

Conditions under which anhydrite precipitation can occur in oil reservoirs as a result of seawater injection

R. A. McCartney (GeoScience Limited)

ABSTRACT

Recently, precipitation of sulphate minerals in oil reservoirs as a result of mixing of injected seawater and formation water has been the subject of extensive investigation. Of particular interest to scale management is that this process causes a reduction in produced water sulphate mineral scaling potential leading to significant reductions in scale mitigation costs against those originally anticipated. Most interest has focused on BaSO_4 because it is a more common scaling mineral but deposition of CaSO_4 (anhydrite) in the reservoir has the greatest potential to reduce sulphate mineral scaling potentials where Ca-rich formation waters are present.

To better understand the conditions under which the latter process will occur, predictions of sulphate mineral deposition in the reservoirs of 81 fields in the UK North Sea (UKNS) and Norwegian Continental Shelf (NCS) have been undertaken. In each case, it has been assumed that the reservoirs are under seawater flood and sulphate mineral deposition occurs only as a result of heating of injected seawater and mixing of seawater and formation water, the mechanisms by which sulphate minerals are most likely to precipitate.

These calculations have shown that deposition of CaSO_4 is likely to be a relatively common process in UKNS and NCS reservoirs, and in almost 1 in 4 fields it is likely to cause a significant reduction in sulphate mineral scaling potential. The amount of deposition of CaSO_4 in the reservoir is mainly dependent on the Ca content of the formation water and the reservoir temperature. The minimum temperature observed where significant deposition has been predicted (and therefore significant SO_4 loss) is 105°C . Generally, significant deposition also occurs where formation water is Ca-rich ($>6,000$ mg/l Ca) but as temperature also plays a role, there are exceptions (i.e. in some cases, below $\sim 133^\circ\text{C}$, Ca concentrations need to be greater and vice-versa). Ca-rich formation water usually has elevated salinity ($>70,000$ mg/l Cl). Significant CaSO_4 deposition and SO_4 removal is predicted to occur in deep reservoirs with Ca-rich formation water and in particular those located in the Skagerrak Formation (Triassic), Pentland (M. Jurassic), Ula/Gyda Formation (U. Jurassic), and Fulmar Formation (U. Jurassic) of the Central Graben overlying the Zechstein Formation, although they can be located elsewhere if geological conditions are favourable.

Based on the results of this study, the anticipated effect of sulphate mineral deposition on produced water compositions during the well life cycle is described with particular reference to reservoirs that are either more, or less, heterogeneous. Tools available for quantitative prediction of produced water compositions when sulphate mineral deposition occurs in the reservoir are also discussed.

The results of this study may aid identification of those fields under development where precipitation of CaSO_4 in the reservoir should be considered during scale management planning. They may also help explain observed trends in produced water scaling ion concentrations and sulphate mineral scaling potentials where CaSO_4 deposition is occurring in the reservoir.

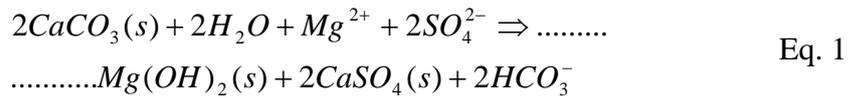
INTRODUCTION

Production wells in many North Sea reservoirs are at risk of BaSO₄, SrSO₄ or CaSO₄ (anhydrite) scaling during seawater flood due to the mixing of SO₄-rich seawater and Ba, Sr-, or Ca-rich formation water. During development planning, scaling risks are identified, scale inhibitors are selected, MICs (Minimum Inhibitor Concentrations) are determined, and scale mitigation costs are estimated, often on the assumption that these two fluids will simply mix in the production well during production. However, several studies have recently shown that BaSO₄ and CaSO₄ can also deposit in the reservoir via the same process (Bertero et al., 1988; Graham et al., 2002; Mackay, 2003a, b; Mackay and Graham, 2003; Mackay and Jordan, 2003; Mackay et al., 2004; Mackay et al., 2003; Mackay et al., 2006; McCartney et al., 2007; Paulo and Mackay, 2001; Petrovich and Hamouda, 1998; Sorbie and Mackay, 2000; White et al., 1999). It is likely that this is also the case for reservoirs where there are SrSO₄ scaling risks. This phenomenon has attracted much interest because where these minerals precipitate in the reservoir, the scaling risks and scale mitigation costs can be much less than originally anticipated. In some cases, it may also be that different inhibitors might have been chosen or lower MICs may have been determined if deposition of scale in the reservoir had been considered.

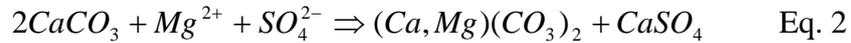
Deposition of CaSO₄ in the reservoir is of particular interest because formation water Ca concentrations are usually significantly in excess of SO₄ in seawater in molal terms. When CaSO₄ deposition occurs in the reservoir, much less SO₄ (and to a lesser extent Ca) will enter the production well than expected. Being the common scaling ion for CaSO₄, BaSO₄ and SrSO₄, this reduction in produced water SO₄ causes a reduction in the scaling risks of all sulphate scale minerals in the production well. In contrast, where BaSO₄ precipitates in the reservoir, because seawater SO₄ is usually significantly in excess of Ba in formation water in molal terms, much less Ba enters the production well than expected for simple mixtures of seawater and formation water, but not so much SO₄ is removed so only the production well scaling risk for BaSO₄ is significantly affected.

CaSO₄ is not a common production well scaling mineral but it has been observed in high temperature fields under seawater flood where Ca-rich formation water and seawater mix in the production well at elevated seawater fractions (e.g. 70-80%) (Graham et al., 2003; Stalker et al., 2005; Todd et al., 1994). It differs from BaSO₄ and SrSO₄ in that not only can it precipitate in the reservoir via this process during seawater flood but it can also precipitate from the injected seawater via several different mechanisms (McCartney et al., 2007):

1. **Heating of seawater.** Because CaSO₄ has retrograde solubility (Figure 1), CaSO₄ solubility can be exceeded when seawater is injected into higher temperature reservoirs (>~130°C) leading to CaSO₄ deposition.
2. **Precipitation of brucite from seawater.** Deposition of brucite (Mg(OH)₂) from seawater can induce calcite dissolution. The released Ca²⁺ ions can cause additional CaSO₄ precipitation. Where this reaction occurs, it can proceed until equilibrium between seawater, calcite, brucite and anhydrite is reached:



3. **Dolomitisation of carbonates by seawater.** Dissolution of calcite in the reservoir by seawater can result in precipitation of dolomite or Mg-calcite and CaSO₄. The reaction proceeds until equilibrium between seawater, calcite, dolomite (or Mg-calcite) and anhydrite is reached:



4. **Release of Ca via ion exchange.** During injection of seawater, Ca is displaced from ion exchange sites (e.g. on clays, micas, etc) and this can lead to CaSO₄ precipitation if CaSO₄ solubility is exceeded.

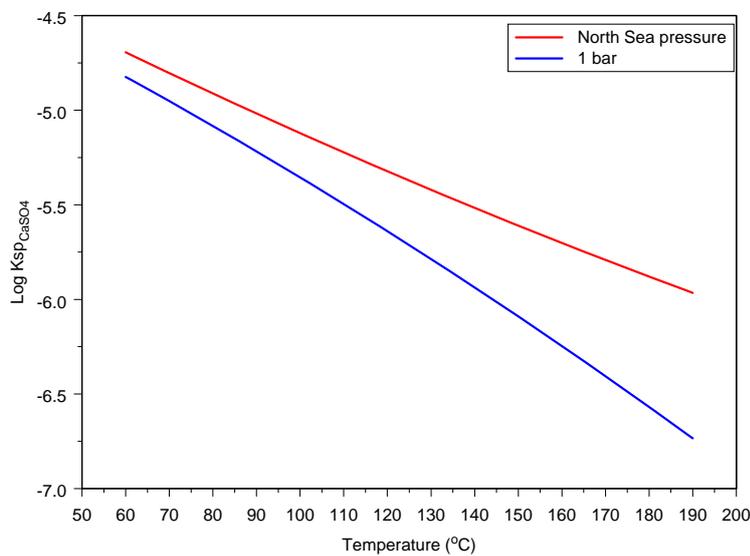


Figure 1 Solubility of anhydrite under increasing temperature at (a) 1 bar and (b) average North Sea reservoir pressures (for the given temperature).

Other than heating of seawater, a common theme in these SO₄ removal mechanisms is Ca release from the formation. Although not yet identified, it is possible that other reactions might release Ca²⁺ ions to seawater and induce CaSO₄ deposition (e.g. plagioclase dissolution). Also, as the solubility of CaSO₄ decreases with decreasing pressure (see Figure 1), it is possible that CaSO₄ precipitation might be induced during flow of fluids, saturated with respect to CaSO₄ at reservoir pressures, toward the production well. These fluids might be seawater, a mixture of seawater and formation water, or formation water.

Although these different mechanisms for deposition of CaSO₄ in the reservoir have been identified, little work has been undertaken to determine (a) how important they are with respect to the reduction of produced water sulphate mineral scaling potentials and (b) under what conditions they occur. In this paper, these aspects have been investigated for the two mechanisms thought to be most important in the Gyda reservoir (McCartney et al., 2007) and probably other reservoirs too: heating of

seawater and mixing between seawater and Ca-rich formation water. The relative importance of these mechanisms for sulphate removal versus BaSO_4 and/or SrSO_4 deposition in the reservoir is also discussed. This has been achieved by undertaking predictions of sulphate mineral deposition in the reservoirs of 81 fields in the UK North Sea (UKNS) and Norwegian Continental Shelf (NCS) under seawater flood conditions and assessing the impact on their produced water sulphate concentrations.

