FLUID-FLOW DURING EOR EXPERIMENTS IN CHALK: INSIGHTS USING SEM-MLA, EMPA AND NANOSIMS APPLICATIONS

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ABSTRACT

Water injection has been applied with great success on the Norwegian continental shelf (NCS) and has in addition to maintaining pore-pressure a significant EOR effect. Understanding rock-fluid interactions during flooding experiments with synthetic seawater under reservoir conditions comparable to the NCS, are of importance in order to decide on the best-suited water-composition and to predict and control compaction-effects. For this objective fractured chalk samples are analysed with Scanning Electron Microscope Mineral Liberation Analyzer (SEM-MLA), Electron MicroProbe Analyses (EMPA) and nano Secondary Ion Mass Spectrometry (nano-SIMS) techniques to observe chemical and mineralogical changes on smallest scale. The results point to a significant influence of rock texture on fluid flow mechanisms and propagation through the sample. Micro- and nano-sized silicates and minute grains of magnesium-rich carbonates most likely grow on larger micron-sized calcite crystals and/or precipitate in pore-spaces. The new grown inner-fracture minerals show higher magnesium-concentrations than those of the surrounding matrix and minute Si-rich minerals have been detected. Remarkable is the observation that shell fragments from macrofossils, orientated perpendicular to the fluid flow, influence the rock-fluid interactions. Moreover, shell fragments of macrofossils resist fluid flow and its effects on mineralogy stronger than micro- and nanofossils and their fragments. This study shows that fluid flow and flooding movements are, even in seemingly homogeneous rocks like chalk, strongly dependent on the texture, which reflects in this case the environmental conditions during deposition of the carbonate or later induced fractures. This has, in turn, a significant effect on the distribution of mineral alteration caused by flooding at micron- and nanoscale. The formation of secondary minerals has a significant effect on the surface properties of the rock, such as surface charge, specific surface area, thus wettability, permeability and porosity, which are control factors for the recovery of hydrocarbons.

INTRODUCTION

Flooding by non-equilibrium brines is an efficient EOR-method in chalk-reservoirs. The composition and temperature of the brine seem to have an effect on oil recovery through chemical and mineralogical alterations as well as changes in mineral surface complexes, thus surface-charge and -potential of the rock [1-4]. The primary composition of the rock controls these interactions and studies have suggested that especially the silica-content in carbonate rocks, may play an important role [5]. Chemical and textural alterations have shown to affect the mechanical strength of the rock and the compaction of chalk, thus the recovery of oil [2, 6-8]. A large variety of experiments carried out on flooded chalk cores has led to a large dataset and reveals an extraordinary complexity of reactions even though the mineralogy of the rock itself seems rather simple. Understanding the mechanisms behind the water induced compaction, often called water weakening of chalk, and its EOR effects is a multi-scale work, ranging from nano- to field-scale. To understand these alterations at larger scale, one must also understand them at smaller scale and as such pore-scale studies are carried out (e.g. [2] and [9]) When flooding samples with synthetic seawater (SSW), anhydrite or gypsum have been found to precipitate together with magnesium-bearing carbonates and silicates. This is linked to dissolution of calcite [2]. The chalk core, which has been the subject of this experiment, is from the Late Campanian to Early Maastrichtian Gulpen Formation [10], sampled from an outcrop near Liège (Belgium). The chalk from this outcrop has a very clean nature, with a non-carbonate content mostly below 5 weight% (wt%). Diagenesis did not affect the rock significantly as such the preservation of mircofossils and pore-space is fairly good. Calcite cementation is absent, however contact cement is commonly found [11]. Most of the oil in chalk reservoirs is trapped in the matrix. In fractured carbonate reservoirs, displacement of oil is mostly related to spontaneous imbibition of water into the matrix [4]. Hence, it is important to understand how fractures in the reservoir behave during flooding to maximize the effect of the injected water, improving the sweep.

