

How sandstone mineral surfaces interact with Ca^{2+} and Cl^- ions

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Sandstone oil reservoirs form an important global resource. Production with the highest possible yield would extend the resources that are currently accessible with existing infrastructure and postpone the need for developing more risky deep water and high Arctic fields. Enhanced oil recovery (EOR) methods, including flooding with low salinity water, have increased oil recovery rates for sandstone reservoirs, even though the mechanisms responsible are not yet fully understood. Linking reservoir scale studies with investigations carried out at the molecular scale would increase our understanding of such mechanisms and allow EOR methods to be optimised.

In this work, we examined the change in surface composition of two natural sandstones (SS1 and SS2) and the associated extracted clay, during exposure to calcium chloride (CaCl_2) solutions at a variety of concentrations. For investigating surface uptake, we used X-ray photoelectron spectroscopy (XPS) on fast frozen samples [1] The sandstones and extracted clay have been thoroughly characterised with X-ray powder diffraction (XRPD) and scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDXS).

The ratio of Ca/Si and Cl/Si , derived from XPS spectra, show which ions stick to the surface at various Ca concentrations (Figure 1). The SS2 sandstone adsorbed more chloride than calcium, no matter what solution concentrations were used, whereas the opposite was observed for SS1. SS2 also had a higher affinity for adsorption in general than SS1. XRPD patterns confirmed a difference in mineral composition.

We are using the information about responses from natural sandstone and natural clay minerals to design model systems for determining the mechanism behind the oil release that is observed on the reservoir scale in response to low salinity water injection.

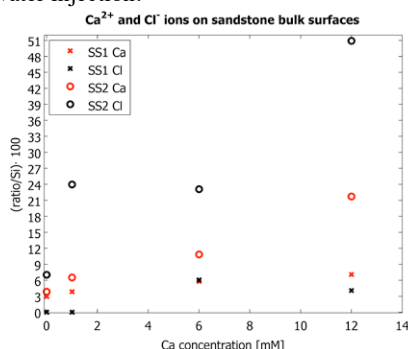


Figure 1: The ratio of Ca/Si and Cl/Si for the two bulk sandstones presented as a function of the calcium concentration of the solution.

Calcite scaling: Growth inhibition by Mg^{2+} , SO_4^{2-} and $\text{Mg}^{2+} + \text{SO}_4^{2-}$

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Calcite precipitation in wells, pipes, boilers and the like causes problems for industry. Effective inhibition would save huge amounts of energy and money. Magnesium (Mg^{2+}) is known to poison calcite growth [1-3], so better understanding of how it works could lead to improved scale inhibitors. It has recently been shown that adsorption of both Mg^{2+} and sulfate (SO_4^{2-}) changes calcite surface tension [4-5].

We investigated the effect of each ion singly and in combination by precipitating calcite at room temperature in a constant composition reactor [6]. Calcite precipitated at constant rate, then ions were added and the change in growth rate was monitored with time.

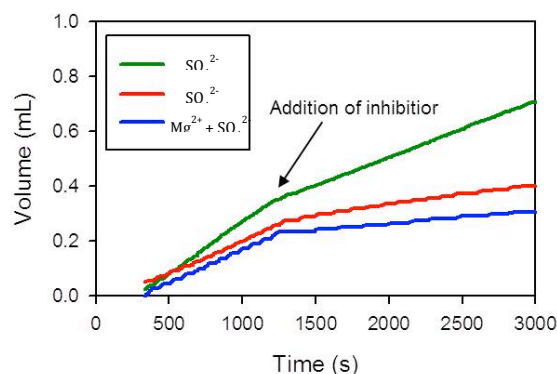


Figure 1. Typical plots for reagent addition versus time. Concentration of the inhibitors was 7.4 mM in all cases

Growth rate for pure calcite ranged from $1.8 \cdot 10^6$ to $6.0 \cdot 10^6$ $\text{mol s}^{-1} \text{m}^{-2}$, consistent with previous data. Increased Mg^{2+} concentration correlated directly with increased inhibition. Dissolved Mg^{2+} decreased with growth, suggesting incorporation into the newly formed calcite. Although there is less inhibition by SO_4^{2-} alone than Mg^{2+} alone, when the two are present together, inhibition is strongest (Figure 1).

[1] Berner (1975) *Geochim. Cosmochim. Ac.* **39**(4) 489-494. [2] Deleuze & Brantley (1997) *Geochim. Cosmochim. Ac.* **61**(7) 1475-1485. [3] Davis *et al.* (2000) *Science* **290**, 1134-1137. [4] Sakuma H. *et al.* (2013) abstract, Goldschmidt Conference, this volume. [5] Zhang, P.; *et al* *Colloid Surf. A-Physicochem. Eng. Asp.* 2007, **301**, 199. [6] Lakshtanov *et al.* (2011) *Geochim. Cosmochim. Ac.* **75**(14) 3945-3955.