Based on the results of this study, the anticipated effect of sulphate mineral deposition on produced water compositions during the well life cycle is described with particular reference to reservoirs that are either more, or less, heterogeneous. Tools available for quantitative prediction of produced water compositions when sulphate mineral deposition occurs in the reservoir are also discussed. The results of this study may aid identification of those fields under development where precipitation of CaSO_4 in the reservoir should be considered during scale management planning. They may also help explain observed trends in produced water scaling ion concentrations and sulphate mineral scaling potentials where CaSO_4 deposition is occurring in the reservoir.

PREDICTION OF RESERVOIR DEPOSITION OF SULPHATES

Model selection

To assess the relative importance of the different processes referred to above with respect to SO_4 removal in the reservoir it is necessary to simulate (a) heating of seawater and (b) mixing of formation water and seawater in the reservoir. Standard oilfield software can be used for the former, but it is not designed to simulate the latter process. Although scaling software can quickly simulate mixing of fluids, the calculations simulate the effects of mixing them in fixed proportions similar to pouring two fluids into a beaker (Figure 2; flash model). The reservoir process is different in that it involves gradual mixing and displacement of formation water by seawater and reactive transport models are ideal for such predictions. The reservoir mixing process can be simulated using reactive transport software via two models. The more complex model accounts for mixing and displacement along a multi-cell flow path (e.g. 1-D flow path). The simpler 'flush' model simulates mixing and displacement in the first cell of this flow path (Figure 2). However, these calculations are time consuming to undertake, particularly for a study of this nature.

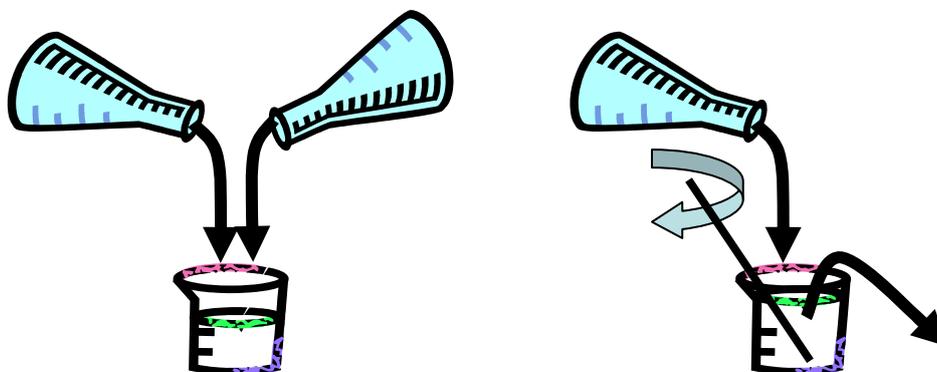


Figure 2 Conceptual models of flash and flush simulations.

An alternative approach is to manipulate flash calculation results to provide estimates of data that can be obtained from flush models. This is possible because both the flush and flash models produce water compositions that are identical after mixing and precipitation. By determining the change in mixing proportions of seawater and formation water with increasing seawater volume added to the cell (or pore space) (Figure 3) and knowing how the mixed fluid composition changes as a result of mixing and precipitation, the amount of precipitation of sulphate minerals in the pore space can be calculated. By comparing the results obtained by this method with those obtained via a reaction transport flush model, it was found that they agreed within 5% (Figure 4) if the cumulative mass precipitated up to 97.5% seawater was used from the flash calculation data (equating to passing ~3.7 pore volumes seawater through the pore). The cumulative mass precipitated from the flash data is significantly in error if it is calculated up to 100% seawater due to numerical errors (relatively large volumes of seawater, ~6, are required to displace the final 2.5% formation water).

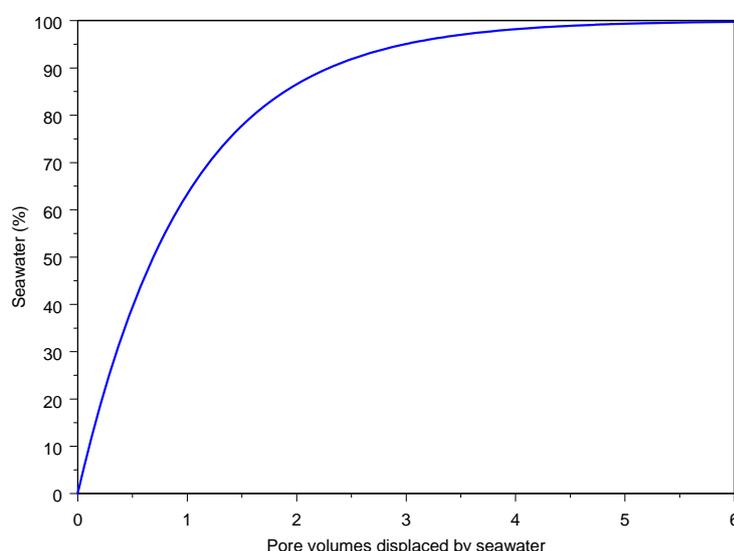


Figure 3 Flush model: Variation in percentage of seawater in a cell volume with increasing volume of injected seawater.

It should be noted that the flush model only predicts mineral deposition on first development of the seawater-formation water mixing zone. With continued seawater injection, this zone is displaced across the reservoir and further dispersion-induced mixing and mineral deposition can occur. Under these circumstances reacted seawater from behind the mixing zone and formation water from in front of it are drawn into the mixing zone. Dispersion effects can be modelled using 1-D (or 2-D or 3-D) reactive transport models. SO_4 loss occurs via mixing with low SO_4 formation water (dilution effect) and additional sulphate mineral precipitation. Figure 5 shows the loss of SO_4 in the mixing zone for Gyda formation water as a result of heating, flush model mixing and 1-D reactive transport model dispersive mixing. It can be seen that SO_4 loss via additional dispersion is minor relative to that discussed above. So, although manipulated flash calculation results are not as accurate as those from the flush model or reactive transport models, it does allow the quick and reasonable estimation of the amount of sulphates that could deposit in the reservoir as a result of initial mixing of seawater and formation water. This method has therefore been used in this study.

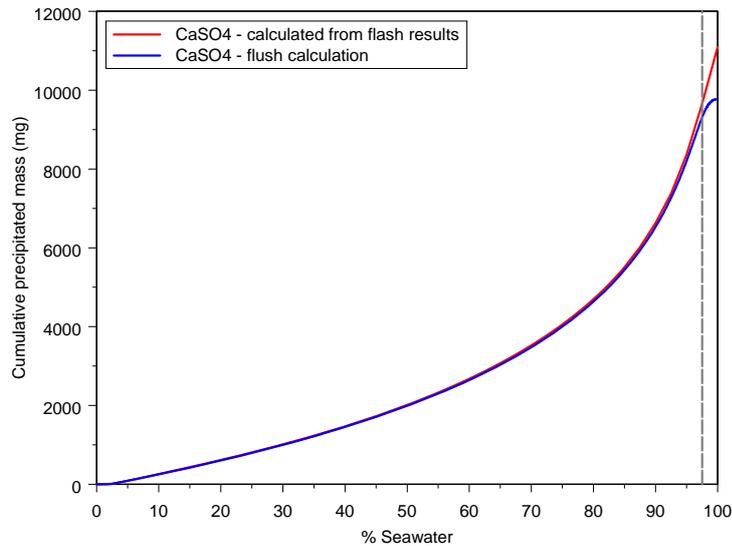


Figure 4 Comparison of the cumulative mass precipitated within the cell via the flush model against that estimated from flash calculations. Vertical line indicates the seawater fraction at which precipitated mass is estimated from flash calculations (97.5% seawater).

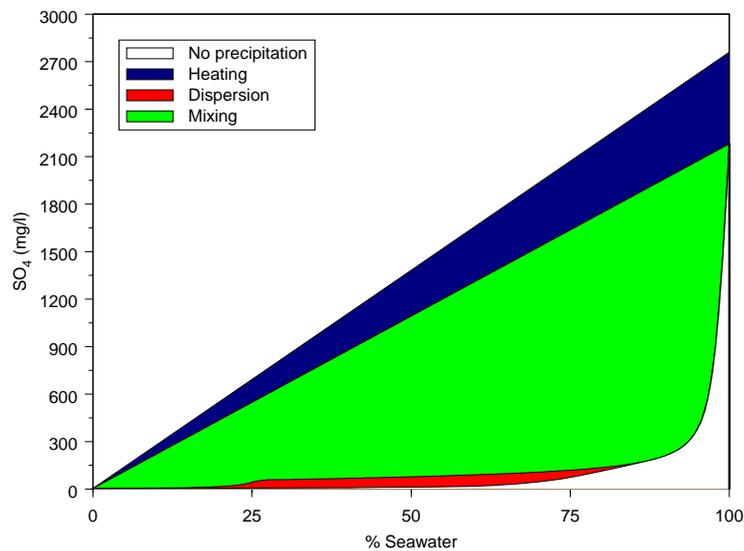


Figure 5 SO_4 loss from seawater-formation water mixtures. Coloured areas show SO_4 loss via heating, mixing (flash model) and dispersive mixing (1-D reactive transport model).

Calculations undertaken

MultiScale 6.1 (Petrotech, 2003) was used to undertake flash calculations involving seawater and formation water obtained from 81 fields (see Tables 1 and 2) in the NCS and central and northern UKNS for which reservoir temperature \pm pressure was

available. A total of 163 published formation water analyses were used (Falla et al., 2005; Graham and Mackay, 2004; Hardy and Simm, 1996; Jasinski et al., 1998; McCartney et al., 2006; McCartney et al., 2007; McCartney and Rein, 2005; Stalker et al., 2005; Stiegler Øye et al., 2006; Warren and Smalley, 1994; Ziegler et al., 2001). These are believed to be of reasonable quality on the basis that there are no comments in the original source publications suggesting they are not. Where Ba, Sr or SO₄ analyses were not available it was assumed that they were 0 mg/l. Where reservoir pressure was not available, it was estimated using a regression through pressure and temperature data in Warren and Smalley (1994) (Figure 6; Eq. 2).

$$P_r = 76.53 \cdot \exp^{(0.0141 \cdot T_r)} \quad \text{Eq. 2}$$

Where:

P_r = Reservoir pressure (bar)

T_r = Reservoir temperature (°C)

Where CaSO₄ deposition as a result of heating of seawater to reservoir temperature was predicted, additional flash calculations were undertaken using CaSO₄ equilibrated seawater (i.e. Ca and SO₄ removed in equimolar proportions until the saturation ratio of CaSO₄ = 1 for the seawater).

