

Rapid fluid-rock interaction in oilfield reservoirs

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ABSTRACT

We report here on production data from a North Sea oilfield that demonstrates that significant mineral-fluid interactions took place in the reservoir on a time scale of months. A time series of produced water compositions from the BP-operated Miller Field, in the UK sector of the North Sea, was generated over a period of more than 7 yr when seawater was being injected for secondary recovery and pressure maintenance. Deviation of the produced water chemistry from linear mixing of seawater and formation water indicates that mineral-water interactions took place in the reservoir. Of particular significance is the evidence for rapid reaction of injected water with silicates. The safety case for CO₂ storage in such reservoirs is greatly facilitated if it can be shown to react with the host pore waters and rocks on a human time scale, and the results of this study indicate that this is indeed the case.

Keywords: CO₂ storage, basinal formation water, chemical composition of fluid, pH, buffering.

INTRODUCTION

The rates of mineral-fluid interactions in natural systems may vary significantly from those measured in the laboratory, but need to be understood for the long-term consequences of the injection of CO₂ into oilfields and aquifers to be evaluated. We report here on a data set that documents field-scale in situ fluid-mineral interactions in a North Sea oilfield. The Miller Field covers an area of 45 km² in the South Viking Graben in the central North Sea. It has been onstream since 1992, and production is supported by water/gas injection wells. Waterflooding was initiated shortly after first oil was produced and has continued to date. Miller reservoir rock consists of fine- to coarse-grained quartzitic sandstones (conglomeratic in parts) of the Brae Formation with trace amounts of feldspar, muscovite, calcite, and heavy minerals. Cementation is commonly by secondary silica with minor authigenic illite. Patchily distributed calcite cement may also be common in shell-rich sandstones (Gluyas et al., 2000; Marchand et al., 2001). The formation water in the reservoir is high-salinity NaCl-CaCl₂ brine, with low sulfate and high barium, and the reservoir is at a relatively high temperature (~120 °C) (Smalley and Warren, 1994).

PRODUCED WATER VARIABILITY

The produced water from each well in Miller was sampled and analyzed for major cations, anions, and transition metals on an almost daily

basis for ~10 yr (Fig. 1). During this time 1.93 × 10¹¹ liters of water were produced, with typical water production rates of 3.75 × 10⁵ liters/day for the main 93-month production period. Figure 1 shows a time series of data for SO₄, Si, Ba, Ca, Mg, and Cl in the produced water from a typical production well; this well is located on a structural high. Production at the well commenced in March 1995, with almost simultaneous start-up of seawater injection at an injection well ~2.5 km away. Pristine formation water exhibited some variability in some of its constituents from this well (apparent from the scatter in the earliest period of water production in Figure 1), but there is good consistency in water composition between wells. We have taken the Miller formation water analysis from Smalley and Warren (1994) as representative. The initial formation water was almost double seawater salinity, and so changes in the concentration of the Cl ion in the produced water can be used to estimate the proportion of injected seawater to formation water in produced water. Lower chloride in the produced water indicates a higher seawater component, i.e., the percentage seawater in each produced water sample is

$$\% \text{ seawater} = \frac{[(\text{Cl}_{\text{FW}} - \text{Cl}_{\text{meas}}) / (\text{Cl}_{\text{FW}} - \text{Cl}_{\text{SW}})] \times 100}{(1)}$$

where the subscripts FW, SW, and meas denote the chloride concentrations in the original formation water, seawater, and produced water, respectively. The proportion of seawater in the water emerging from a production well varies with time and is a function of many factors,

including the injection and production rates, the saturation distribution within the reservoir, the distance between the injector and producer wells, and the connectivity of the sandstone reservoir rocks.

Figure 1 demonstrates that the initial produced water was formation water. After ~600 days, Cl decreased rapidly as injected seawater reached the producer. Subsequently, Cl showed a slow increase accompanying increased formation water production. Later changes in Cl relate to specific water shutoff activities in the well to reduce water production and maintain oil flow. After periods of zero production, the proportion of formation water in the produced water always increased. The overall Cl data set indicates significant variation in the proportion of seawater produced through time. Almost all analyzed species showed some variation through time, and are linked to changes in the relative proportions of formation water and seawater in the produced water, as monitored by chloride.