EXPERIMENTAL SET-UP AND METHODOLOGY

For this experiment, the chalk-core was fractured in two directions (Figure 1). One perpendicular to the flow, cut by a saw, and one along the core-axis, induced by uniaxial stress in a so-called Brazilian test cell. Parts of the latter fracture is the focus of this paper. The experiment was performed in a tri-axial cell at 130℃, pore pressure of 0.7 MPa and two injection brines, NaCl and Synthetic seawater (SSW). After an initial loading phase beyond the yield stress, a creep phase at 11.4 MPa followed with NaCl injection for 5.7 days, before SSW was flooded through the core at the rate of one pore-volume a day (PV/D) for 34 days. After this phase, the core clogged and was bypassed with SSW for another 24 days and was subsequently cleaned by distilled water. Before flooding, porosity was measured to 40.1 % and permeability to 5 mD. More detailed description of the experimental set up can be found in [2].

The here presented data is based on the following analytical methods; field emission gun Scanning Electron Microscope (SEM) with Energy-Dispersive X-ray Spectroscopy (EDS), Mineral Liberation Analysis software (MLA; FEI Quanta 650 FEG with EDAX-EDS and Quantix Esprit 1.8 software; 25 kV acceleration voltage 12 mm working distance at TU Freiberg/Saxony), Electron MicroProbe Analyses (EMPA; JEOL JXA-8900RL; 15 kV acceleration voltage, 20 nA current and 2 μm beam; TU Freiberg/Saxony) and nano Secondary Ion Mass Spectrometry (NanoSIMS 50; 16 kV impact energy, 2 pA current and 150 nm probe size; LIST). Detailed methodologies are described in [9]. In fine-grained chalk, it is difficult to resolve the composition of all minute grains by MLA, and areas with different content of magnesium (Mg), were classified into two so-called “mixed spectra”, in addition to minerals such as calcite, magnesite, quartz, clay minerals, and feldspars. The names of the mixed spectra are denoted “Low Mg calcite” (Mg wt% <1%) and “High Mg calcite” (Mg wt% >1%). The spatial resolution is between 1 and 2 μm per pixel.

RESULTS

MLA-images show that inside fractures there is in general a higher concentration of magnesium (Mg), silicon (Si) and aluminium (Al). Shells of micro- and macrofossils stand out as to have very low Mg content, even contain pure calcite, while the matrix of the rock has a mixture of high and low Mg concentrations. Figure 2 shows the fracture running from the bottom to the top of the figure with fluid-flow direction along the fracture. A shell from a macrofossil is embedded perpendicular to the fracture. This texture provokes a significant difference in Mg content between the concave side of the shell, with higher Mg concentrations, and the area of the convex side of the obstruction. This trend is confirmed by EMPA data along the profile A-A’ in Figure 2, showing higher values for MgO, SiO_2 and Al_2O_3 on the concave side of the shell (Figure 3). Analyses by nanoSIMS show that another fragment of a shell embedded in the matrix, also exhibit different behavior than the surrounding particles (Figure 4). It does not seem altered by flooding of SSW and the shell shows a clear depletion of Si and Mg while, compared to the matrix, it seems to have kept its original calcitic composition. With the methods used, no precise evidence of calcite dissolution is identified in the core, but as at least part of the newly precipitated material is assumed to be Mg-bearing carbonate, dissolution of calcite is a pre-requisite for having CO_3^{2-} available in the fluid. In addition, dissolution is confirmed by presence of calcium (Ca^{2+}) in the produced water from the experiment (not shown in this paper).

