamine (Ni-en) as the leaching solution. EID tests are undertaken to help determine the initial composition of exchangeable ions on ion exchange surfaces (i.e. prior to the leaching step during ERSA). To date, this correction method has only been applied to core samples with high clay content (~40%) and not to typical oilfield reservoir sands.

Given (a) the potential usefulness of ERSA-derived data for scale management purposes, (b) the availability of a method for ‘correcting’ reaction associated biases and (c) uncertainties over the influence of different aspects of ERSA procedures on the quality of the results, a study was conducted with the following objectives:

1. To evaluate the effect of variations in ERSA/EID procedures on leachate compositions obtained using core samples flooded with synthetic formation water of known composition and with clay content more typical of oilfield sandstones.

2. To generate estimates of formation water compositions using the normal mass balance method and that of Bradbury and Baeyens (op cited) to assess the validity of results generated via ERSA/EID tests.

In this paper we describe the laboratory work undertaken and results obtained, and discuss the implications with respect to use of ERSA-derived formation water compositions in scale management.

EXPERIMENTAL STUDIES

Core samples

Core plug samples for the study were obtained from a horizontal well section comprising a very fine grained Devonian sandstone facies from Reservoir Unit V of the Clair Field, West of Shetland. This facies was selected because, typically, it contains moderate concentrations of clay (approximately 10-13% point counted). These clays were expected to induce ion exchange reactions during the ERSA leaching step which would allow us to more easily identify reaction effects and test correction methods. “Vertical” core plugs (4 inch by 30mm) were taken from the centre of unpreserved, slabbed (half-cut) sections of core (i.e. parallel to the bedding of the horizontal well). Sampled sandstone sections appeared to be homogenous and “clean” (i.e. free of fractures, pervasive cement or mudstone/clay beds). However, some of the core plugs contained horizontal and ripple cross laminae which ran approximately parallel with the length of the plugs.

The core plugs used in this study are listed in Table 1 along with their measured permeabilities and flowing porosities (derived from core flood experiments, see below). The permeabilities of individual plugs vary between 2 and 42mD. Flowing porosities are generally between 17.3% and 21.6% (except core plug A3; 10%). Table 2 shows XRD analyses for some of the samples. It can be seen that the mineralogy is dominated by quartz and feldspar, with lesser amounts of carbonates and clays. The clay content is variable and lower than was expected for these samples (0.5 to 4.4 wt%). The relatively low clay abundance is most likely the result of selection of samples with homogeneous and “clean” texture. Table 3 shows the formation water composition in the area of the Clair Field where the core was obtained.

Task	Description	Core plug	Core flood procedure	Connected core porosity (%)	Brine permeability (mD)
A	Ni-en isotherm	B1	S	17.26	3
B	ERSA grinding assessment	D1	S	20.55	29
B	EID grinding assessment	E1	S	20.39	26
C	ERSA leaching time assessment 1	G1	S	17.47	2.18
C	ERSA leaching time assessment 2	G2	S	20.36	38
D	ERSA agitation assessment	F1	S	19.21	12.69
E	ERSA/EID method validation 1	A1	MV	21.60	41.8
E	ERSA/EID method validation 1	A3	MV	10.00	3.88
E	ERSA/EID method validation 2	C2	MV	18.59	2.41
E	ERSA/EID method validation 2	C3	MV	17.87	19.21

Table 1 Summary of core plugs used in laboratory tests, the core flood procedures applied (S=standard, MV=method validation), and measured permeability and connected porosity of the core plugs.

Prior to use in the core floods, the core plugs were trimmed and cleaned by hot solvent Soxhlet extraction. All samples were successfully cleaned except G1 (see Figure 1). Repeated attempts to clean this core showed that the residual oil was 'immobile'. As further attempts to clean the core were unlikely to be successful, this core plug was flooded in the condition shown in Figure 1.

Synthetic formation water

The composition of the synthetic formation water used to flood the core plugs is shown in Table 3. A stock solution was prepared at the start of the study and was analysed by both Heriot-Watt University and the Macaulay Institute. The former sampled this solution, diluted it into analytical range and analysed it regularly during the core floods (see Table 3).

Sample	**Top plug A1**	**Base plug A3**	**Top plug C1**	**Base plug C1**	**Top plug C3**	**Base plug C3**
Depth (m)	2030.16	2530.55	2523.62	2523.75	2523.88	2524.00
Mineral	**Wt%**	**Wt%**	**Wt%**	**Wt%**	**Wt%**	**Wt%**
Quartz	75.7	72.3	80.3	73.8	72.3	74.8
Plagioclase	8.4	9.1	8.7	10	9.1	9.1
K-feldspar	9.6	12.6	9	13.8	13.4	11.8
Calcite	0.6	0.5	0.6	0	0.1	0.3
Dolomite	1	0.7	0.8	0.4	0.4	0.8
Siderite	0.5	0.4	0.1	0.1	0.6	0.4
Pyrite	0	0	0	n/a	n/a	0
Chlorite	1.7	1.2	0.4	0	0.3	1.1
Illite*	0.29	0.40	0.01	0.11	0.21	0.12
Illite-Smectite*	2.01	2.80	0.09	1.89	3.69	1.68
Total	99.8	100	100	100.1	100.1	100.1
	Relative Wt%	**Relative Wt%**	**Relative Wt%**	**Relative Wt%**	**Relative Wt%**	**Relative Wt%**
Chlorite	12	12	5	4	4	8
Kaolinite	0	0	0	1	1	0
Illite	11	11	5	5	5	6
Illite-smectite	76	77	90	90	90	86
Total	99	100	100	100	100	100
%Exp**	20-25	20	20-25	20-30	20-30	20-25
	CEC^	**CEC^**	**CEC^**	**CEC^**	**CEC^**	**CEC^**
Low	1.27	1.64	0.09	0.99	1.96	1.00
Medium	1.94	2.38	0.17	1.34	2.70	1.49
High	2.62	3.13	0.26	1.69	3.43	1.99

Note:
* Estimated from original Illite + smectite analyses and clay fraction analyses.
** %Expandability of smectite layers in illite-smectite.
^ meq/100g rock. Estimated from XRD analyses and typical low, medium and high CEC for pure minerals.

Table 2 Summary of XRD bulk rock quantitative analyses (weight %), relative percentage (by weight) of clay minerals in the <2mm clay size fraction (Reference Intensity Ratio method), and CEC.

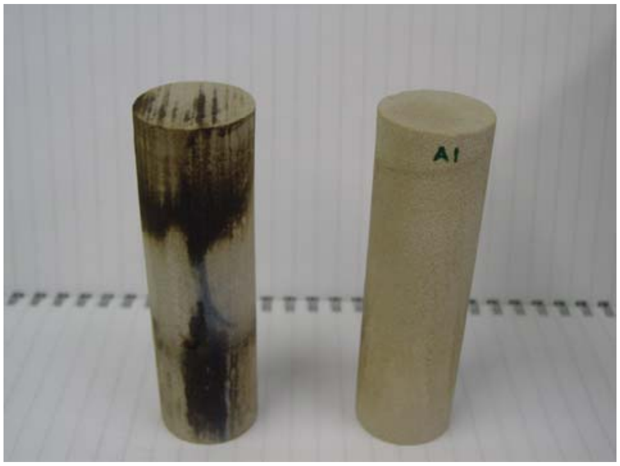

Figure 1 Photograph showing the residual oil staining on Core G1 (left) compared with the cleaned A1 core.