Amongst other information, the following were calculated for each formation water sample and are discussed in the remainder of the paper:

1. The saturation state of seawater and the formation water with respect to CaSO₄ at reservoir temperature and pressure (SR_{CaSO4}).
2. The amount of SO₄ removed from seawater as a result of heating it to reservoir temperature.
3. The types of sulphate mineral that precipitate in the reservoir.
4. The average amount of SO₄ removed from seawater during initial development of the seawater-formation water mixing zone as a result of CaSO₄, BaSO₄ and SrSO₄ precipitation.

It is important to emphasise that these predictions have been made to understand the conditions under which CaSO₄ might precipitate in the reservoir. In some cases the calculations are hypothetical because a seawater flood has not been undertaken on fields identified.

RESULTS

Anhydrite deposition from injected seawater

CaSO₄ precipitation from seawater as a result of heating to reservoir temperature was predicted in 31 cases (19%) from 22 fields (27%; Table 1). The trend in SR_{CaSO4} is primarily determined by the temperature; the solubility of CaSO₄ decreases with increasing temperature thereby causing SR_{CaSO4} to increase (Figure 7). Scatter about this trend reflects variations in reservoir pressure.

Table 1 Fields affected by CaSO₄ precipitation or where SR_{CaSO4} (mix) > 1.

Field	Mixing seawater and formation water				Heat
	SR _{CaSO4} >1	Reservoir precipitates			CaSO ₄
		CaSO ₄	BaSO ₄	SrSO ₄	
Albuskjell	✓	✓	✓	✓	✓
Asgard	✓		✓	✓	
Auk	✓	✓	✓	✓	
Birch			✓	✓	✓
Brage	✓	✓	✓	✓	
Brage*	✓		✓	✓	
Bruce	✓	✓		✓	
Buchan	✓	✓	✓	✓	
Clyde	✓	✓	✓		✓
Crawford	✓	✓			
Crawford*	✓		✓	✓	
Cyrus	✓	✓	✓	✓	
Don	✓		✓		
Edda					✓
Ekofisk	✓	✓	✓	✓	
Ekofisk*	✓	✓	✓		✓
Ekofisk*	✓	✓	✓	✓	✓
Eldfisk			✓	✓	✓
Elgin	✓	✓	✓		✓
Forties	✓		✓	✓	
Fram			✓		✓
Fulmar	✓	✓		✓	✓
Gyda	✓	✓	✓		✓
Heidrun	✓	✓	✓		
Heimdal	✓	✓	✓	✓	✓
Heron	✓	✓	✓		✓
Highlander	✓	✓	✓	✓	
Hild	✓	✓	✓		✓
Ivanhoe	✓	✓	✓	✓	
Kittiwake	✓	✓	✓		✓
Kristin	✓	✓	✓		✓
Njord	✓	✓	✓	✓	
Njord*	✓		✓	✓	
Oseberg East			✓	✓	✓
Oseberg East*			✓		✓
Oseberg South	✓	✓	✓	✓	
Oseberg Vestflanken	✓	✓	✓	✓	
Rob Roy	✓	✓	✓	✓	
Scott	✓	✓	✓	✓	
Shearwater	✓	✓	✓		✓
Skua	✓	✓	✓		✓
Sleipner West	✓	✓	✓		✓
Snorre	✓	✓		✓	
Statfjord			✓		✓
Tambar	✓	✓	✓		✓
Tor	✓	✓	✓		✓
Varg	✓	✓	✓		
Varg*	✓	✓	✓	✓	

* Variation in formation water composition causes variation in results.

Table 2 Fields not affected by CaSO₄ precipitation and where SR_{CaSO4} (mix) < 1.

Argyll	Deveron	Hutton	Scapa
Beatrice	Duncan	Magnus	Sleipner East
Beryl	Dunlin	Miller	Snorre*
Birch*	Eider	Murchison	South Brae
Brae	Ekofisk*	Ninian	Statfjord*
Brage*	Emerald	Norne	Statfjord North
Brent	Forties	North Brae	Tern
Brent South	Gjoa	Ormen Lange	Thistle
Bruce*	Grane	Oseberg	Tordis
Central Brae	Gryphon	Oseberg South*	Troll
Cormorant	Gulfaks	Oseberg West	Tyrihans
Cormorant North	Heidrun*	Osprey	Veslefrikk
Crawford*	Highlander	Piper	Visund

* Due to variation in formation water compositions in some fields, some samples for these fields are also included in Table 1.

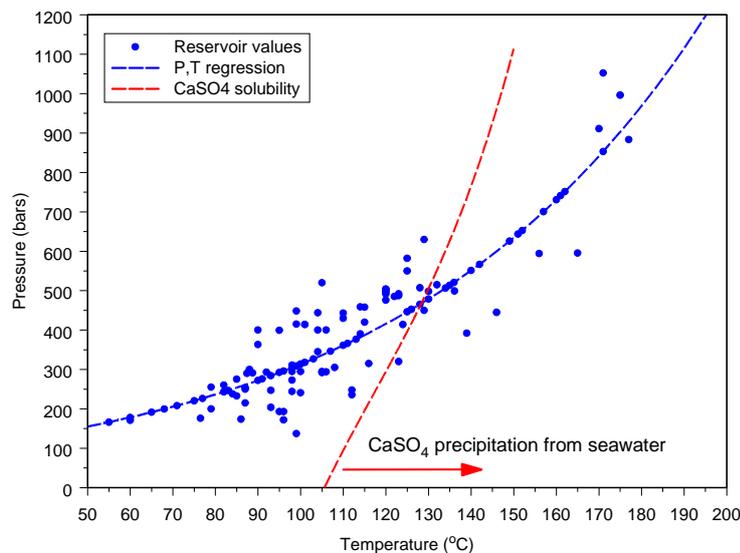


Figure 6 Variation of reservoir pressure and temperature in UKNS and NCS fields (Warren and Smalley, 1994) and comparison with CaSO₄ solubility in seawater (CaSO₄ precipitates from seawater to the right of the dashed red line). The blue dashed line is a regression through the reservoir pressure and temperature data.

The solubility of CaSO₄ increases with increasing pressure (Figure 1) so data lying below the general trend in Figure 7 are associated with higher pressure reservoirs and vice-versa.

Above ~129°C, seawater becomes oversaturated with respect to CaSO₄ so it can precipitate in the reservoir following injection and heating to reservoir temperature (Figure 7). The actual temperature at which SO₄ starts to be removed from injected seawater by this process is pressure sensitive (Eq. 3) and can occur at <129°C where the reservoir pressure is low.

$$P = -1.2649 \times 10^4 + 290.1192.T - 2.3041.T^2 + 0.0065.T^3 \quad \text{Eq. 3}$$

Given the range of reservoir pressures observed in the UKNS and NCS, the lowest temperature at which SO_4 is removed from heated seawater via CaSO_4 is likely to be $\sim 120^\circ\text{C}$ (reservoir pressure = 295 bar; see Figure 6). The depth at which this temperature is exceeded will vary with the geothermal gradient but based on a temperature–depth correlation for the North Sea, such temperatures are likely to occur at depths of greater than 2,700–4,200m.

Heating of seawater and consequent deposition of CaSO_4 in the reservoir is evidently not an important mechanism of removal of SO_4 at temperatures below ~ 120 – 129°C . However, as the reservoir temperature increases above this range it becomes increasingly important. In the highest temperature reservoir (177°C), 505 mg SO_4/kg H_2O is removed from seawater by this process (18% of seawater SO_4).

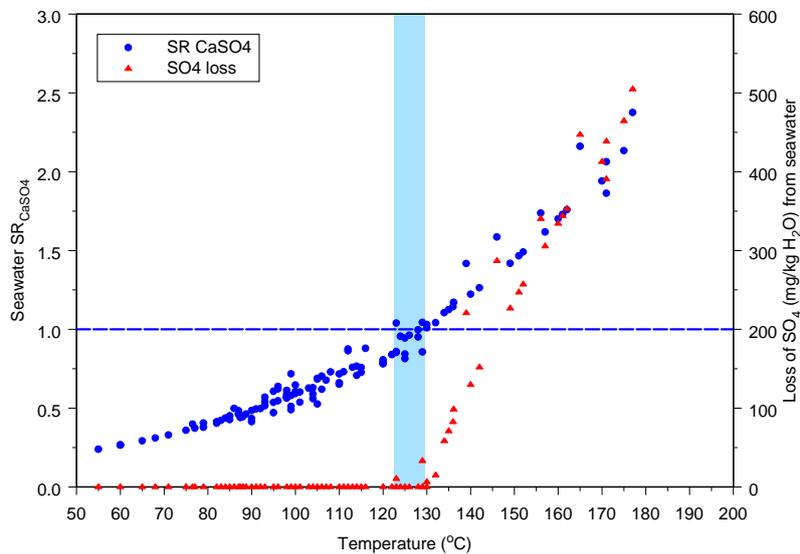


Figure 7 Variation of $\text{SR}_{\text{CaSO}_4}$ for seawater, and predicted loss of SO_4 from seawater as a result of CaSO_4 precipitation, with increasing reservoir temperature. Dashed blue line, $\text{SR}_{\text{CaSO}_4} = 1$. Blue band shows the temperature range over which precipitation of CaSO_4 from seawater may start.