DISCUSSION

In the fracture, enrichments of Mg, Si and Al could be observed, measured as either oxides, elements or isotope clusters. This is compatible with the results from studies identifying precipitated clay-minerals and/or Mg-rich carbonates in fractured areas [12]. Even though the resolution of MLA measurements does not enable identification of the mineralogy of single grains in every case, the increase in concentrations of Mg, Al and Si corresponds to an increase in silicates and alumo-silicates, most probably clay precipitates, in addition to Mg-rich carbonates including minute particles of magnesite. A general increase in Mg content in the sample after flooding agrees with the information from studies using effluent profiles in chalk-flooding experiments which show retention of Mg^{2+} and production of Ca^{2+} [9, 12]. Remarkable is how the concentration of Mg, Si and Al varies between the concave and the convex side of the shell-fragment perpendicular to fluid flow and how the shells in Figures 3 and 4 resist to the effect of the fluid. The flow is clearly obstructed by the shell-fragments (Figure 2 and Figure 4) and cannot infiltrate the shell during the here used flooding time. Although most of the surrounding matrix seems affected by the flooding of SSW, the shells and microfossils seem inert to the flooding agent and show to much less degree, if any, mineralogical changes. There may be several reasons for this differentiation: 1) The size of the carbonaceous particle matters for the chemical stability of the grain. Smaller particles may be more prone to alteration and mineralogical changes than larger ones. 2) The initial composition of the fossils differs from the finer-grained matrix, such as Mg/Ca ratio depending on e.g. age, seawater composition and temperature at formation. 3) Curvature and surface properties affect the dissolution rates of the initial grains and fossils [13]. 4) The increase in Mg-, Si- and Al-concentration may be due to precipitation of smaller crystals/grains in the pore-spaces or in the fractures where there is more free space and the stress state is different. If all these points would be deciding factors, then the mineralogical composition of the rock itself is paramount for the fluid flow in chalks. Without the knowledge of the micro-facies, fluid flow is barely predictable even on core scale for the length of the experiment here. It is possible that these criteria are of less significance when massive fluid flow affects entire rocks over a longer time. However, they affect definitely simulation and modelling at core scale, assuming homogeneous rock and rock-fluid interactions, which function for the entire rock in a similar way. Chalk with large amounts of micro- or macrofossil shells, will react differently than those rocks with fewer shell fragments. Furthermore, these chemically more resistant components influence the fluid flow through the core and play an important role to understand the progression of fluid in a core sample. As the rock-fluid interactions are the key components controlling compaction in chalk during flooding, this factor is important when studying the geo-mechanical behaviour of chalk. Obstruction of fluids may also cause unpredicted high concentrations of ions in the fluid, which in turn would change the equilibrium and influence the rock-fluid interactions in certain locations, enhancing coupled dissolution and precipitation locally. At macro-scale this may cause sealing of fractures, thus affecting the sweep and imbibition of water into the matrix.

CONCLUSION

The results from this study show clearly that chemical and textural alterations do take place when flooding non-equilibrium synthetic seawater (SSW) through an onshore Liège chalk-core with two fracture systems. Fluid flow through the core is significantly influenced by the fractures and the texture of the rock. Microfossils and shell debris of macrofossils play an important role in the rock-fluid interplay and affect estimates of rock-fluid interaction as they react differently from the much finer-grained matrix in chalk. Measurable differences in Mg-, Si- and Al-concentrations on either side of the shell lying perpendicular to the fluid flow in the natural fracture, proves disturbances of the fluid flow and variable alterations of the core at micro-scale. Hence, the presented results imply that occurring heterogeneities in chalk after flooding can occur and should be controlled before modelling the impact on a larger scale. This accounts also for the texture and the pattern of existing fractures. Such alterations may lead to sealing of fractures or heterogeneous alterations and may therefore be important to control fluid-flow and imbibition of water and compaction in reservoirs.