Sample	Clair Field FW (mg/l)	Synthetic formation water			
		Mean HW (mg/l)	RSD (%)	Mean MI (mg/l)	RSD (%)
Na	4,920	9,883	3.5	9,887	0.76
K	119	210	4.6	204	1.76
Mg	23.2	50.6	2.9	58.1	1.72
Ca	919	98.6	3.1	104	1.44
Sr	35.2	80.2	3.2	86.5	1.73
Ba	4.5	20.7	8.7	21.2	1.42
Cl	9,080	14,919	5.7	15,789	3.62
SO_4	31	6.01	2.7	<1	
Br	n.d.	1.2	284	<3	
I	n.d.	12.3	14.5	2.07	3.38
Alkalinity (as HCO_3)	559	n.d.		891	24

Table 3 Composition of Clair Field formation water (FW) and synthetic formation water. HW = Heriot-Watt University (mean of 17-22 analyses). MI = Macaulay Institute (mean of 2 analyses). RSD = Relative Standard Deviation. n.d. = not determined.

The results from the two establishments are in reasonable agreement with any differences probably reflecting the different analytical procedures adopted by each. The composition is close to that of formation water from the Magnus and Statfjord fields of the North Sea (Warren and Smalley, 1994). Iodide was added to act as a tracer for the synthetic formation water. Br was not deliberately added to the synthetic formation water because it was to be used as an aid to detect remnant Clair formation water in the ERSA leachate solutions (Br is expected to be present in Clair formation water). Br in the synthetic formation water in Table 3 may have inadvertently entered the fluid with Cl during its preparation.

Core floods

Core floods were undertaken at ambient temperature and pressure. Different flooding procedures were utilised depending on whether a core plug was designated a 'standard' core plug or 'method validation' core plug (see Table 1). The 'standard' core plugs were used to assess the influence of variations in ERSA/EID procedures. For these tests, it was only necessary to ensure that the core plug was homogeneously flooded so variations in formation water composition along each core did not occur. The standard core plug flooding procedure involved:

1. **Initial brine saturation:** Formation water containing 10 mg/l iodide was vacuum-degassed and filtered before being injected into the core under vacuum at a flow rate of 150ml/h. A leak test was then undertaken. The sample was saturated until steady state ∆P was reached.

2. **Measurement of absolute brine permeability at 100% brine:** ∆P was measured at 30, 60, 90, 120, and 150ml/h and permeability was calculated using Darcy's Law.

3. **Measurement of connected pore volume:** Iodide-free formation water was injected at 150ml/h and the effluent analysed for iodide using in-line UV spectrometry analysis. A post-flush with formation water containing 10ppm iodide was then performed with the effluent again being analysed for iodide using in-line UV spectrometry analysis. Throughout both injections, 2ml samples were collected for manual back-up analysis if required. Connected pore volume was calculated using the iodide tracer analysis to determine the volume of dosed or undosed brine that had been displaced from the core.

4. **Brine saturation 2:** Approximately 10 pore volumes of formation water containing 10ppm iodide were then injected at a flow rate of 150ml/h. Samples of the effluent were collected every 0.5 pore volumes throughout the saturation period.

5. **Shut-in:** Flow was then stopped overnight (~0.75 days).

6. **Brine saturation 3:** Step 4 was repeated.
7. **Removal of Core:** The core was removed from the core holder under a nitrogen atmosphere and place in foil bag which had been purged with oxygen-free nitrogen. After the first bag was heat-sealed, this was placed in a second bag and the procedure was repeated. Care was taken to prevent addition or removal of water from the core.

The method validation core plugs were used to assess the accuracy of the estimated formation water compositions (see below). Therefore, the procedure was modified to (a) try to confirm that reactions were not occurring in the core during ‘standing’ time (i.e. whilst waiting to make use of the flooded core) and (b) understand the effect of the reactions on the formation water composition if this was not the case. The flooding procedure was the same as that described above except that shut-in times were 4-6 days, Steps 5 and 6 were repeated an additional 3 times and selected samples collected during the brine saturation steps were analysed to monitor the extent of reaction occurring in the core during flowing and shut-in periods. pH was analysed by electrode, and Na, K, Mg, Ca, Sr, Ba, Br, I, S (SO_4) and Cl by ICP-OES. All samples were diluted into analytical range. Where possible, those samples for analysis that were collected during a flowing period were analysed together. Calibration standards and stock formation water were analysed before and after each batch. Drift corrections were made to effluent and stock formation water analyses using the calibration standard results.

ERSA/EID experiments

All core plug handling was undertaken in an anaerobic cabinet containing a water-saturated, oxygen-free, nitrogen atmosphere to restrict oxidation and drying of the samples. Prior to each experiment, the relevant core plugs were removed from their sealed bags. The bags were then weighed, dried and weighed again to determine how much water had drained from the core during storage. Drainage losses varied between 0.07 and 17.25% of the pore volume. Storage times for core used in Tasks A-D were 3-59 days. Those for Task E were 2-7 days. The total weight, length and end diameter of the plugs were measured using a balance and vernier calipers, from which the plug volume and density were calculated. For all tests, pieces of the core plug were broken off and their volumes calculated from their weight and the core plug density.

Ni-en isotherm

A Ni-en isotherm was measured on core plug B1 (Task A). This was undertaken to determine what concentration of Ni-en was required to fully displace all exchangeable ions from the ion exchange sites of the core samples during the EID tests. The procedure involved making up a stock solution of Ni-en, preparing various solutions of Ni-en from this (0.000025 to 0.03 M Ni-en), and adding 400ml of each solution to ~11g of disaggregated core (solid:liquid, S:L, ratio of 0.0275) in a polypropylene centrifuge tube. These were sealed and the solutions agitated for two days before the solution was analysed for Ni via ICP-OES. Repeat analyses were undertaken on these to provide an estimation of measurement uncertainty. Similarly, repeat analyses were also undertaken on various procedural blanks and the original stock solutions.

The sorption isotherm and procedural blank results for this task are shown in Figure 2. Based on these results the CEC of Core B1 is approximately 20 meq/kg rock although there is significant uncertainty on this value reflecting the uncertainty on the leachate analyses, the low CEC of the rock and adsorption of Ni on the equipment as indicated by the results for the procedural blanks.

For the Unit V sands, there is a positive correlation between permeability and clay content. The low permeability of this core (3mD) indicates that Core B1 probably has one of the highest clay contents of the core plug samples and a Ni-en concentration of approximately 0.03M should be sufficient to displace all exchangeable ions from the EID samples obtained from other core plugs. However, to allow for uncertainties in the isotherm and in the clay content-permeability correlation, a 0.09M Ni-en solution was selected for use in subsequent tasks (i.e. 3 times the maximum used to generate the isotherm).

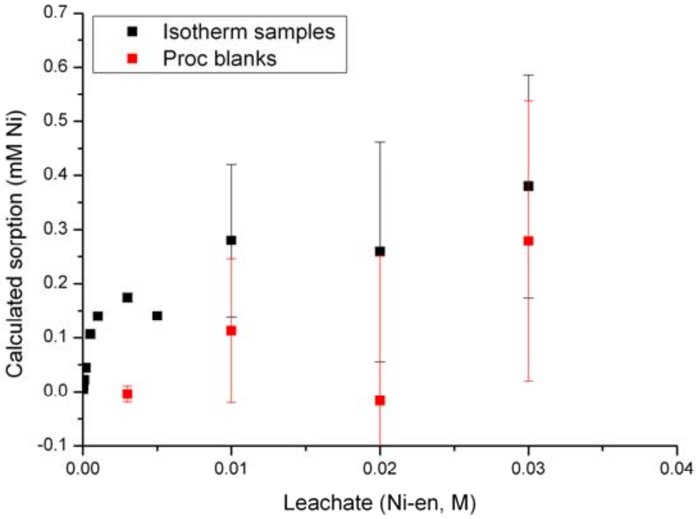

Figure 2 **Ni-en isotherm results ('Proc blanks' = procedural blanks). Error bars = 1 S.D. (n=6).**

Evaluation of ERSA/EID methods

For the purposes of this study, the 'standard' ERSA technique involved adding a known weight of standard flooded core to a known volume of leachate (de-oxygenated, $18M\Omega cm^{-1}$ de-ionised water) to give S:L=1. The volume of the core was checked by displacement of the leachate. The core was then removed, disaggregated in an agate mortar and rinsed into a plastic bottle using the leachate. The bottle was sealed, shaken thoroughly and then agitated periodically (i.e. once every hour during the working day) over a period of 24 hours. After 24 hours, when the bulk of the particle matter has settled, as much as possible of the leachate was removed by pipette, centrifuged and then analysed using ICP-OES (Na, K, Mg, Ca, Sr, Ba), Dionex ion chromatography (SO_4, Br, Cl), ICP-MS (total Iodine), discrete analyzer (alkalinity) and electrode (pH). Procedural blank samples were collected during each task. The EID procedure was the same as that for the ERSA tests except that de-oxygenated, 0.09M Ni-en solution was used as the leachate and Ni analyses were also undertaken by ICP-OES.