Anhydrite deposition during mixing of seawater and formation water

Removal of SO_4 from mixtures of equilibrated seawater (i.e. after loss of CaSO_4 via heating to reservoir temperature) and formation water, as a result of CaSO_4 precipitation during development of the mixing zone, was predicted for 48 cases (29% of the samples) from 32 fields (40% of the field studied; Table 1).

In these cases, the amount of SO_4 loss is dependant on pressure, temperature and formation water composition (particularly Ca, Ba, Sr, SO_4 and salinity). The most important factor is the Ca content of the formation water which is positively correlated with both SO_4 loss and the peak $\text{SR}_{\text{CaSO}_4}$ observed during mixing (Figure

8). The lowest Ca content of formation water where CaSO_4 is predicted to deposit in the reservoir is 1,455 mg/l. The average amount of SO_4 loss per kg H_2O from seawater within the mixing zone was calculated by dividing the cumulative loss of SO_4 in the cell volume by 3.7 (number of cell volumes injected into the cell). The greatest average amount of SO_4 loss predicted to occur as a result of mixing of equilibrated seawater with formation water is 1977 mg/kg H_2O (70% of seawater SO_4 ; for formation water containing 45,200 mg/l Ca). In this case the peak $\text{SR}_{\text{CaSO}_4}$ during mixing was 13.1.

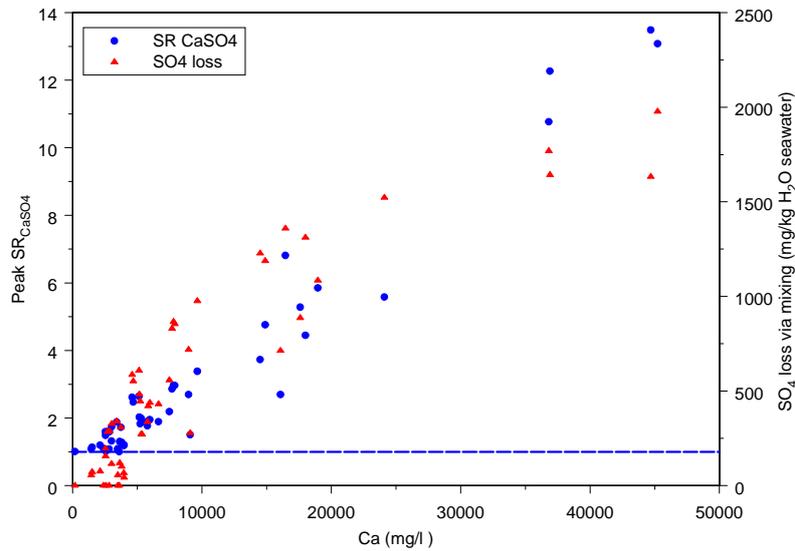


Figure 8 Peak $\text{SR}_{\text{CaSO}_4}$ and predicted average loss of SO_4 from seawater in the mixing zone via CaSO_4 precipitation with increasing formation water Ca content. Dashed blue line, $\text{SR}_{\text{CaSO}_4}=1$.

The scatter about the dominant trends in Figure 8 reflects the influence of the other variables. The influence of temperature on CaSO_4 solubility has been shown in Figure 1. After the Ca content of the formation water, temperature is the most important variable determining the occurrence of CaSO_4 precipitation in the mixing zone. For example, SO_4 loss in the mixing zone as a result of CaSO_4 precipitation can be predicted from reservoir temperature (T) and the Ca content of the formation water (FW_{Ca}) where (see Figure 9):

$$\text{FW}_{\text{Ca}} > 16594 - 197.9935.T + 0.632.T^2 \quad \text{Eq. 4}$$

The lowest temperature at which SO_4 removal via CaSO_4 deposition during mixing occurs is 87°C (9,100 mg/l Ca in formation water) whilst the highest temperature at which SO_4 removal does not occur via this process is 149°C reflecting the low Ca content of this formation water (76 mg/l).

The effect of pressure on CaSO_4 solubility has also been demonstrated in Figure 1. The effect of salinity is shown in Figure 10 where Cl is used as a proxy indicator of salinity. CaSO_4 solubility increases with salinity before decreasing again at elevated salinity.

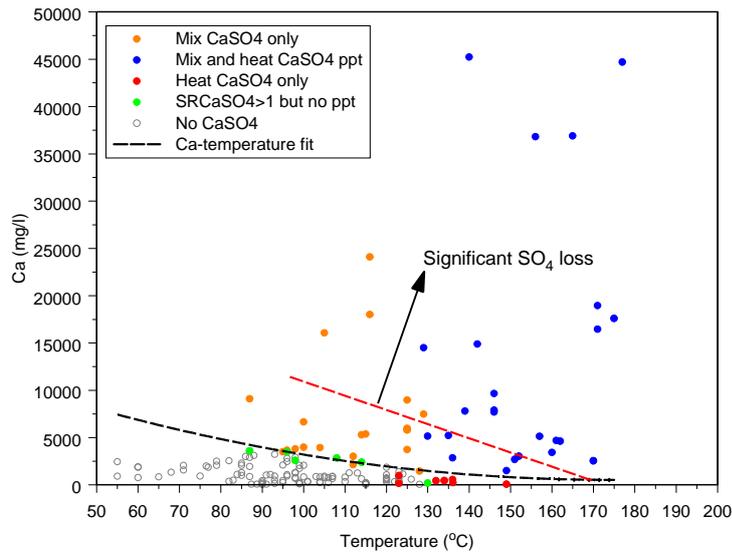


Figure 9 Variation of formation water Ca content and temperature. The Ca-temperature fit line shows the approximate relationship between these variables for the onset of CaSO₄ deposition during mixing with seawater. The dashed red line shows onset of significant SO₄ loss (see main text). Samples are categorised: (a) affected by mixing related CaSO₄ deposition only, (b) affected by mixing and heating associated CaSO₄ deposition, (c) affected by heating related CaSO₄ deposition only, (d) no CaSO₄ deposition but $SR_{CaSO_4} > 1$, and (e) no CaSO₄ deposition and $SR_{CaSO_4} < 1$.

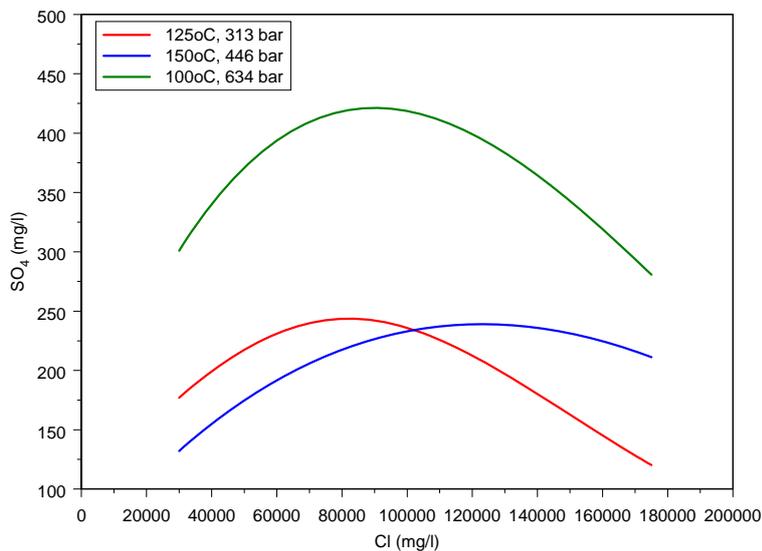


Figure 10 Variation of anhydrite solubility (as indicated by equilibrium SO₄ content of water) with increasing Cl (Ca fixed at 10,000 mg/l, Na set by ion balance with Na). Pressure at each temperature is an average at that temperature for the North Sea.

The peak solubility varies with both salinity and temperature (e.g. ~100, 80, and 125 g/l Cl at 100, 125 and 150°C respectively). As a result, some samples from higher pressure reservoirs or with formation water with moderate-high Cl content can lie above the line shown in Figure 8 without precipitation of CaSO₄ and vice-versa.

In only one case was CaSO₄ the sole sulphate mineral predicted to precipitate in the mixing zone. In most cases either BaSO₄ (19 cases) or BaSO₄ and SrSO₄ (23 cases) are predicted to co-precipitate with CaSO₄ (Table 1). In the other three cases, SrSO₄ is predicted to co-precipitate with CaSO₄. Co-precipitation of these additional sulphate minerals can remove SO₄ from solution and so reduce the amount of SO₄ precipitated in CaSO₄. So, some samples from reservoirs with formation water that is relatively enriched in Ba and/or Sr compared with Ca might lie above the line in Figure 9 without precipitation of CaSO₄ and vice-versa. For example, in 6 cases, mixing of formation water and equilibrated seawater resulted in fluids where SR_{CaSO₄}>1 (up to 1.1), but due to precipitation of BaSO₄ and SrSO₄, no CaSO₄ was predicted to precipitate from these fluids (see Table 1, Figure 9). It should be noted that CaSO₄ did precipitate from other samples with SR_{CaSO₄} up to 1.1 when relatively little BaSO₄ and/or SrSO₄ precipitation occurred.

Relative importance of CaSO₄ precipitation for SO₄ removal for water in the mixing zone

Figure 11 shows the average SO₄ loss from seawater in the mixing zone as a result of four processes: heating of seawater to reservoir temperature, and precipitation of CaSO₄, BaSO₄ and SrSO₄ on mixing the reacted seawater with formation water. Only those cases where SR_{CaSO₄} exceeds 1 are shown. The average removal of SO₄ from seawater in the mixing zone as a result of these processes can be as high as 2,360 mg/kg H₂O (84% of that in the injected seawater).