If produced waters were simply binary mixtures of formation water and injected water, all ions, when plotted against Cl, should show linear mixing relations. Many ions do not; this indicates that dissolution or precipitation occurred, probably both in the reservoir (water-rock interaction) and in the wellbore (e.g., precipitation of barite scale through water-water interaction). To monitor these reactions, we calculated the deviation between the analyzed concentration of each component in the produced water and the value predicted from linear mixing of seawater and formation water to produce the observed chloride (Figs. 2–4).

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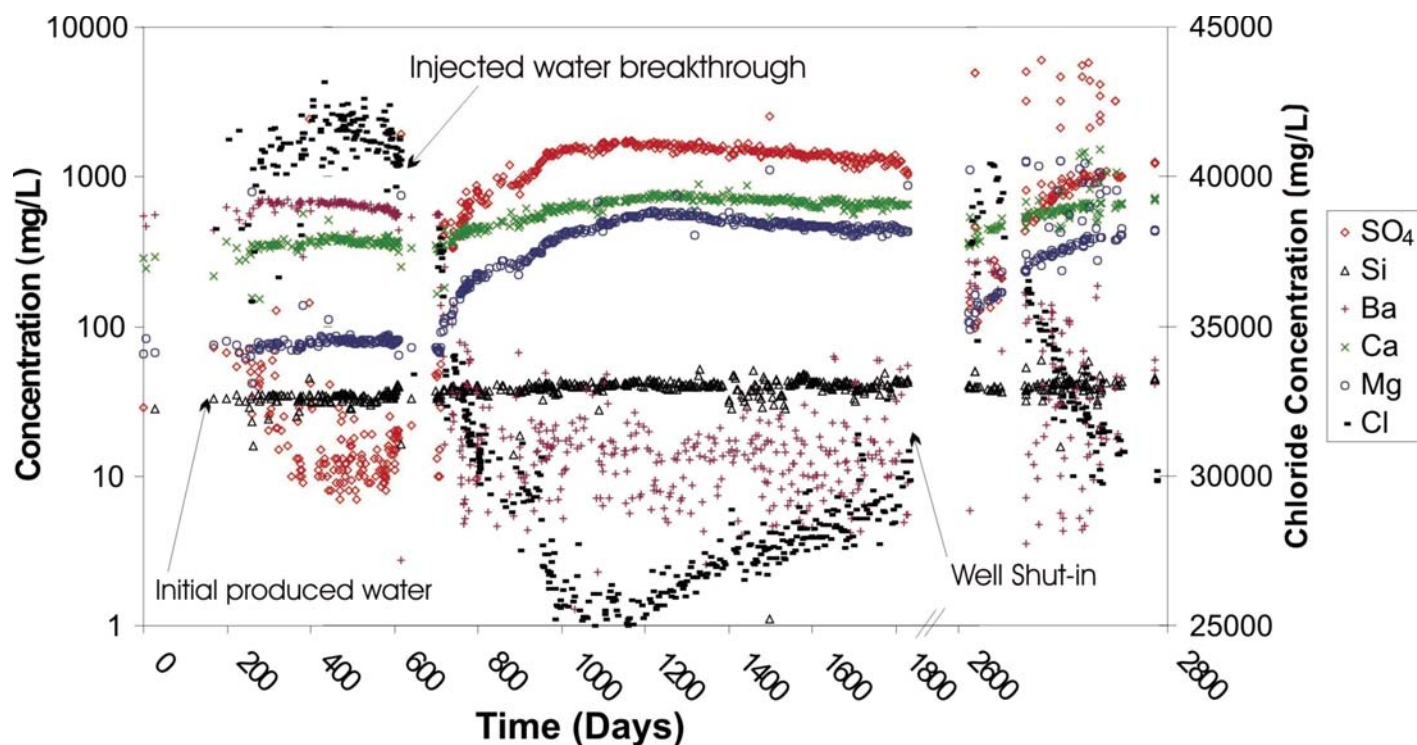


Figure 1. Variation through time in the concentrations of the major solute components in produced water from a well in the Miller Field, as injected seawater displaces original formation water. Note the different scale for chloride concentration. Note that the silica concentration is almost constant throughout.