A number of variations on this standard technique were undertaken:

1. **Task B.** Standard ERSA and EID techniques were each applied to 4 core samples to test reproducibility of the methods.

2. **Task C.** Standard ERSA technique was applied to core samples except that the agitation frequency and leaching times were varied. Two samples were leached for 15 minutes and agitated once (at the start). Two samples were leached for 2 hours and agitated at the start and at 30 minutes intervals (4 times total). Two samples were leached for 6 hours and agitated at the start and at 1 hour intervals (6 times total). Two samples were leached for 24 hours and agitated at the start and at 1 hour intervals during the working day (10 times total).

3. **Task D.** Standard ERSA technique was applied to core samples except that the leaching time was only 1 hour and the agitation frequency was varied. Four samples were gently shaken and then left for one hour before the leachate was removed. One of these was left undisturbed for the hour, one was also shaken after 30 minutes, one was also shaken every 15 minutes and the last was also placed on a motorized roller and rolled constantly.

Based on the results of these tests, Task E was undertaken to generate a set of data to which the Bradbury and Baeyens correction method could be applied. In addition, the effect of varying the S:L ratio was investigated. Again the standard ERSA technique was used except that the core was flooded using the method validation procedure. Also, after adding the leachate, the sealed sample bottle was initially shaken, and then shaken again a further 3 times at 15 minute intervals. The sample was then left undisturbed for the last 15 minutes (i.e. total leaching time of 1 hour), before the water was removed and centrifuged for 30 minutes before analysis. Two batches of tests were undertaken, with each batch consisting of 4 ERSA and 4 EID tests. The S:L ratios for the 4 tests in each case were ~0.25, ~0.5, ~1 and ~1.5. For each ERSA and EID test at a given S:L ratio, adjacent core samples were used to minimise variations associated with changes in mineralogy along the core plugs. The samples for the 0.25, 0.5 and 1 S:L tests were taken from one core plug (A1 and C3 respectively) and that for the 1.5 S:L tests were taken from an adjacent or nearby plug (A3 and C2 respectively).

RESULTS

Core flooding

To assess the validity of the ERSA-derived formation water compositions, the composition of the formation water in the core sample prior to the ERSA/EID tests needs to be known. However, the composition of the formation water might change during the storage period between completion of the core flood and the start of the ERSA/EID tests as a result of water-rock reactions. Evaluation of time-dependent trends in method validation core flood effluent compositions can provide clues as to whether such reactions are significant.

Trends early in brine saturation following shut-in periods demonstrate that the synthetic formation water was reacting with the core. Ca, Mg and SO_4 concentrations increased rapidly during the shut-in period, suggesting that they were being gained by the formation water in the core, and then declined toward formation water compositions during the next core flood (see Figure 3; only results for Ca and S shown). Such reactions probably also occurred during brine saturation but were less easy to detect outside of sampling/analytical uncertainty. The gain in Ca and Mg is most likely due to either release from clays (ion exchange) or dissolution of calcite and dolomite/chlorite respectively (the rate of dissolution of plagioclase will be slow). The gain in S may reflect gain in SO_4 due to either dissolution of soluble sulphates or oxidation of sulphides that were not detected by XRD. If the latter is correct, this suggests that efforts to remove oxygen from the formation water by degassing may not have been completely successful. The reaction effects decline as the number of shut-in periods increase which may reflect gradual achievement of equilibrium between ion exchange sites and the injected formation water, or gradual reduction of accessible minerals for dissolution/oxidation, or reduction of more reactive surfaces (e.g. fines). Although there appears to be a ‘reaction’ effect in the iodide analyses where iodide consistently decreases over time following most shut-in periods, this is likely to be an effect of analytical drift that was not adequately corrected for during analysis. Therefore, it is possible that Ca, SO_4, and Mg might be released to the formation water between completion of the core floods and the start of the Task E tests (2-7 days; core plugs A1, A3, C2 and C3).

Storage times for the standard core plugs were much longer (3-59 days). Given that these are expected to have similar mineralogy to the method validation core plugs, it is possible that the reaction effects noted above may be enhanced in the standard core plugs during storage, possibly even affecting other ions (e.g. Na, K, Sr, etc). The potential influence of reactions occurring during storage is considered further below.

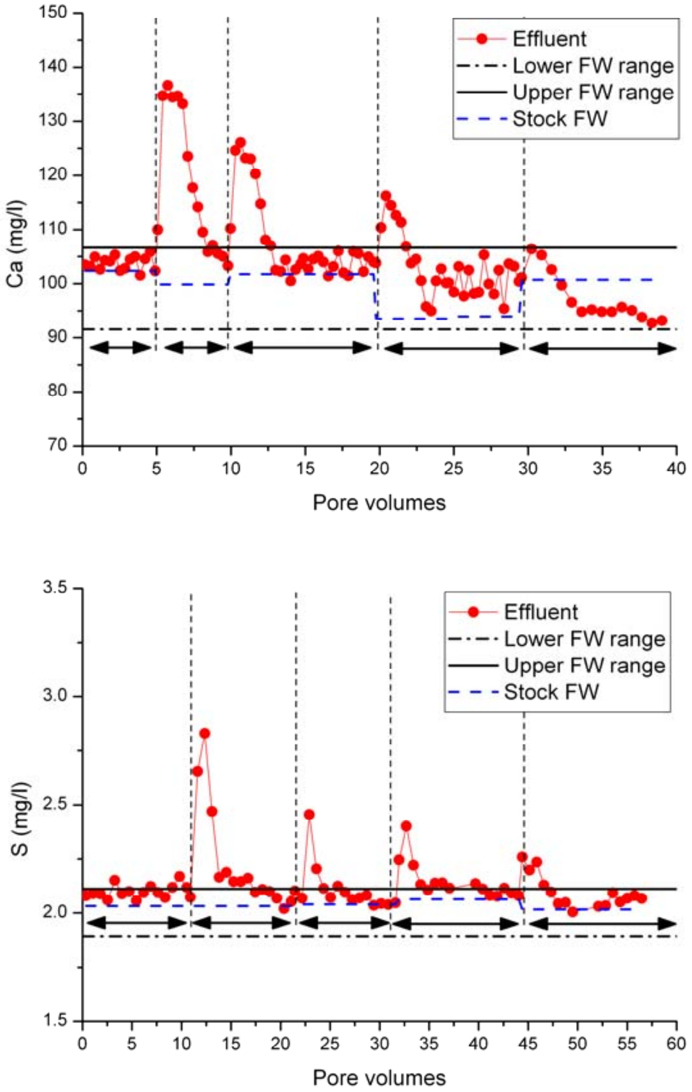

Figure 3 **Effluent Ca and S analyses from the A1 and A3 (respectively) method validation core floods. Upper and lower FW range is the range of stock formation water analyses observed during the core flood. Dashed horizontal lines show the mean stock formation water composition for each flowing period. Vertical dashed lines show shut-in periods.**