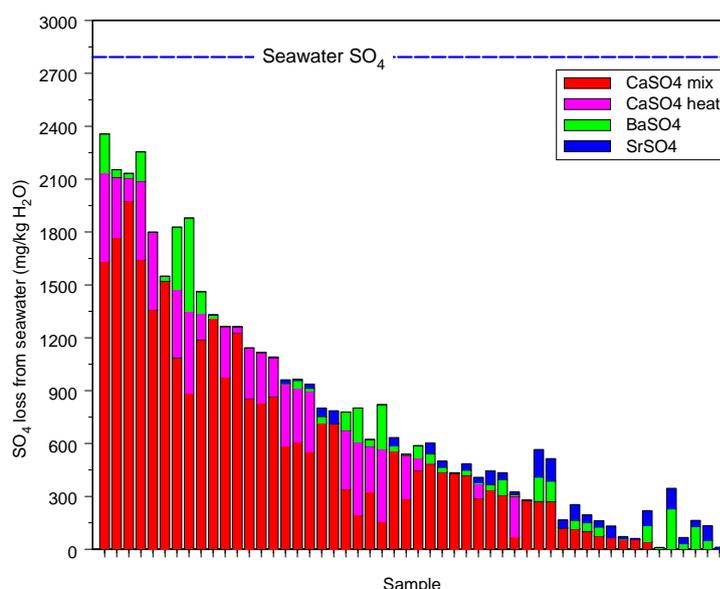


Figure 11 Comparing SO₄ loss resulting from heating of seawater and mixing of seawater and formation water (average SO₄ loss) as a result of CaSO₄, BaSO₄ and SrSO₄ deposition for all samples where SR_{CaSO₄}>1. Blue dashed line indicates unreacted seawater.

Mixing associated CaSO_4 deposition dominates SO_4 loss for all samples where formation water Ca content is greater than $\sim 6,000$ mg/l (Figure 12). Where the formation water is very Ca-rich ($> \sim 10,000$ mg/l), heating and mixing induced CaSO_4 deposition can remove between ~ 3 to 7 times the amount of SO_4 removed by BaSO_4 and SrSO_4 precipitation. Where Ca is less than $\sim 6,000$ mg/l Ca, the dominant source of SO_4 loss varies depending on the relative concentrations of Ba, Sr and Ca and the reservoir temperature. For example, when formation water Ca is less than 6,000 mg/l, and the temperature is elevated (> 120 - 129°C), heating might be the dominant SO_4 removal process; where Ba and/or Sr are elevated, BaSO_4 and/or SrSO_4 deposition may be dominant.

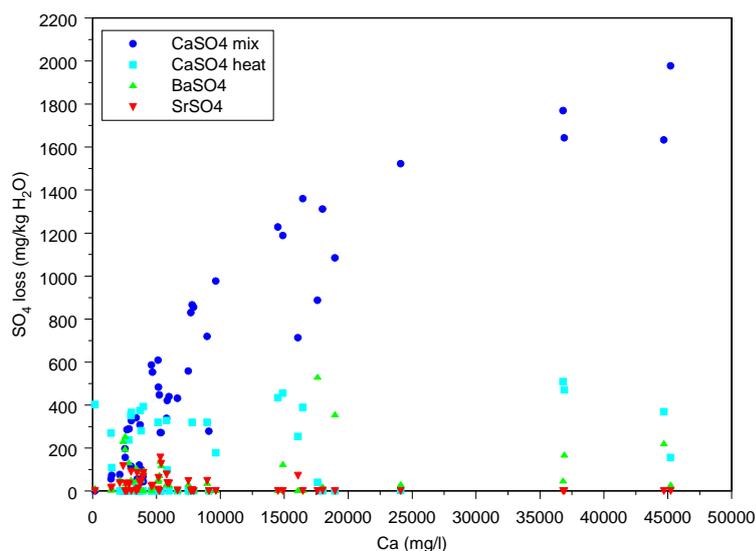


Figure 12 Average SO_4 loss from seawater in the reservoir mixing zone versus formation water Ca content for four different processes: CaSO_4 deposition (via mixing or heating), BaSO_4 deposition and SrSO_4 deposition.

CaSO_4 was predicted to deposit in the reservoir by mixing and/or heating in $\sim 26\%$ of cases (representing $\sim 46\%$ of the fields). Given that we have used a ‘random’ set of formation water analyses, this suggests that, unlike deposition of CaSO_4 in production wells, deposition of CaSO_4 in the reservoir is likely to be common. In those cases where SO_4 removal is greatest, the primary cause is CaSO_4 deposition via mixing and/or heating. Indeed, in 25 cases ($\sim 15\%$ of samples) from 19 fields ($\sim 23\%$ of fields), the average removal of SO_4 from seawater in the mixing zone by these processes was significant (at least 20%, see Figure 8). This level of SO_4 removal occurred where:

$$FW_{Ca} > 43200 - 386.2603.T + 0.7996.T^2 \quad \text{Eq. 5}$$

In most of these cases the Ca concentration in the formation water exceeded 6,000 mg/l but as temperature also plays a role, there are exceptions (i.e. in some cases, below $\sim 133^\circ\text{C}$, Ca concentrations need to be greater and vice-versa). The minimum temperature at which significant SO_4 loss via CaSO_4 deposition has been observed is 105°C .

Rate of CaSO₄ deposition in the reservoir

These predictions provide estimates of the effect of deposition of sulphates in the reservoir assuming there is sufficient time for this process to occur before the relevant water reaches the production well. In their study of the Gyda Field, McCartney et al. (2007) found that deposition of CaSO₄ in the injection well area, and CaSO₄ and BaSO₄ in the mixing zone in the reservoir, probably occurred within hours under their reservoir conditions (156°C). In most cases, transit times between injection and production wells will be of the order of months or more. Therefore although requiring further investigation it is believed that, at the temperatures at which Ca-rich formation waters are typically found (>~100°C), there will normally be sufficient time for deposition of sulphate minerals in the reservoir to occur, with the waters probably approaching equilibrium with respect to these minerals. The only time when this might not occur will be when a short transit time flow path is located between the injection and production wells.

Distribution of fields where significant CaSO₄ deposition is predicted

Figure 13 shows the distribution of fields in the UKNS, NCS and Danish sector where formation water Ca concentrations are known to exceed 6,000 mg/l (please note there may be other fields with Ca-rich formation waters of which the author is unaware). As discussed above, in most cases significant deposition of CaSO₄ is expected in these fields under waterflood conditions except in two cases where the temperature is too low (<~133°C, Auk Field and Crawford Field, see Figure 13). Generally Ca-rich formation waters occur in the Central Graben with further occurrences in the Outer Moray Firth and South Viking Graben. These formation waters are most prone to occur in particular formations. The highest Ca concentrations occur in the Skagerrak Formation (Triassic), followed by the Ula/Gyda Formation (U. Jurassic), the Fulmar Formation (U. Jurassic) and Pentland (M. Jurassic) Formation. These formations are consistently associated with high Ca formation waters. The reason why Ca-rich formation waters should be associated with these particular formations is not known with any certainty but it is likely to be related to a combination of coincident factors.

Firstly, the origin of these Ca-rich formation waters is likely to be related to the distribution of the Zechstein (salt) Formation because:

1. Ca-rich formation waters tend to have high salinity (>~70,000 mg/l Cl; Figure 14).
2. Most locations where they have been identified are underlain by the Zechstein Formation (Figure 13).
3. Most Ca-rich formation waters occur just above the Zechstein Formation (i.e. the Skagerrak Formation).
4. Within each of these formations, Ca and Cl increase with depth at the field or local scale (i.e. where two or more fields are in close proximity) toward the Zechstein Formation. The lack of regional depth correlations reflects the complex geology of this area.