Barium and Sulfate

Of particular interest for production is the relationship between barium and sulfate because of the potential impact of barite precipitation on reservoir permeability and flow in and around the producing wellbore. Relative to the linear mixing line, both barium and sulfate are strongly depleted, due to mixing to produce barite scale (Fig. 2). Over the production period monitored in one well, the amount of barite precipitation amounts to 589 tonnes, equivalent to a volume of $\sim 131 \text{ m}^3$. This barite will be located in regions of fluid mixing, and may therefore be concentrated in and near the wellbores. Between 200 and 600 days, barite precipitation accounts for the loss of sulfate in full, but an additional sink for sulfate was present between 700 and 1800 days when there is an excess of sulfate depletion relative to Ba. This sink might be reduction to sulfide (Worden and Smalley, 2001), anhydrite precipitation, or ion exchange/adsorption onto authigenic clays. High water-rock ratios may maintain low enough temperatures for bacterial sulfate reduction, while injected water will not remain oxygenating in the subsurface.

Calcium and Magnesium

Calcium and magnesium exhibit opposite deviations from the mixing line, with Ca enriched and Mg depleted in the produced water. This may in part reflect conversion of calcite to

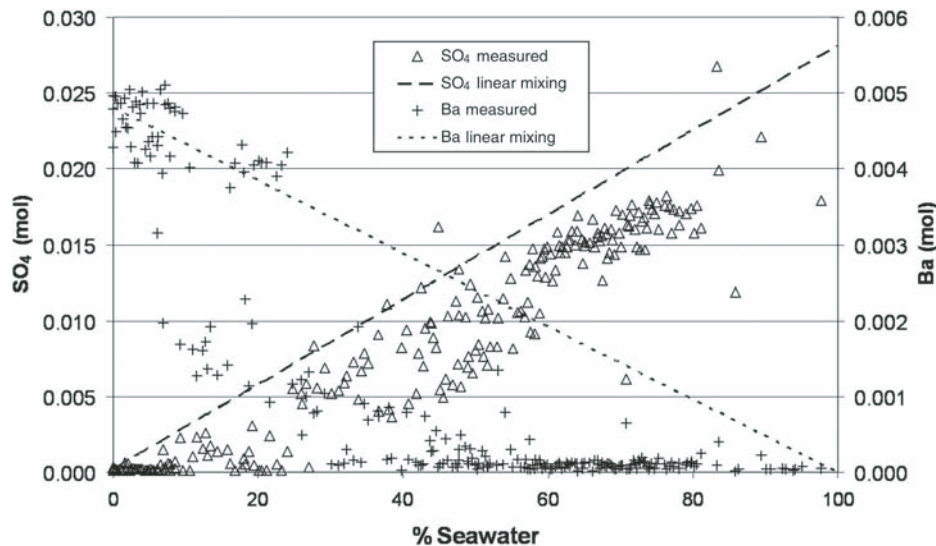


Figure 2. Variation in concentration of sulfate and barium with proportion of seawater relative to a linear mixing trend based on conservative chloride. Open triangles— SO_4 ; plus sign—Ba. At 20% seawater the Ba depletion is 0.004 mol and the sulfate depletion 0.005 mol, while at 70% seawater the values are 0.0015 mol and 0.004 mol, respectively.

dolomite, but comparison of the Ca and Mg deviations from the mixing line on a molar basis shows that the Mg depletion is normally greater than the Ca enrichment (Fig. 3). This suggests that there must be an additional rapid mechanism for fixation of Mg from the water, prob-

ably by incorporation into and/or sorption onto clay minerals. In this case, simple calcite dissolution may also have taken place. Bicarbonate alkalinity was not reported as part of the data set; thus evidence for the controls on Ca and Mg behavior must come from geochemical model-