ERSA/EID tests

The quality of the ERSA leachate analyses is generally good (<±5% ion balance) with no evidence of contamination in the procedural blank samples. Where simple dilution of formation water has occurred during the leaching step, the leachate analyses should lie on the synthetic formation water dilution line on Cl-X scatter plots (where X is Na, K, Ca, etc). Where sampling/analytical uncertainty is present, the analyses should lie both above and below the line within the limits of uncertainty. Also, given the lack of Cl minerals in the core samples, the ERSA/EID leachate Cl analyses should not be affected by water-rock reactions. Therefore, analyses lying consistently above or below the dilution line may reflect the effects on X of reactions occurring during storage, or reactions between the core and de-ionised water or Ni-en during the leaching step. In addition, minor Br was detected in many of the samples (Figure 4) indicating that some remnant Clair formation water or salts from this formation water, may have been present in the core plugs within the unconnected (non-flowing) porosity and was released from pores during sample disaggregation. Therefore, consistent deviations from the dilution line might also reflect mixing with original Clair formation water or dissolution of remnant salts from this water. Each of the above processes may be affecting the ERSA/EID results where they lie off the dilution line. However, in most cases, one factor appears to dominate.

Na, alkalinity and iodide leachate analyses are generally grouped about the dilution line (Figure 4; only Na shown) with the range of concentrations observed primarily reflecting variations in the S:L ratios (i.e. higher concentrations at high S:L ratios). This suggests that the sampling/analytical uncertainty dominates the effects of reaction or mixing with original formation water. In the case of alkalinity, the proximity of the detection limit has added to the uncertainty of these analyses. The ERSA iodide analyses for core plugs C2 and C3 are anomalously high. The reason for this is currently unknown although they were analysed in one batch and so there may be an analytical explanation.

In contrast, ERSA leachate K analyses lie above the dilution line, indicating a gain from some source, whilst Ca, Ba and Sr lie below it indicating a loss (Figure 4; only Sr shown). The ERSA leachate Mg analyses display a transition from samples with lower leachate Cl content (lower S:L ratios) lying above the synthetic formation water dilution line to those lying on and below it at higher leachate Cl content (higher S:L ratios) (Figure 4). All the EID leachate analyses for Na, K, Mg, Ca, Sr and Ba lie above the line (see Figure 4 for Na, Sr and Mg results). Considering the biased deviations expected during storage, and those expected for mixing with Clair formation water, it is considered that reactions occurring during the ERSA/EID leaching step probably account for most of the biases observed in Na, K, Ca, Mg, Ba and Sr data.

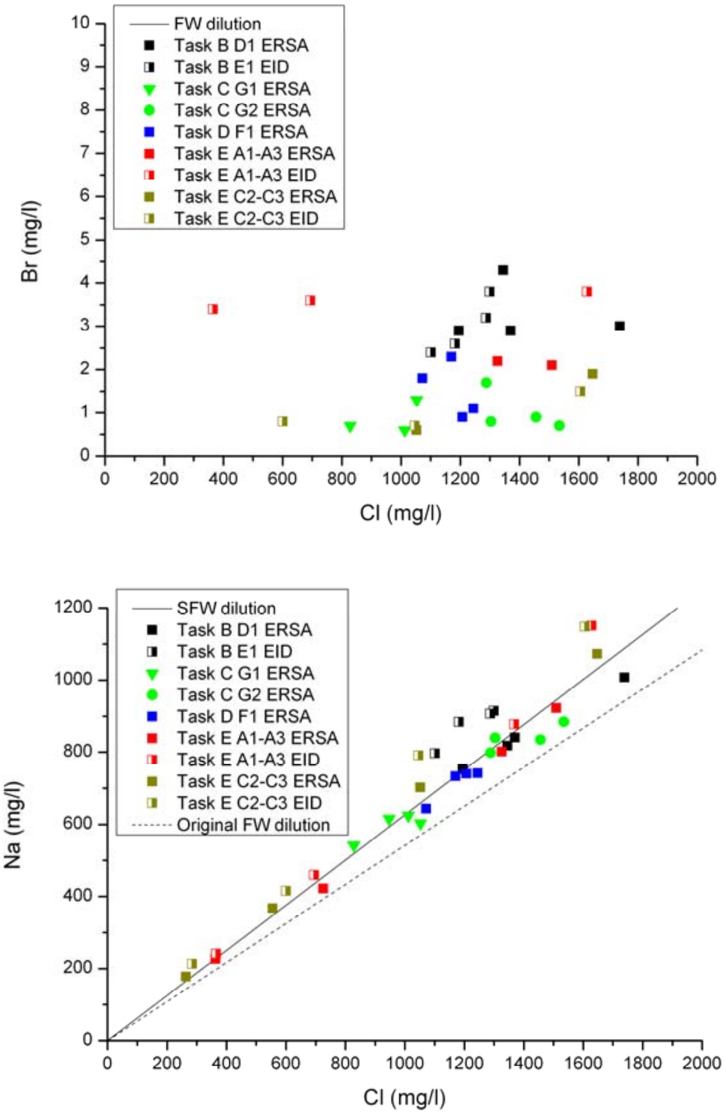

Figure 4 **ERSA and EID leachate analyses: (a) Cl v Br, (b) Cl v Na. Solid symbols = ERSA tests, half-filled symbols = EID tests. SFW = synthetic formation water. Original FW = Clair Field formation water.**

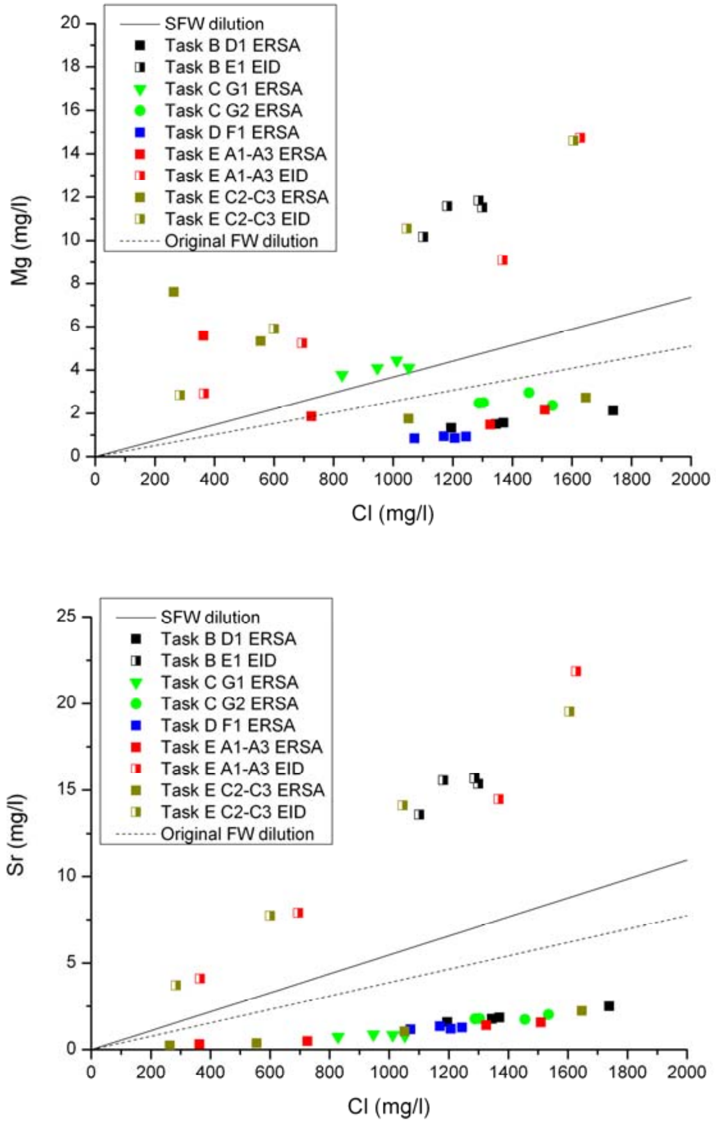

Figure 4 ERSA and EID leachate analyses: (c) Cl v Mg, (d) Cl v Sr. Solid symbols = ERSA tests, half-filled symbols = EID tests. SFW = synthetic formation water. Original FW = Clair Field formation water.