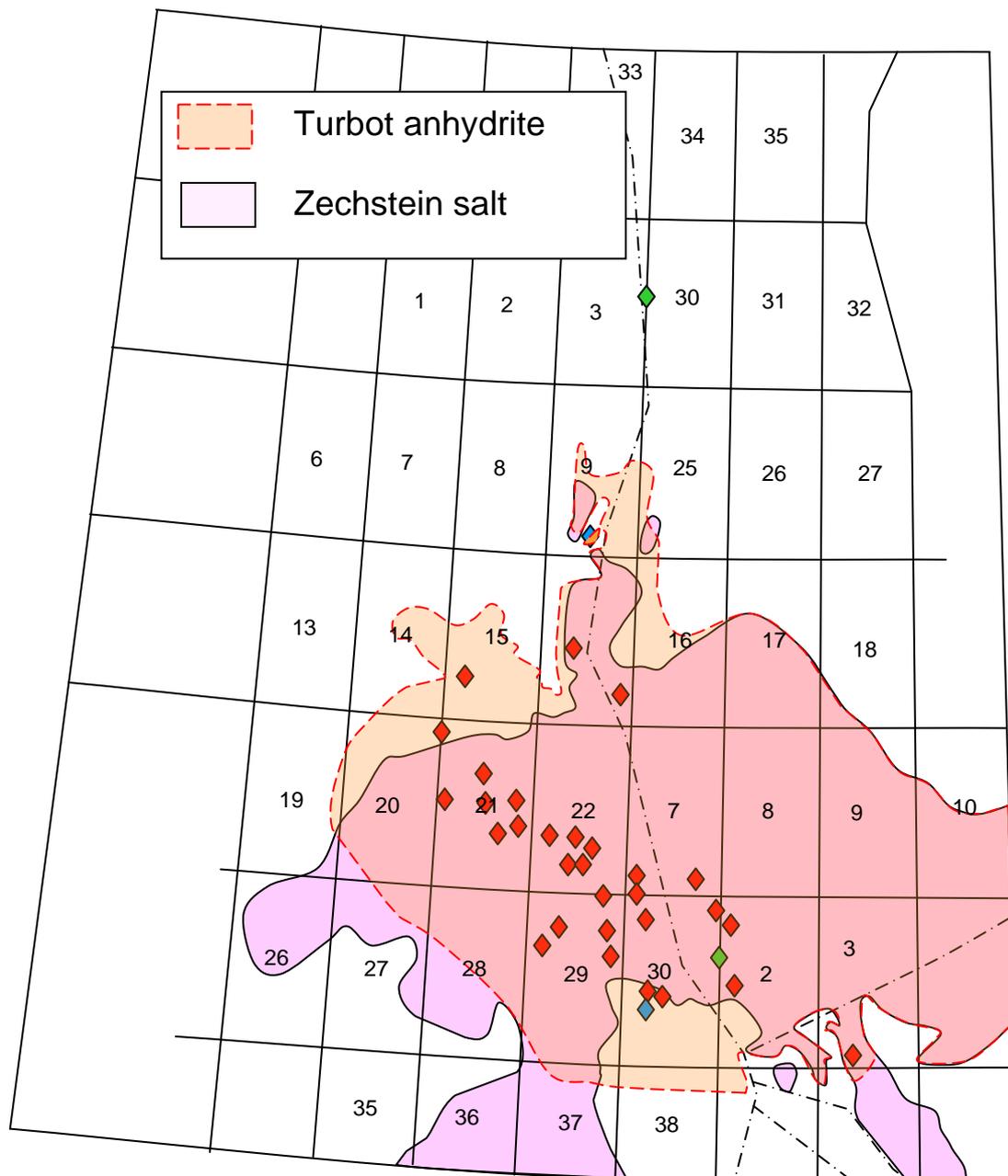


Figure 13 UKNS and NCS: Red symbols are Ca-rich (>6000 mg/l Ca) formation waters where significant SO₄ loss is expected under seawater flood conditions. Blue symbols show Ca-rich (>6000 mg/l Ca) formation waters where significant SO₄ loss is not expected under seawater flood conditions due to low reservoir temperature. Green symbols are Ca-poor (<6000 mg/l Ca) formation waters where significant SO₄ loss is expected under seawater flood conditions due to high reservoir temperature.

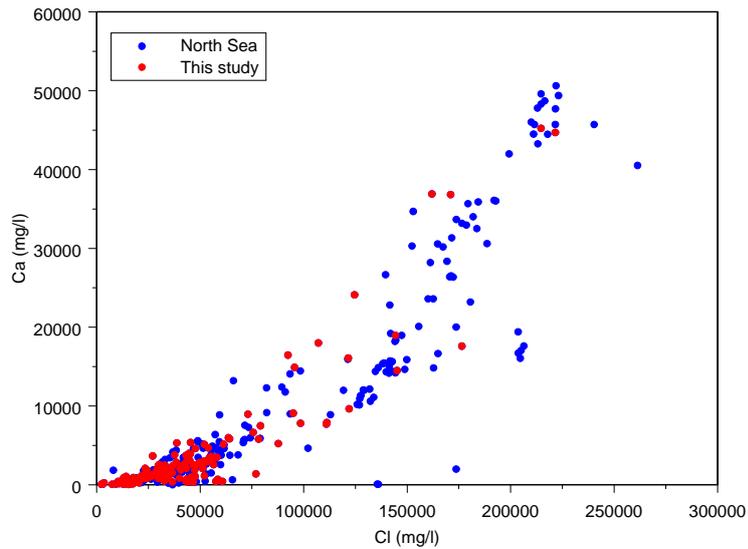


Figure 14 Ca and Cl content of formation water samples from the North Sea and those used in this study.

The Ca-rich, high salinity formation water may have gained its salinity via (a) dissolution of halite or mixing with a brine itself generated by halite dissolution, or (b) mixing with residual evaporative water deposited with the Zechstein Formation. On burial, water within the Zechstein Formation would be expelled into adjacent formations and with continuing burial the fluid would migrate upward relative to the sedimentary column. Upward diffusion of salinity might also occur. For this higher salinity formation water to be present in these reservoir formations there must have been permeable flow paths connecting them with the Zechstein at some time in the past.

The brines associated with the Zechstein Formation would initially be Na-rich. It has been shown that in deeper sedimentary environments such brines are unstable and tend to gain Ca and lose Na in approximately equivalent amounts (i.e. 2 moles Na lost to 1 mole Ca gained) (Hanor, 1994). Although this implies that an ‘exchange’ reaction is occurring, it may also be that separate Na-removing and Ca-releasing reactions are occurring together. The actual reactions responsible for generating Na-Ca-Cl formation waters from Na-Cl brines are not known for certain but may include albitisation of plagioclase (Na removal, Ca release), dissolution of calcite or anhydrite, dolomitisation of calcite, and illitisation of smectite (all Ca release) (e.g. Carpenter, 1978; Davisson and Criss, 1996; Hanor, 1994; Land, 1995). Therefore, the minerals dissolving in these reactions would need to be present either in the reservoir formations or in the formations lying between them and the Zechstein. These reactions are likely to proceed at a greater rate at higher temperatures, hence explaining the tendency of Ca-rich formation waters to occur at temperatures of $>\sim 100^{\circ}\text{C}$ in the North Sea.

For the samples considered in this study, Ca-enrichment of formation water by dissolution of anhydrite on its own does not appear to be significant because the vast majority of formation waters have $\text{SR}_{\text{CaSO}_4}$ less than 0.1 (see Figure 15). There are however, 6 samples with $\text{SR}_{\text{CaSO}_4}$ greater than 0.9 (up to 1.2), these coming from the Kittiwake, Auk, Clyde and Fulmar fields. Allowing for uncertainties in the

thermodynamic data and analyses, these samples may be saturated with respect to CaSO_4 . They all have a similar composition (moderate-high Ca, SO_4 , and Cl; e.g. see Figure 16) implying a similar genetic origin. The latter three fields are all located in UK Blocks 30/16 and 30/17 with the Auk sample being collected from the Chalk Formation (100°C) and the other samples being obtained from Fulmar Formation sandstones (139-146°C). This area is underlain by the Turbot Anhydrite Formation, and the Zechstein salt (which also contains anhydrite) is present in the Auk Field. So, it is possible that these formation waters have dissolved anhydrite in these formations before flowing into the overlying reservoirs. A similar explanation may be valid for the Kittiwake Field (U. Jurassic, UK Block 21/18) which is underlain by both formations.

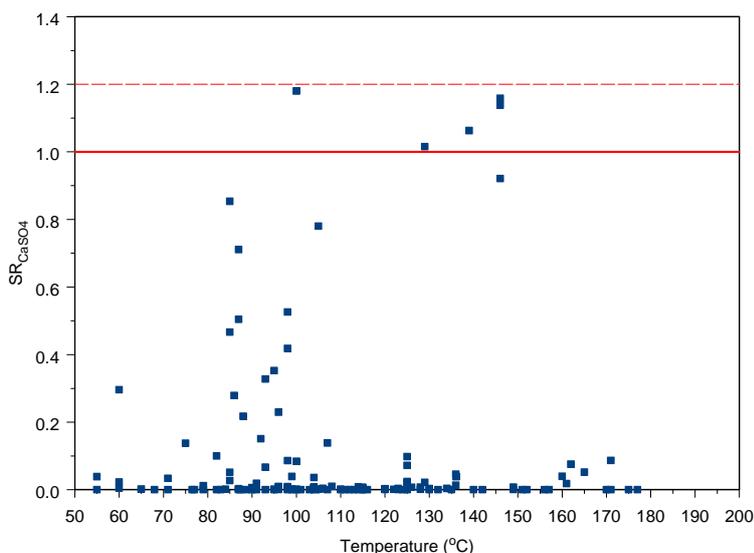


Figure 15 Variation of formation water Saturation Ratio for CaSO_4 with reservoir temperature.

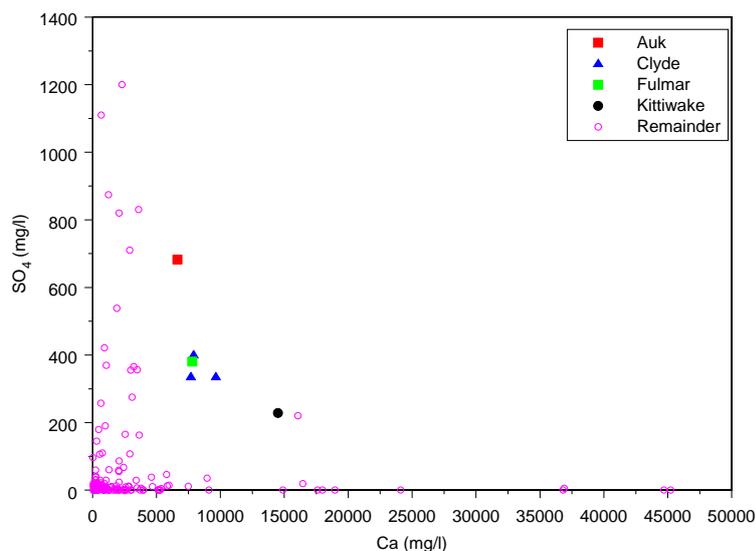


Figure 16 Variation of Ca and SO_4 in formation waters from the North Sea and NCS (analyses for Auk, Clyde, Fulmar and Kittiwake fields are highlighted).

There are also isolated occurrences of higher salinity, Ca-rich formation waters in the Old Red Sandstone (Devonian; e.g. Buchan Field), Piper formation (U. Jurassic; e.g. Scott Field), Palaeocene sandstones (e.g. Machar Field) and the Chalk Formation (U. Cretaceous; e.g. Ekofisk). In some cases, these overlie the Zechstein Formation, so it may be that the vertical connectivity in these areas has been enhanced in the past relative to other areas where such formation water is absent. The presence of these formation waters in the Chalk Formation demonstrates that their occurrence is not limited to sandstones. In some cases, saline Ca-rich formation waters are laterally displaced from the Zechstein Formation (e.g. Scott Field, Buchan Field). These tend to have lower salinity and are not so Ca-rich. It is possible that in these cases, the formation waters have migrated laterally and vertically away from the Zechstein Formation, being diluted by mixing with other lower salinity formations waters in the process.