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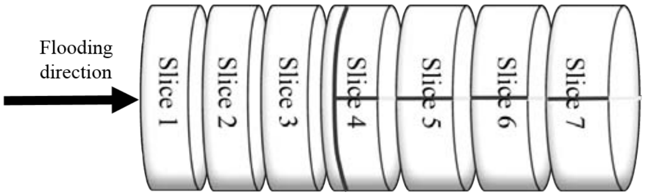

Figure 1. Sketch of the chalk core and how it was cut after flooding. Dark grey lines showing the positions of the fractures created before flooding

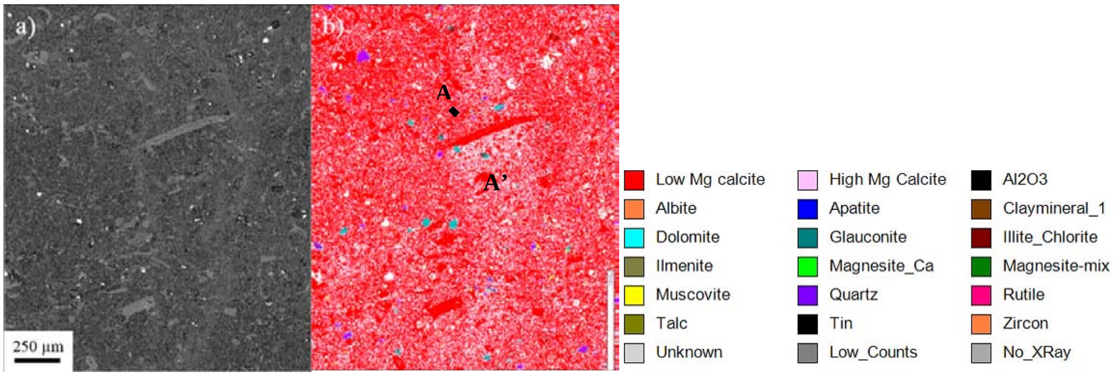

Figure 2: SEM-BSE micrograph (a) and MLA scan (b) of the same area of the fracture. The Mg-content is higher on the concave side (below) of the shell than on the convex side (above). White areas relate to pore space.

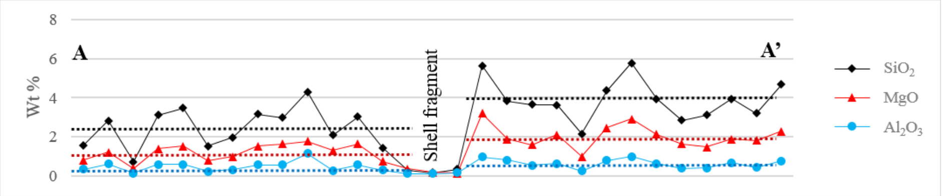

Figure 3: Oxide values measured by EMPA along the profile A - A' in Figure 2. Dotted lines are average values

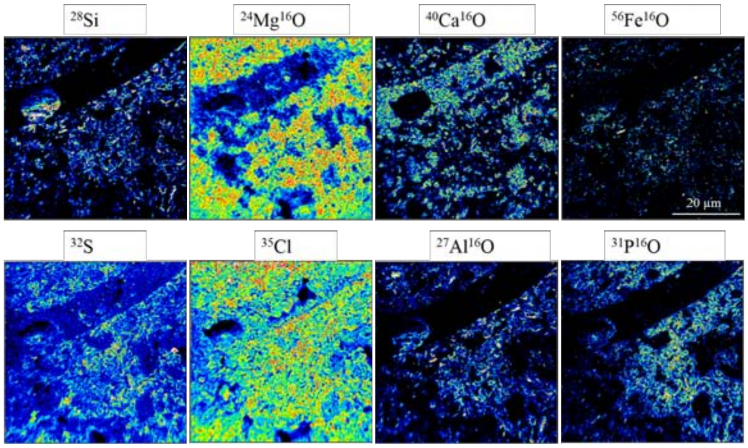

Figure 4: NanoSIMS images showing relative concentrations of elements between a shell-fragment and the surrounding matrix in fractured Liège chalk flooded with synthetic seawater (SSW). Notice the enrichment of Mg in the surrounding matrix compared to the concentration of Mg in the shell-fragment