For some EID and ERSA samples, SO_4 is below detection which is consistent with simple dilution of formation water. However, for other samples, SO_4 lies significantly above the dilution line and the cause of SO_4 enrichment is less clear. For example, SO_4 is present, albeit at low levels, in the original formation water. Also, although neither sulphides nor sulphates were detected in the A and C core plugs in this study, both pyrite and barite have been detected as trace constituents in petrographic studies of other Clair Unit V sandstones. As the

ERSA and EID solutions are undersaturated with respect to barite, and as sulphide oxidation may have occurred during core flooding and storage, both reaction effects and mixing with original formation water might account for the SO_4 gains observed.

Given the mineralogical composition of the core and the short duration of the leaching step during these tests, the reactions most likely to dominate the other ions during this step are ion exchange and dissolution of carbonates because:

1. Speciation calculations indicate that the ERSA and EID leachate solutions are undersaturated with respect to carbonate minerals.

2. The presence of ion exchange sites has been demonstrated by the generation of the Ni-en isotherm.

3. Ion exchange reactions and dissolution of carbonates are fast reactions relative to the dissolution and precipitation of silicates within the pH range of the ERSA leachate solutions (6-7.5).

The gains in Na, K, Mg, Ca, Ba, and Sr during the EID leaching step are most likely to be caused by displacement of exchangeable ions from exchange sites by Ni although dissolution of carbonates (calcite, dolomite) may also have contributed to the gains in Mg and Ca.

The losses of Mg, Ca, Ba and Sr from the ERSA leachate samples are most likely to have occurred via replacement of Na and K on ion exchange sites. Uptake of divalent cations and release of univalent cations via ion exchange is common during reduction of water salinity (Appelo and Postma, 1999). The gain in Na is too small to be detected outside the sampling/analytical uncertainty. Perhaps surprisingly, there is no strong evidence for the variations in procedures to have significantly affected the compositions of the leachate solutions suggesting that the ERSA/EID procedures are robust. Slight increases in Ca, Sr, and Ba concentrations occur with increasing ERSA leaching times (Task C).

This raises the possibility that although the general behaviour of these constituents is dominated by ion exchange during the ERSA leaching step, with increasing reaction time, dissolution of certain mineral constituents may contribute to their concentration in the leachate. Alkalinity also increases with reaction time supporting the possibility that carbonates may be dissolved and suggesting that sampling/analytical uncertainty may be masking reaction effects on this constituent. Much of the Mg and Ca released via dissolution of carbonates has been taken up on ion exchange sites, at least at higher S:L ratios. At lower S:L ratios it may be that Mg released by dissolution of dolomite has exceeded that capable of being taken up on ion exchange sites (possibly due to greater undersaturation of leachate solutions with respect to dolomite and the smaller number of ion exchange sites?). With increasing S:L ratios, the effects of reaction on the EID and ERSA leachate samples increases as shown by the increasing deviation between the leachate analyses and formation water dilution line (see Figure 4). Given the nature of the reactions thought to be occurring during the leaching steps this result is expected.

Estimated formation water compositions

In this study, formation water concentrations are calculated from ERSA leachate analyses using:

$$FW_x = C_{L,x} \cdot \left(\frac{V_L}{\varphi . S_W . V_C} + 1 \right) \qquad \text{Eq. 1}$$

Where: FW_x = Concentration of constituent X in the formation water (mg/l).
$C_{L,x}$ = Concentration of constituent X in the leachate (mg/l).
V_L = Volume of leachate (cm^3).
V_C = Volume of core (cm^3).
φ = Fractional porosity of core.
S_W = Fractional water saturation of core.

For Cl, the majority of calculated formation water concentrations are within ±10% of that of the synthetic formation water (see Figure 5a). Such results are good given that uncertainty on the formation water analyses themselves is ~±3.6%RSD (±7.2% for 2xRSD). Other studies have also shown that it is possible to obtain reasonable estimates of formation water Cl using the ERSA technique (McCoy et al., 1994; Woulé Ebongué et al., 2005).

There are, however, some samples lying outside this range (both above and below). The causes of these higher and lower values are not certain because there is not a good correlation between calculated formation water Cl and either the procedures adopted (i.e. leachate reaction time, degree of sample agitation, S:L ratio) or other sample variables (amount of drainage, permeability, porosity, presence of original formation water). Variations in procedure generally appear to have little effect on the estimated formation water Cl concentration except that lower values (but still within 10% of the expected values) were obtained when samples were shaken only once during the leaching step. The need to agitate the samples more frequently to release the formation water is consistent with the findings of Woulé Ebongué et al. (2005) who found that for their core samples, repeat leaching of core was necessary to release all the pore water.

The low estimated formation water Cl concentration obtained from a sub-sample of core G1 (Figure 5a) appears to be an isolated 'error' that may be the result of greater drainage from this section of the core plug during storage relative to other sections, lower porosity in this section, an isolated error in procedure (e.g. incomplete grinding of the sample) or a combination of these factors. It is notable that this sample was incompletely cleaned although it is not known whether or how this might have affected the estimated formation water Cl concentration.

The high estimates of formation water Cl concentration could be the result of the presence of original formation water (or remnant salts from this formation water) in the unconnected porosity of the samples. Equally, the high formation water Cl might be due to the porosity in the sample being higher in that section of core relative to that recorded for the whole core plug during the core flood. Core plug A3 is notable for its unusually low flowing porosity (Table 1) combined with low permeability relative to the other samples. Also, the A3 samples have Br concentrations at the higher end of values observed in the samples overall. Assuming the original Clair formation water contains ~24-27 mg/l Br, calculations indicate that the A3 results are most likely to be the result of the presence of ~0.13 unconnected porosity filled with remnant salts of the original formation water. So, the total fractional porosity of the A3 core (~0.23) may be similar to that of the other core samples (see Table 1). For the sub-samples of D1 and G2 giving high formation water Cl concentrations, it is less clear which of the two possible causes might explain the results and so it may be a combination of each. These examples demonstrate that multiple factors can cause the observed ‘anomalous’ results and therefore may explain why there is no strong correlation between the different factors and calculated formation water Cl concentrations. It is also possible that the effects of some of the factors oppose each other resulting in more samples giving ‘reasonable’ results.

The factors affecting calculated formation water Cl concentrations should also affect those of the other ions in a similar way if they are not significantly affected by reaction or sampling/analytical uncertainty. This can best be seen in the calculated Na concentrations which like Cl, also generally lie within ±10% of the expected values (Figure 5a). However, for all the other constituents, additional and more dominant factors result in the estimated formation water compositions being ‘poor’ (i.e. deviate from the synthetic formation water composition by more than ±10%). For alkalinity and iodide the results are within ±65% and ±75% of the actual synthetic formation water concentration respectively (except for C2 and C3 samples which give anomalously high iodide) primarily due to high sampling/analytical uncertainty. For the other ions, the effects of reactions occurring in the leaching step result in biases in the calculated formation water concentrations relative to those of the synthetic formation water:

1. All calculated K concentrations are more than 10% higher, and particularly those derived from samples with low leachate Cl concentrations and S:L ratios.