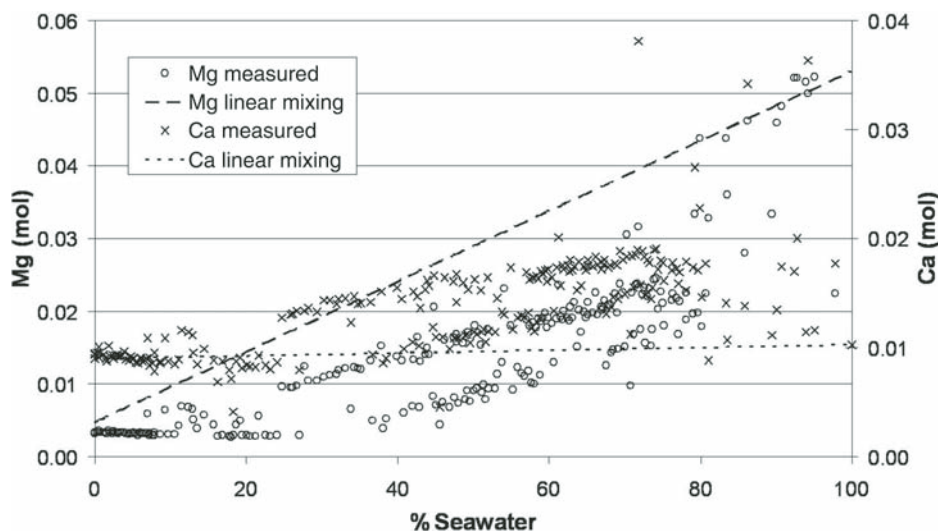


Figure 3. Variation in concentration of magnesium and calcium with proportion of seawater relative to a linear mixing trend based on conservative chloride. Open circles—Mg; multiplication sign—Ca. Note the depletion in magnesium and increase in calcium. This may be due to dolomitization, but an additional sink for Mg is required, possibly clay minerals.

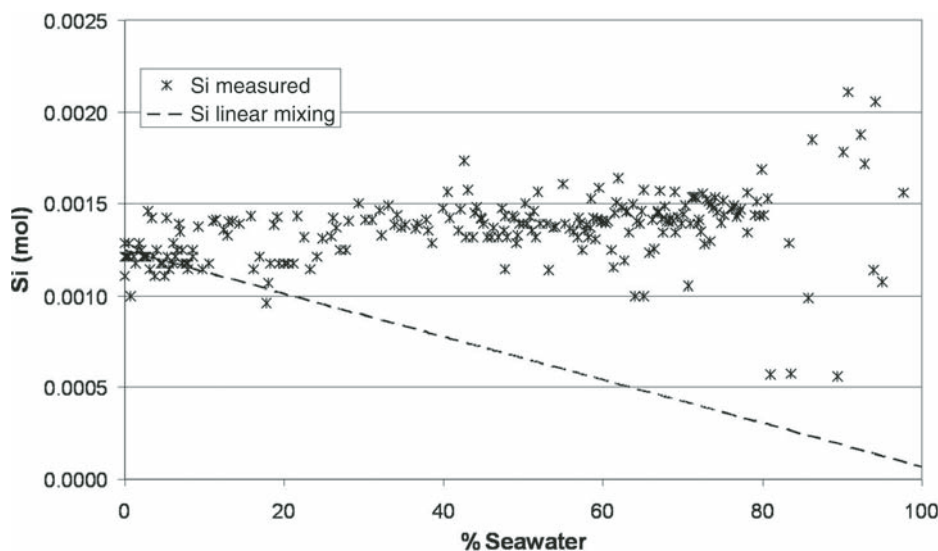


Figure 4. Variation in concentration of Si with proportion of seawater relative to a linear mixing trend based on conservative chloride. Note the almost constant concentration of Si regardless of time and seawater proportion, the only change being a slight increase due to either a salting-out effect, temperature effects, or increased silicate dissolution.

ing alone. Typical seawater and pristine formation water were modeled using the geochemical code PHREEQE (Parkhurst et al., 1980) in the program PHREEEQC and suggest that on heating to 120 °C they were close to saturation with anhydrite, but not supersaturated.