Significant deposition of CaSO_4 can also occur at temperatures greater than 133°C when formation water contains less than 6,000 mg/ Cal. However, there are few additional fields in this category because most with temperatures greater than 133°C have Ca-rich formation waters. Two of the additional fields are located in the Haltenbanken of the NCS (Kristin, Heidrun) which overlie Triassic evaporites. Further fields are located in the South Viking Graben (Thelma) and in the Central Graben (Albuskjell), again both overlying the Zechstein evaporites. Thelma contains formation water with elevated salinity and just less than 6,000 mg/l Ca. The other fields are characterised by their lower salinity suggesting that poor connectivity with the underlying evaporite formations is the cause of their relatively low Ca given the reservoir temperatures.

IMPLICATIONS FOR SCALE MANAGEMENT

Predicting the occurrence of significant reservoir deposition of CaSO_4

Where the Ca-concentration of the formation water and the reservoir temperature are known, calculations similar to those used in this study can be applied to determine whether significant deposition of CaSO_4 is likely to occur in the reservoir. In some cases, the reservoir temperature will be known but a formation water sample may not have been obtained or it may be of poor quality. It may be feasible to qualitatively assess whether the Ca concentration is likely to be sufficiently high at the reservoir temperature (i.e. using Eq. 5) by evaluating the geological conditions at that location and comparing them to the geological conditions where Ca-rich formation water is known to occur in the North Sea basin. Based on the above evaluation, we know that Ca-rich formation waters are most likely to occur where (a) the reservoir is in close proximity to the Zechstein Formation, and (b) reservoir temperature is $>\sim 100^\circ\text{C}$, and (c) vertical, and in some cases, lateral flow paths between the reservoir formation and the Zechstein Formation that have been operative at some time in the past, and (d) minerals required for conversion of Na-Cl type to Na-Ca-Cl type formation waters are present either along these flow paths or within the reservoir formation. More detailed investigation of the geological environments where Ca-rich formation water occurs would help reduce uncertainties in such predictions.

Predicting the effect of CaSO₄ deposition on produced water compositions

Qualitative predictions

The results of this study can be used to provide qualitative predictions of the effects of sulphate mineral deposition in the reservoir on produced water compositions. This information can help explain observed trends in produced water compositions and lower than expected sulphate mineral scaling potentials for fields where CaSO₄ deposition is important. It can also help constrain various scale management activities such as (a) undertaking scaling predictions to assess future scaling risks, (b) selecting or changing of inhibitors, (c) determination or re-evaluation of MICs, and (d) estimating future scale mitigation costs.

The principal factors determining produced water compositions are the types of water entering the well, their compositions, and their fractions in the total water flow. In this respect, two types of reservoir can be considered: those that have no marked heterogeneity in permeability and those that do. The particular nature of each reservoir can be ascertained from the reservoir model.

In the former case, assuming maintenance of reservoir pressure and consistent water injection, it would be expected that over time and under seawater flood the fraction of formation water produced from the well would progressively decrease and that of the equilibrated mixing zone water would increase along with the seawater fraction of the latter. These trends have been observed at the Clyde and Gyda Fields and explain observed changes in produced water SO₄ concentrations over time (Wright et al., 2008).

Under these conditions, with Ca-rich formation water, and earlier in well life (i.e. following seawater breakthrough), produced water Ca and SO₄ concentrations and sulphate mineral scaling potentials will be lower than expected as a result of CaSO₄ deposition nearer the injection well (from seawater) and within the reservoir (from mixing zone water). These effects will be heightened where temperatures are in excess of 129°C and formation water Ca concentrations are in excess of 6,000 mg/l; the greater the excess, the lower the produced water Ca and SO₄ concentrations and sulphate mineral scaling potentials at lower to moderate seawater fractions. The reduction in produced water Ca concentrations will be less noticeable than those of SO₄ when the formation water is Ca-rich. Where the formation water is also Ba- and/or Sr-rich, deposition of BaSO₄ and SrSO₄ will contribute to lowering produced water SO₄ concentrations (and Ba and Sr concentrations) and sulphate minerals scaling potentials at lower seawater fractions. This is because these minerals tend to deposit in the reservoir toward the front of the mixing zone (at lower seawater fractions due to their lower solubility). For example, at Gyda the formation water is Ca- and Ba-rich and so produced water Ba and SO₄ (but not Ca) concentrations in produced water are much lower than expected for simple seawater-formation water mixing. SO₄ concentrations remained below ~30 mg/l up to a seawater fraction of ~0.7 so the BaSO₄ and CaSO₄ scaling potential was very low to negligible. In contrast, scaling predictions that ignored reservoir reactions had indicated that the scaling potential would be high (BaSO₄) to moderate (CaSO₄) (McCartney et al., 2007).

Later in well life, as the seawater fraction of produced water increases and Ca concentrations in the produced water decrease (due to CaSO₄ deposition and dilution

by seawater), SO_4 concentrations will increase, as expected for CaSO_4 solubility control. The Ca and SO_4 concentrations will still be lower than expected. Processes affecting the injected seawater will become more important because the SO_4 concentration of seawater determines the highest SO_4 content expected from late-stage produced water. The 'ceiling' SO_4 content of produced water will be lower for reservoirs at higher temperature and in reservoirs where Ca-releasing reactions occur in the injection area. For example, if dolomitisation of calcite were to be occurring under the conditions in the Gyda Field, and abundant calcite were present, the injected seawater SO_4 concentration could be reduced to only ~365 mg/l (McCartney et al., 2007). Where Ca-sources are limited, these reactions might not go to completion and so the amount of SO_4 removal might be reduced. Again, using the Gyda Field as an example and ignoring Ca-releasing reactions, later in well life SO_4 actually increased to ~320 mg/l (0.85 seawater fraction) and theoretically could reach a maximum of 2,180 mg/l. Extrapolating trends in scaling ions in produced water between seawater fractions of 0.85 and 1.00, the maximum CaSO_4 and BaSO_4 scaling potentials are expected to be low, as opposed to moderate to high respectively if reservoir reactions were to be ignored.

Where reservoirs have marked heterogeneity in permeability, there is greater potential for flow paths connecting the injection and production wells to become completely swept with equilibrated seawater (e.g. short-circuit flow paths) whilst formation water is still being produced from other flow paths. Depending on the specific conditions in the field this situation might occur at any stage of well life. In this case, the scaling risk will be relatively high because once the mixing zone water has been produced from the short-circuit flow path, reduction in produced water scaling potential is limited to that associated with loss of SO_4 from the equilibrated seawater during heating; again, the higher the reservoir temperature the greater this effect. In this case, where the temperature is less than 120-129°C, no loss of SO_4 from seawater will occur and the scaling potential will be correctly predicted by standard flash calculations. If the formation water is Ca-rich but depleted in Ba and Sr, there will only be a CaSO_4 scaling risk. If the formation water is also Ba- and/or Sr-rich, and the proportion of produced equilibrated seawater is low, the principal risk will be for BaSO_4 and/or SrSO_4 scale deposition. Where the proportion of produced equilibrated seawater is high, the principal risk will be for CaSO_4 deposition.

Quantitative predictions

Ultimately, scale management activities will benefit most from the availability of quantitative predictions of produced water compositions that account for both reservoir reactions and mixing in the reservoir/well. Although tools are available for this purpose, there are uncertainties in the results that they generate and it is an ongoing challenge to reduce these uncertainties.

Quantitative predictions of produced water compositions over time can be generated by reactive transport reservoir simulators (e.g. Daher et al., 2005; Mackay et al., 2003; Paulo et al., 2001) and this technique accounts for both deposition of sulphates in the reservoir and mixing of fluids in the reservoir and production well. Potential limitations of this approach are that the underlying reservoir models are often uncertain, particularly prior to production. In addition, the approach is costly and time-consuming.

Recently, Wright et al. (2008) proposed a model to explain produced water SO_4 concentrations at the Clyde and Gyda Fields. This model assumes that the water being produced from a well is a mixture of formation water and mixing zone water that has equilibrated in the reservoir. The composition of the latter can be estimated using a simple 1-D reactive transport model or a flash model. Variations in produced water SO_4 were shown to be the result of variations in the proportions of these fluids, and the seawater fraction of the mixing zone water ('fluid parameters'). Once the mixing zone water composition has been estimated, on producing fields this model can be used to calculate trends in the fluid parameters over time from trends in produced water SO_4 . By extrapolating trends in these parameters, future produced water SO_4 concentrations (and those of other scaling ions) can be estimated using the model. For fields that have not previously been under waterflood (e.g. new developments, reservoirs under natural depletion) but where predictions of produced water compositions are required under waterflood conditions, the model might also be useful. However, under these circumstances an analogue field under seawater flood is required from which fluid parameters can be obtained. These would then be applied to the target field but using formation water and mixing zone water compositions estimated for the target field. Although there are evidently uncertainties in this approach, the method is relatively fast and simple, and will provide more realistic information than models that ignore reservoir reactions and mixing. It also provides alternative predictions to those derived from reactive transport reservoir simulators.

CONCLUSIONS

Predictions of deposition of sulphate minerals in the reservoirs of 81 fields in the UKNS and NCS have been undertaken assuming seawater flood conditions. These have shown that of all sulphate minerals, deposition of CaSO_4 has the greatest capacity to cause a significant reduction in sulphate mineral scaling potentials in produced water.

The principal processes by which CaSO_4 deposition occurs in the reservoir are likely to be heating of seawater and mixing of seawater and Ca-rich formation water. The amount of CaSO_4 deposited in the reservoir is mainly dependent on the Ca content of the formation water and the reservoir temperature although other factors which are also an influence are reservoir pressure, and formation water salinity and Ba and Sr content.