2. Calculated Ba, Sr and Ca concentrations are more than 10% lower (Figures 5b and 5c; only Ca and Ba shown).

3. Most calculated Mg concentrations lie below the 10% band except for those derived from samples with low leachate Cl concentrations and S:L ratios which lie within or above the 10% band.

4. Where SO_4 is above the detection limit in the leachate, all calculated SO_4 concentrations are more than 10% higher (Figure 5d).

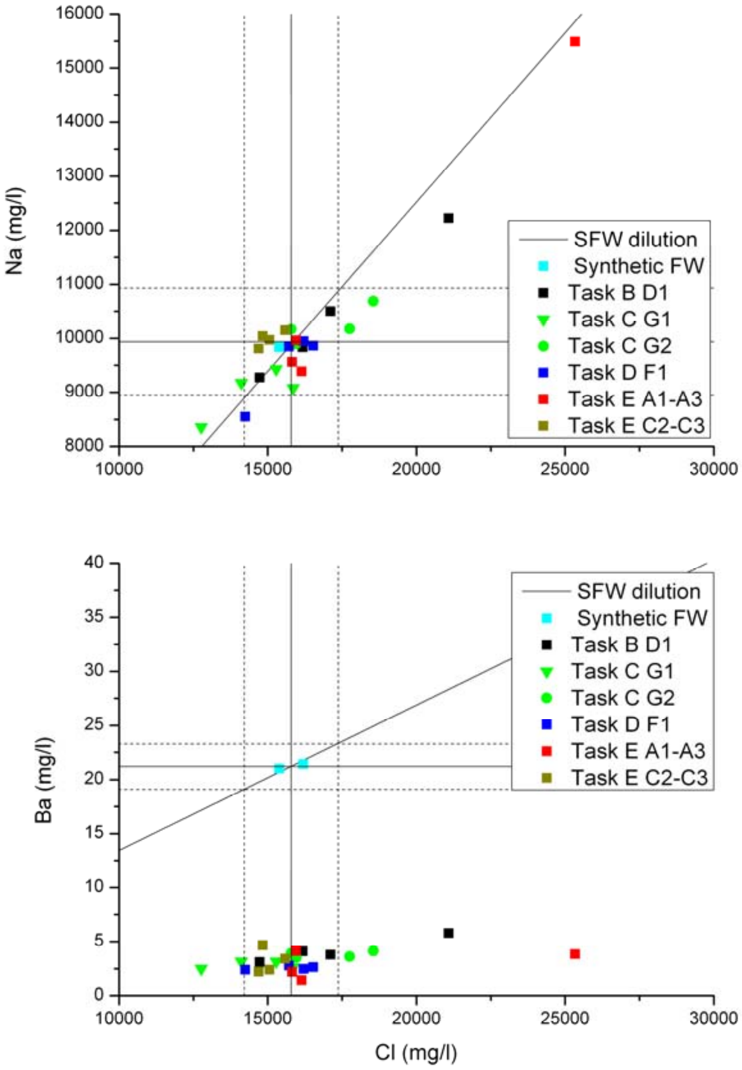

Figure 5 **ERSA-derived formation water compositions: (a) Cl v Na, (b) Cl v Ba. Also shown are the synthetic formation water dilution line, and the synthetic formation water composition (solid lines) (± 10% = dotted lines).**

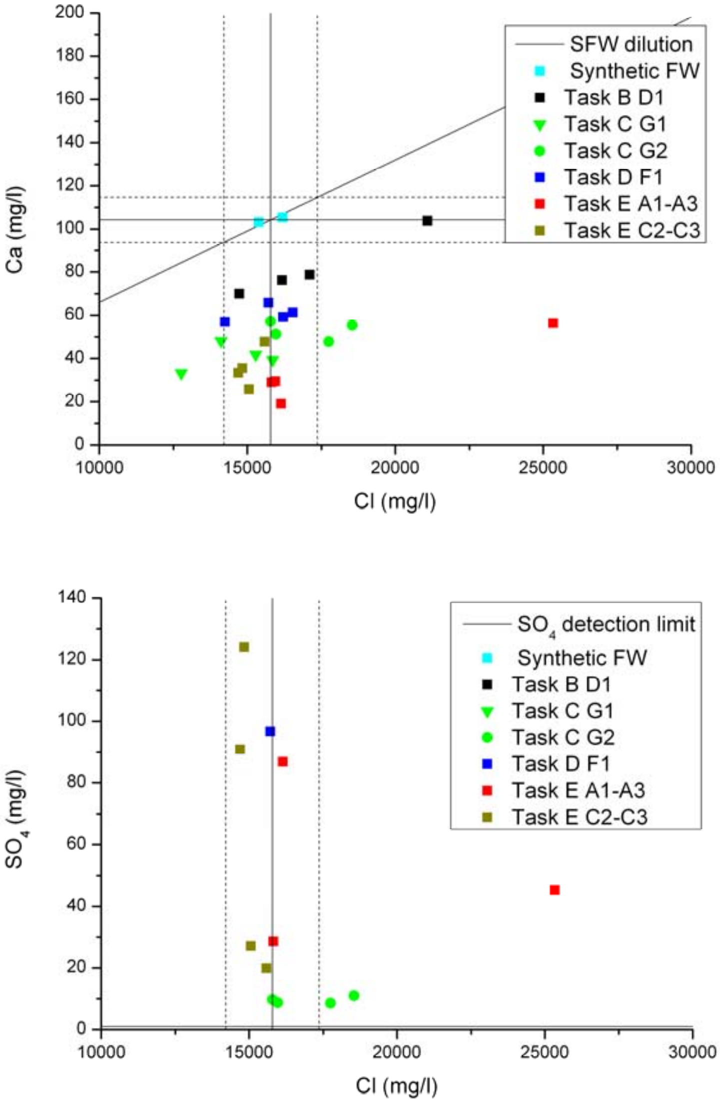

Figure 5 **ERSA-derived formation water compositions: (c) Cl v Ca, (d) Cl v SO_4. Also shown are the synthetic formation water dilution line, and the synthetic formation water composition (solid lines) (± 10% = dotted lines).**

These biases are expected for a method that does not account for the effects of reaction during the leaching step. Indeed, this is the reason why Bradbury and Baeyens developed their method which attempts to correct for these reaction effects.

Correcting for reaction effects

The Bradbury and Baeyens (1998) method of correcting for reaction effects involves using both ERSA and EID leachate analyses obtained from adjacent core samples. The method requires several assumptions to be made:

1. All Cl and SO_4 released during the EID/ERSA leaching steps is associated with formation water.

2. The formation water has a Na/Cl mole ratio of 1 so that the amount of Na displaced from ion exchange sites during the EID/ERSA leaching steps is the excess of Na over Cl (in meq/kg rock).

3. K, Ca, and Mg (meq/kg rock) in the EID leachate solution after leaching has only been displaced from the ion exchange sites (i.e. none from the formation water).

4. K in the ERSA leachate has been released from ion exchange sites only.

5. The formation water is originally in equilibrium with calcite and dolomite

The method allows the original ion exchange site occupancy of the core to be calculated along with Na-K, Na-Mg, and Na-Ca ion exchange selectivity coefficients from which formation water Ca, Mg and K concentrations can be calculated. Formation water Cl and SO_4 concentrations are calculated using Equation 1 and Na is calculated by charge balance. Although not part of their model, Ba could be estimated assuming $BaSO_4$ saturation in the reservoir (where this is present) and alkalinity and pH can be estimated assuming equilibrium with calcite and petroleum CO_2. At present, Sr concentrations cannot be calculated unless equilibrium with $SrSO_4$ in the reservoir can be assumed.