Silica

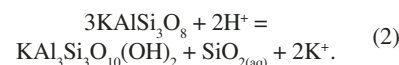
The deviation from the conservative mixing line for silica is particularly distinctive. Figure 4 shows that the silica concentration remains almost constant in the produced water irrespective of the proportion of seawater present, and

is always close to quartz saturation at 120 °C (~60 mg/L $\text{SiO}_{2(\text{aq})}$). Based on the produced water from one well (proportionally <1% of the field), this requires dissolution of ~80 tonnes of silica from the formation over the production cycle, equivalent to removal of ~30 m³ of quartz. The rate of silicate dissolution is evidently fast enough to maintain a high silica concentration in the fluid throughout the period of monitoring.

In detail, there is actually a slight increase in silica with the increasing proportion of seawater in the later produced waters, and possible causes of this include either the lower salinity of

these waters, because silica solubility is subject to a salting-out effect (Shmulovich et al., 2006; Von Damm et al., 1991), or metastable enhancement of the degree of silica saturation.

Calculations based on a solvation number of 4 (Shmulovich et al., 2006) indicate that the lowered water activity can account for only 4–5 mg/L of the increase in silica observed in the more dilute waters. Alternatively, levels may be enhanced metastably due to fluid-rock interactions on a time scale of months. Cases of rapid silica dissolution have elsewhere been ascribed to the presence of reactive metastable sponge spicules in the rocks (Aase and Walderhaug, 2005; Bjørlykke and Egeberg, 1993; Icenhower and Dove, 2000). While there is evidence for the presence of sponge spicules in trace amounts in Miller (Bjørlykke and Egeberg, 1993), their dissolution cannot account for the fact that Si concentrations in the produced water actually exceed those in the original formation water, which was itself buffered by coexistence with the same spicules. An alternative mechanism for enhanced silica in solution is the breakdown of silicates in response to the ingress of cold seawater, which is heated as it passes through the formation. For example, alteration of feldspar to clay (illitization) is widespread at 120 °C in North Sea reservoirs as a diagenetic process (Bjørlykke, 1998). K-feldspar dissolution occurs more rapidly than quartz dissolution at temperatures as low as 65 °C, partly as a result of the high surface area caused by abundant microtextures on feldspar overgrowths (Aagaard et al., 1990; Worden and Rushton, 1992). Feldspar alteration can be written to a first approximation as

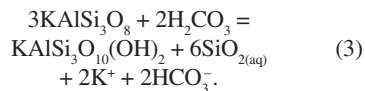


This reaction can drive the concentration of silica in solution above the equilibrium level for quartz saturation. This is our preferred explanation for the enhanced values measured, and in less than 600 days (the time to seawater breakthrough) the injected seawater traveling across the field had been able to attain a silica content comparable to that of the original formation water by this means.

DISCUSSION AND CONCLUSIONS

The results obtained here are of value for evaluating the likely consequences of carbon dioxide injection into North Sea reservoirs, and in particular whether it is likely to be fixed as required, for 1000 yr (Wawersik et al., 2001). The initial effect of CO_2 injection is to lower the pH by forming carbonic acid, thereby promoting dissolution of calcite rather than its precipitation (Kharaka et al., 2006). This could lead to breakout by destroying seals. However, silicate reactions can also lead to stabilization of CO_2 as

alkali bicarbonate, either by ion exchange reactions after initial calcite dissolution, or by direct neutralization of carbonic acid:



Since few North Sea oilfields contain appreciable silicate Ca, and levels of CaCl_2 in pore fluids are also generally rather low, formation of alkali bicarbonate is likely to be the main type of reaction to irreversibly fix dissolved CO_2 .

The relevance of the field rate of silica release documented here to CO_2 sequestration is that it is an indicator of the rate at which water can interact with silicate minerals at the field scale. Our observations demonstrate that silicate-water reactions proceed on a time scale of months in the Miller Field, and so such reactions are likely to have the potential to provide an effective means of fixing CO_2 as alkali bicarbonate on a similar time scale.