These calculations have shown that deposition of CaSO_4 is likely to be a relatively common process in UKNS and NCS reservoirs, and in almost 1 in 4 fields it is likely to cause a significant reduction in sulphate mineral scaling potential. The amount of deposition of CaSO_4 in the reservoir is mainly dependent on the Ca content of the formation water and the reservoir temperature. The minimum temperature observed where significant deposition has been predicted (and therefore significant SO_4 loss) is 105°C . Generally, significant deposition also occurs where formation water is Ca-rich ($>\sim 6,000$ mg/l Ca) but as temperature also plays a role, there are exceptions (i.e. in some cases, below $\sim 133^\circ\text{C}$, Ca concentrations need to be greater and vice-versa). Ca-rich formation water usually has elevated salinity ($>70,000$ mg/l Cl). Significant CaSO_4 deposition and SO_4 removal is predicted to occur in deep reservoirs with Ca-rich formation water and in particular those located in the Skagerrak Formation (Triassic), Pentland (M. Jurassic), Ula/Gyda Formation (U. Jurassic), and Fulmar Formation (U. Jurassic) of the Central Graben overlying the Zechstein Formation,

although they can be located elsewhere if geological conditions are favourable. Further investigation of the geological conditions under which Ca-rich formation waters are found will improve prediction of their occurrence. This will help scale management planning when formation water analyses are not available for a field.

The results of this study will help identify those fields under development where precipitation of CaSO₄ in the reservoir should be considered during scale management planning and explain observed trends in produced water scaling ion concentrations and sulphate mineral scaling potentials where CaSO₄ deposition is occurring in the reservoir. A continuing challenge is to produce reliable predictions of produced water compositions. These could provide (a) more realistic indications of future scaling risks, (b) more accurate conditions for selection of inhibitors and determination of MICs, and (c) more realistic scale mitigation costs. Predictive tools are available but would benefit from further development.

ACKNOWLEDGEMENTS

The author thanks the management of GeoScience Limited for permission to publish this paper.

REFERENCES

- Bertero, L., G. L. Chierici, G. Gottardi, E. Mesini, and G. Mormino. 1988. Chemical equilibrium models: their use in simulating the injection of incompatible waters. *SPE Reservoir Engineering*, v. February, p. 288-294.
- Carpenter, A. B., 1978, Origin and chemical evolution of brines in sedimentary basins: 13th Annual Forum on Geology of Industrial Minerals,
- Daher, J. S., J. A. T. Gomes, F. F. Rosario, M. C. M. Bezerra, E. J. Mackay, and K. S. Sorbie, 2005, Evaluation of inorganic scale deposition in an unconsolidated reservoir by numerical simulation: SPE 7th International Symposium on Oilfield Scale, Aberdeen, United Kingdom, 11-12 May.
- Davison, M. L., and R. E. Criss. 1996. Na-Ca-Cl relations in basinal fluids. *Geochimica Cosmochimica Acta*, v. 60, p. 2743-2752.
- Falla, M., K. Orski, D. Frigo, J. S. James, G. M. Graham, S. Heath, C. Strachan, and C. MacPherson, 2005, Design and laboratory testing of scale-inhibitor squeeze packages for HP/HT gas-condensate reservoirs: SPE 7th International Symposium on Oilfield Scale, Aberdeen, United Kingdom, 11-12 May.
- Graham, G. M., D. M. Frigo, and N. Poynton, 2003, Calcium sulphate (anhydrite) scale control in a mature asset - the Kittiwake and Fulmar reservoirs: SPE 5th International Symposium on Oilfield Scale, Aberdeen, United Kingdom, 30-31 January.
- Graham, G. M., and E. J. Mackay, 2004, A background to inorganic scaling - mechanisms, formation and control: SPE short course, Aberdeen, UK.,
- Graham, G. M., E. J. Mackay, S. J. Dyer, and H. M. Bourne, 2002, The challenges for scale control in deepwater production systems: Chemical inhibition and placement: Corrosion 2002, Denver, Colorado, 7-14 April.
- Hanor, J. S., 1994, Origin of saline fluids in sedimentary basins, *in* J. Parnell, ed., *Geofluids: Origin, migration and evolution of fluids in sedimentary basins: Geological Society Special Publication*, v. 78, Geological Society, p. 151-174.

- Hardy, J. A., and I. Simm. 1996. Low sulfate seawater mitigates barite scale. *Oil & Gas Journal*.
- Jasinski, R., P. Fletcher, K. Taylor, and W. Sablerolle, 1998, Calcite scaling tendencies for North Sea HTHP wells: Prediction, authentication and application: SPE Annual Technical Conference and Exhibition, New Orleans, Louisiana, U.S.A., 27-30 September.
- Land, L. S. 1995. Na-Ca-Cl saline formation waters, Frio Formation (Oligocene), south Texas, USA: Products of diagenesis. *Geochimica et Cosmochimica Acta*, v. 59, p. 2163-2174.
- Mackay, E. J. 2003a. Modelling in-situ scale deposition: The impact of reservoir and well geometries and kinetic reaction rates. *SPE Production and Facilities*, p. 45-56.
- Mackay, E. J. 2003b. Predicting in-situ sulphate scale deposition and the impact on produced ion concentrations. *Trans IChemE*, v. 81(A), p. 326-332.
- Mackay, E. J., and G. M. Graham, 2003, The use of flow models in assessing the risk of scale damage: SPE International Symposium on Oilfield Chemistry, Houston, Texas, U.S.A., 20-21 February.
- Mackay, E. J., and M. M. Jordan, 2003, Natural sulphate ion stripping during seawater flooding in chalk reservoirs: Chemistry in the oilfield VIII, Manchester, UK.,
- Mackay, E. J., M. M. Jordan, N. D. Feasey, D. Shah, P. Kumar, and S. A. Ali, 2004, Integrated risk analysis for scale management in deepwater developments: 6th International Symposium on Oilfield Scale, Aberdeen, U.K.,
- Mackay, E. J., M. M. Jordan, and F. Torabi. 2003. Predicting brine mixing deep within the reservoir and its impact on scale control in marginal and deepwater developments. *SPE Production and Facilities*, p. 210-220.
- Mackay, E. J., K. S. Sorbie, V. Kavle, E. Sørhaug, K. Melvin, K. Sjursæther, and M. M. Jordan, 2006, Impact of in-situ sulphate stripping on scale management in the Gyda Field: SPE 8th International Symposium on Oilfield Scale, Aberdeen, U.K., 31 May-1 June.
- McCartney, R. A., G. Coghlan, and A. White, 2006, Identification of the source of low salinity water produced from a subsea well in the Birch Field and implications for scale management: SPE 8th International Symposium on Oilfield Scale, Aberdeen, U.K., 31 May-1 June.
- McCartney, R. A., K. Melvin, R. Wright, and E. Sørhaug, 2007, Seawater injection into reservoirs with ion exchange properties and high sulphate scaling tendencies: Modelling of reactions and implications for scale management, with specific application to the Gyda Field: 18th International Oilfield Chemistry Symposium, Geilo, Norway, 26-28 March.
- McCartney, R. A., and E. Rein, 2005, Formation waters of the Norwegian Continental Shelf: 16th International Symposium on Oilfield Chemistry, Geilo, Norway, 13-16 March.
- Paulo, J., and E. J. Mackay, 2001, Modelling of in-situ scale deposition: 12th International Symposium on Oilfield Chemistry, Geilo, Norway, 1-4 April.
- Paulo, J., E. J. Mackay, N. Menzies, and N. Poynton, 2001, Implications of brine mixing in the reservoir for scale management in the Alba Field: SPE International symposium on oilfield scale, Aberdeen, UK,
- Petrotech. 2003. MultiScale Version 6.1 User Manual. Haugesund, Norway.
- Petrovich, R., and A. A. Hamouda, 1998, Dolomitisation of Ekofisk oilfield reservoir chalk by injected seawater: Proceedings of the 9th International Symposium on Water- Rock Interaction, Taupo, New Zealand,

- Sorbie, K. S., and E. J. Mackay. 2000. Mixing of injected, connate and aquifer brines in waterflooding and its relevance to oilfield scaling. *Journal of Petroleum Science and Engineering*, v. 27, p. 85-106.
- Stalker, R., G. M. Graham, G. Hellings, J. C. Williams, and I. J. Littlehales, 2005, Downhole scale formation and inhibition in mild sulphate scaling conditions: SPE International Symposium on Oilfield Chemistry, Houston, Texas, U.S.A., 2-4 February.
- Stiegler Øye, K. M., B. M. Hustad, and R. Wat, 2006, Challenges in qualifying environmental acceptable production chemicals for a HTHP field: 17th International Oilfield Chemistry Symposium, Geilo, Norway,
- Todd, A. C., M. D. Yuan, and I. R. McCracken, 1994, Part 3: Sulphate and carbonate scale prediction in North Sea oil and gas fields, *in* E. A. Warren, and P. C. Smalley, eds., *North Sea Formation Water Atlas*, v. 15, Geological Society Memoir, p. 105-118.
- Warren, E. A., and P. C. Smalley, eds., 1994, *North Sea Formation Water Atlas: Memoir No. 15*: London, Geological Society, 208 p.
- White, R., J. Brookley, and N. Menzies, 1999, Practical experiences of a Gel diversion technique and an overview of scale management for the Alba field: SPE Symposium Oilfield Scale: Field applications and novel solutions, Aberdeen, Scotland,
- Wright, R., R. A. McCartney, and E. Sørhaug, 2008, Understanding trends in sulphate concentrations in produced water within oilfields under seawater flood and with Ca-rich formation water: SPE 9th International Symposium on Oilfield Scale, Aberdeen, U.K., 28-29 May.
- Ziegler, K., M. L. Coleman, and R. J. Howarth. 2001. Palaeohydrodynamics of fluids in the Brent Group (Oseberg Field, Norwegian North Sea) from chemical and isotopic compositions of formation waters. *Applied Geochemistry*, v. 16, p. 609-632.