Although it was originally intended that this methodology would be applied to the A and C core sample results (Task E), it was only possible to apply this methodology to the latter. This was because there was no molar excess of Na over Cl in the ERSA leachate solution for the A core. Although not evident from the XRD analyses, after allowing for the presence of formation water in the EID solutions, and assuming the remaining concentrations are the result of displacement from ion exchange sites, the CEC for the A1, A3, C2 and C3 cores were calculated to be ~0.3-0.5, ~0.7, ~0.75 and ~0.7-0.95 meq/100g rock respectively. Therefore, it appears that the lower CEC of the A cores may have resulted in insufficient release of Na from ion exchange sites during the ERSA leaching step for it to be ‘detected’.

The results for the C core samples are summarised in Table 4. It can be seen that Ca, Mg, K and SO_4 concentrations are too high and Ba and Na concentrations too low relative to the synthetic formation water values. Also, the results vary significantly. The variability in the results and the differences between the calculated and actual formation water compositions are again probably due to the low CEC of even these samples. With low CEC, after correction for the presence of formation water, the amount of Na affected by ion exchange reactions is of a similar order to the uncertainty on the Na analyses. Also, the bias introduced by assuming Na/Cl mole ratio = 1 is relatively large when the amount of Na affected by ion exchange is low. The large uncertainty on the amount of Na released by ion exchange, results in large uncertainty in both original ion occupancy and ion exchange selectivity coefficients, hence affecting the quality of the estimates of formation water Ca, Mg and K concentrations. The elevated SO_4 in the leachate (due to reaction or presence of original formation water) results in low calculated Ba. These biases also result in a bias in Na which is calculated by ion balance.

The impact of low CEC and relatively large uncertainty on the leachate analyses is confirmed in Table 5. This shows estimates of formation water composition after (a) isolating the reaction component of the EID and ERSA leachate compositions by subtracting the component due to the presence of formation water, and (b) using a similar approach to that used in the Bradbury and Baeyens method to calculate the original ion exchange site occupancy and Na-K, Na-Mg, Na-Ca, Na-Ba, and Na-Sr ion exchange selectivity coefficients. It can be seen that even when corrections for the presence of formation water are accurate, the results are variable and although in some cases the estimates are improved (e.g. sample A1e), in others they are worse (e.g. sample C3c) than those shown in Table 4.

Constituent	**Synthetic FW (mg/l)**	**ERSA C3c (mg/l)**	**ERSA C3e (mg/l)**	**ERSA C2a (mg/l)**
Na	9,887	6,439	8,835	9,037
K	204	2564	453	606
Mg	58	409	98	125
Ca	104	922	249	426
Ba	21	2	1	3
Cl	15,790	15,063	14,694	15,590
SO_4	<1	27	91	20

Table 4 Estimated formation water compositions using the Bradbury and Baeyens methodology. Synthetic formation water analyses from Macaulay Institute (mean of 2 analyses, see Table 2).

Parameter	Synthetic FW	ERSA A1c	ERSA A1e	ERSA C3c	ERSA C3e	ERSA C2a
Solid: Liquid ratio		0.5	0.97	0.5	1	1.5
Na (mg/l)	9,887	8,567	10,032	2,039	8,439	9,108
K (mg/l)	204	415	190	709	378	414
Ca (mg/l)	104	244	57	57	354	350
Mg (mg/l)	58	715	27	3836	235	158

Table 5 Estimated formation water compositions using the mass balance approach. Synthetic formation water analyses from Macaulay Institute (mean of 2 analyses, see Table 2).

IMPLICATIONS FOR SCALE MANAGEMENT

Formation water Cl concentrations

Concentrations of scaling ions are often positively correlated with salinity (e.g. McCartney and Rein, 2005) and so understanding variations in formation water salinity across a field may aid predictions of scaling potential in wells. It may also help explain the unexpected occurrence of scaling in wells where it correlates with changes in salinity unrelated to injection water breakthrough. Therefore, it may be beneficial to obtain ERSA-derived estimates of formation water Cl concentrations from across the field during field development or subsequently if unexpected scaling occurs.

In agreement with other studies, we have demonstrated that reasonable estimates of formation water Cl can be obtained from ERSA samples although the conditions under which these can be obtained warrant further comment. Firstly, the need for accurate total porosity values for the core has been highlighted. Where porosity is homogeneous with depth over the cored interval, reasonable estimates of formation water Cl concentration would be expected using porosity determined from wireline logs or adjacent core samples. However, where porosity varies with depth, it is important to understand the variability and assess the potential impact of an incorrect total porosity being used (e.g. due to differences in log and core depths or due to differences in porosity between adjacent core samples). For a given percentage error in total porosity, a reciprocal percentage error in formation water Cl concentration will result. When porosity is low, the formation water Cl concentration will be particularly susceptible to large absolute errors with small percentage errors in porosity (see Equation 1).

In this study, water saturated core was used. However, undertaking ERSA on core from the transition zone or oil-leg is of interest because the formation water composition in these zones may differ from that in the underlying aquifer (e.g. (Coleman, 1993; Coleman, 1999) and obtaining samples of formation water from these zones may be difficult or impossible. Water saturation (S_W) is usually derived from adjacent core but again, it is important to understand variations in S_W where they occur to appreciate potential errors in the calculated formation water Cl concentration. This is particularly so in the oil-leg where S_W is low because small percentage errors in S_W can lead to large, reciprocal absolute errors in Cl concentration. For high temperature and pressure reservoirs, when using core S_W measurements, a further consideration is any bias caused by the transfer of H_2O between the petroleum phase and residual water as a result of pressure and temperature changes during core retrieval (McCartney and Østvold, 2005).

Drainage of formation water from our core samples does not appear to have significantly affected estimated formation water Cl concentrations, although their permeabilities were low. It is possible that core samples with higher permeabilities may suffer greater drainage prior to ERSA being undertaken on them leading to underestimates of formation water Cl. To minimise the effects of drainage, use of preserved core is recommended. Where cores have not been preserved the possibility of drainage should be considered. If cores are left unpreserved without drainage occurring (e.g. low permeability cores) there is a possibility that the formation water may evaporate, leaving residual salts in the pores. Due to the high solubility of evaporative Cl-bearing salts, these should easily be dissolved given sufficient reaction time and agitation. Although variants of the ERSA methods used in this study have been proposed to give reasonable estimates of formation water Cl concentration from dry core (e.g. American Petroleum Institute, 1998; Woulé Ebongué et al., 2005) our use of wet core means that it has not been possible to independently confirm the reaction time and degree of agitation required to completely dissolve Cl salts. Where Cl has not been completely dissolved, the formation water Cl concentration will be underestimated.

Core retrieved from a well might have been contaminated by drilling mud filtrate invasion during coring, by water used for washing down the core, by lubricant during core plugging, or by rainwater if the core is left exposed. Various precautions can be adopted to minimise/identify such problems. For example, using oil-based mud with tracer, minimizing mud overbalance, obtaining large diameter core (e.g. >5 inches), using low invasion coring techniques, plugging with base oil lubricant, obtaining vertical core plugs from the central axis of the core, avoiding exposure of the core to rain, and minimizing washing of the core. Depending on the relative concentrations of Cl in the formation water and in the mud/water, the ERSA-derived Cl concentration of formation water may be under- or overestimated.

Finally, we have shown that ERSA-derived Cl concentrations might be prone to local variations in core conditions or variations in some aspects of the ERSA procedure. It is therefore recommended that multiple ERSA analyses are undertaken on individual core samples to allow outlying data to be identified and experimental uncertainty to be determined.

Concentrations of scaling ions in formation water

Although understanding salinity variations may be useful in some aspects of scale management, it is an understanding of the variability of formation water scaling ions (Ba, Ca, Sr, and SO_4 assuming that alkalinity and pH can then be estimated via equilibrium with petroleum CO_2 and calcite) that is likely to be more widely useful. Like Cl, these ions are also subject to errors of the type discussed above, but in addition, they are prone to errors resulting from reactions occurring during the leaching step and as a result of retrieval of the core and drying of the core during storage.