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REFERENCES CITED

Aagaard, P., Egeberg, P.K., Saigal, G.C., Morad, S., and Bjørlykke, K., 1990, Diagenetic albitisation of detrital K-feldspars in Jurassic, Lower Cretaceous and Tertiary clastic reservoir rocks from offshore Norway, II: Formation water

- chemistry and kinetic considerations: *Journal of Sedimentary Petrology*, v. 60, p. 575–581.
- Aase, N.E., and Walderhaug, O., 2005, The effect of hydrocarbons on quartz cementation: Diagenesis in the Upper Jurassic sandstones of the Miller Field, North Sea, revisited: *Petroleum Geoscience*, v. 11, p. 215–223.
- Bjørlykke, K., 1998, Clay mineral diagenesis in sedimentary basins—A key to the prediction of rock properties: Examples from the North Sea Basin: *Clay Minerals*, v. 33, p. 15–34, doi: 10.1180/claymin.1998.033.1.03.
- Bjørlykke, K., and Egeberg, P.K., 1993, Quartz cementation in sedimentary basins: *American Association of Petroleum Geologists Bulletin*, v. 77, p. 1538–1548.
- Gluyas, J., Garland, C., Oxtoby, N.H., and Hogg, A.J.C., 2000, Quartz cement: The Miller's tale, in Worden, R.H., and Morad, S., eds., *Quartz cementation in sandstones*. Special Publication of the International Association of Sedimentologists: Oxford, UK, Blackwell, v. 29, p. 1–20.
- Icenhower, J.P., and Dove, P.M., 2000, The dissolution kinetics of amorphous silica into sodium chloride solutions: Effects of temperature and ionic strength: *Geochimica et Cosmochimica Acta*, v. 64, p. 4193–4203, doi: 10.1016/S0016-7037(00)00487-7.
- Kharaka, Y.K., Cole, D.R., Hovorka, S.D., Gunter, W.D., Knauss, K.G., and Friefeld, B.M., 2006, Gas-water-rock interactions in Frio Formation following CO_2 injection: Implications for the storage of greenhouse gases in sedimentary basins: *Geology*, v. 34, p. 577–580, doi: 10.1130/G22357.1.
- Marchand, A.M.E., Haszeldine, R.S., Smalley, P.C., Macaulay, C.I., and Fallick, A.E., 2001, Evidence for reduced quartz cementation rates in oil-filled sandstones: *Geology*, v. 29, p. 915–918, doi: 10.1130/0091-7613(2001)029<0915:EFRQCR>2.0.CO;2.
- Parkhurst, D.L., Thorstenson, D.C., and Plummer, L.N., 1980, A computer program for geochemical calculations: U.S. Geological Survey Water-Resources Investigations Report, p. 80–96.
- Shmulovich, K.I., Yardley, B.W.D., and Graham, C.M., 2006, Solubility of quartz in crustal fluids: Experiments and general equations for salt solutions and $\text{H}_2\text{O}-\text{CO}_2$ mixtures at 400–800 °C and 0.1–0.9 GPa: *Geofluids*, v. 6, p. 154–167, doi: 10.1111/j.1468-8123.2006.00140.x.
- Smalley, P.C., and Warren, E.A., 1994, The Miller Field, in Warren, E.A., and Smalley, P.C., eds., *North Sea formation waters atlas*: Geological Society [London] Memoir 15, 52 p.
- Von Damm, K.L., Bischoff, J.L., and Rosenbauer, R.J., 1991, Quartz solubility in hydrothermal seawater: An experimental study and equation describing quartz solubility for up to 0.5 M NaCl solutions: *American Journal of Science*, v. 291, p. 977–1007.
- Wawersik, W.R., Orr, F.M., Rudnicki, J.W., Ortoleva, P.J., Dove, P., Richter, F., Harris, J., Warpinski, N.R., Logan, J.M., Wilson, J.L., Pyrak-Nolte, L., and Wong, T.F., 2001, Terrestrial sequestration of CO_2 : An assessment of research needs: *Advances in Geophysics*, v. 43, p. 97–177, doi: 10.1006/ageo.2001.0002.
- Worden, R.H., and Rushton, J.C., 1992, Diagenetic K-feldspar textures: A TEM study and model for diagenetic feldspar growth: *Journal of Sedimentary Petrology*, v. 62, p. 779–789.
- Worden, R.H., and Smalley, P.C., 2001, H_2S in North Sea oil fields: Importance of thermochemical sulphate reduction in clastic reservoirs, in Cidu, R., ed., *Water-rock interaction*, 10: Lisse, Abingdon, Exton, Tokyo, A.A. Balkema, p. 659–662.

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