Reactions may occur within the core during/after retrieval as a result of de-pressurisation and cooling of the formation water. Geochemical modelling might be used to investigate the reactions that could occur and how they may affect the ERSA-derived formation water compositions. Reactions can also occur as formation water evaporates resulting in changes to ion occupancy of the ion exchange sites and deposition of minerals that might not re-dissolve during leaching (e.g. $BaSO_4$). This can be avoided by using preserved core for ERSA.

It is evident from our study that reactions during leaching are not avoidable and for low clay content samples, with moderate formation water salinity, corrections are required for their effects. Although Bradbury and Baeyens (1998) have shown that their method appears to be successful on high clay content samples, this is not the case on the low clay content samples used in this study. The critical factor for successful use of the method is that a significant Na excess from ion exchange reactions (i.e. mNa/mCl >1) is identified in the leachate. This is likely to occur where CEC is high, mNa/mCl in the formation water is close to but less than 1, the S:L ratio is low and the formation water Na concentration and salinity is not high.

Geochemical modelling was used to help quantify these variables. Assuming leachate is added to a rock containing 10-15% mixed-clay (kaolinite, illite, smectite), with S:L=0.1 (a lower practical limit given the formation water compositions used in these calculations), a Na excess would not be detected once the TDS exceeded ~70,000 mg/kg because the analytical uncertainty ($2\sigma=\pm4\%$) on the leachate Na analyses would be too great. Significant increases in clay content and CEC raise this salinity but only by a few thousand mg/kg TDS. For this moderate clay content example, the minimum formation water mNa/mCl ratio required for excess Na to be identified in the leachate increases from 0.85 to 0.98 as the salinity rises from ~17,000 to ~48,000 mg/kg TDS and from 0.98 to 1 between ~48,000 and ~70,000 mg/kg TDS. With higher clay content, the minimum formation water mNa/Cl ratio required is reduced and vice-versa.

These preliminary calculations do not encompass all possible combinations of these variables, but they do suggest that this correction method might be successfully used on core samples containing moderate to high clay content (>10-15%) and low-moderate pore water salinity (<~50,000 mg/kg?). The higher the mNa/mCl ratio of the formation water, the better but some screening of formation water compositions would need to be undertaken to ensure that formation waters with mNa/mCl>1 are unlikely to occur in the area. Any molar Na excess over Cl in the formation water would be interpreted as an effect of ion exchange in the leachate and lead to over-correction for reaction effects.

Although the Bradbury and Baeyens method did not originally account for Ba, an upper limit for its concentration in the formation water can be estimated assuming equilibrium with $BaSO_4$ in the reservoir. However, it is important to avoid oxidation of core samples and use of $BaSO_4$ in the drilling mud if reliable formation water SO_4 concentrations are to be obtained. In formation containing $SrSO_4$, formation water Sr might also be estimated assuming equilibrium with this mineral, but otherwise, methods for correcting for reaction effects on Sr are currently not available.

Evidently, where sands are clean, with no clay content, corrections for ion exchange reactions would not be required although where carbonates and more soluble sulphates are present, it may be that reaction times would need to be limited to minimise their dissolution. Also, as formation water salinity increases, the effects of reaction will decrease relative to the concentrations in the leachate. For example, Tables 6 and 7 show original formation water compositions for Gyda (McCartney et al., 2007) and another North Sea field (unpublished). Geochemical modelling was used to predict ERSA leachate compositions for each assuming S:L=1, only ion exchange reactions occur and the clay content is ~4% and 15% mixed clay ('low' and 'high' clay respectively). The formation water compositions have then been re-calculated using Equation 1. It can be seen that when salinities are high (e.g. for Gyda with 230,000 mg/kg TDS) and clay content is low, the calculated formation water compositions are good (i.e. within typical sampling/analytical uncertainty for water samples, other than for K). This may explain why, in some cases, ERSA-derived formation water compositions appear to be consistent with those obtained from water samples (e.g. McCartney et al., 2004; Webb and Kuhn, 2004). However, when clay contents are high at these salinities, or when the clay content is low to moderate with formation water salinity ~100,000 mg/kg (e.g. North Sea Field A), the errors in the estimated formation water compositions are again significant.

Constituent	**Actual FW (mg/l)**	**Low Clay**		**High Clay**	
		Re-calculated FW (mg/l)	**Error (%)**	**Re-calculated FW (mg/l)**	**Error (%)**
Na	47,570	49,342	4	54,392	14
K	5,234	5,959	14	7,382	41
Ca	32,190	30,485	-5	25,903	-20
Mg	1,718	1,616	-6	1,354	-21
Ba	885	829	-6	686	-22
Sr	1,125	1,055	-6	879	-22
Cl	141,400	141,400	0	141,400	0
SO_4	4.37	4.37	0	4.37	0

Table 6 Comparison of original and re-calculated formation water composition for the Gyda Field.

Constituent	**Actual FW (mg/l)**	**Low Clay**		**High Clay**	
		Re-calculated FW (mg/l)	**Error (%)**	**Re-calculated FW (mg/l)**	**Error (%)**
Na	34,930	36,579	5	38,087	9
K	722	816	13	815	13
Ca	2,947	1,740	-41	671	-77
Mg	336	202	-40	82	-75
Ba	166	91	-45	35	-79
Sr	190	104	-45	41	-78
Cl	60,950	60,950	0	60,950	0
SO_4	4.7	4..7	0	4.7	0

Table 7 Comparison of original and re-calculated formation water composition for North Sea Field A.

CONCLUSIONS

1. ERSA-derived formation water compositions are potentially a very useful aid to scale management but there are uncertainties over the quality of these data.

2. This study has shown that core can be flooded to generate core samples of sufficiently good quality to allow the accuracy of ERSA technique to be assessed.

3. Application of ERSA to such core samples has shown that ERSA can provide reasonable estimates of formation water Cl concentrations in the water-leg where S_W and porosity data for core can be obtained. However, to obtain reliable results from field core samples, careful planning is

required to ensure optimum coring, core plugging and core storage conditions.

4. With the core used in this study, estimates of formation water concentrations of other ions were prone to error, primarily as a result of ion exchange reactions occurring during the ERSA leaching step.

5. However, geochemical modelling suggests that reasonable estimates of formation water concentrations of these other ions might also be obtained from water-leg core where it is either clay-free or if the formation water salinity is high (>~200,000 mg/l TDS) and the clay content is low (<~5%) because reaction effects may not be significant. Validation of these conclusions could be achieved via additional laboratory experiments of the type reported in this paper.

6. Under all other conditions, correction for reaction effects is likely to be required. Published correction methods may be successful where the formation water salinity has mNa/mCl close to, but less than, 1, where clay contents are moderate to high (>10-15%) and salinity is low to moderate (<~50,000 mg/l). For other conditions, new correction methods need to be developed if ERSA-derived formation water compositions are to be more widely used.

7. Although ERSA can also be used to estimate formation water compositions from oil-leg core samples, these results may be particularly prone to uncertainty where small errors in S_W or porosity occur.

8. This study has shown that geochemical modelling is a useful tool for predicting, at least qualitatively, effects of reactions on ERSA-derived formation water compositions. It can therefore help with decisions to obtain ERSA data and also highlight uncertainties in data already obtained.

ACKNOWLEDGEMENTS

We thank the management of BP, GeoScience Limited, Isotopic Ltd and Heriot-Watt University for permission to publish this paper. The ERSA and EID tests and associated water analyses were carried out by Macaulay Analytical, the analytical laboratory of the Macaulay Institute.

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