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Changes in surface chemistry and wetting state during aging and flooding of carbonate rocks and implications for recovery mechanisms

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The efficiency of displacement of oil in tight reservoirs largely depends on the physicochemical properties of the Crude Oil-Brine-Rock (COBR) three phase system. Understanding the interfacial phenomena involved in fluid flow in subsurface reservoirs such as tertiary recovery methods and CO_2 injection is critical for developing novel processes to improve oil production while reducing emissions and other environmental impacts at a lower operating cost. Prior to conducting displacement experiments rock samples are typically "aged" in oil containing surface-active compounds to replicate the wetting state of the reservoir. The wetting state is traditionally defined by contact angle changes and the injection profile during displacement experiments, however, an improved understanding of the chemistry that defines these surface properties can be obtained by advanced surface imaging and chemical analysis. This study presents an investigation of the surface chemistry of chalk samples from the Danish North Sea reservoirs during aging in crude oil, before and after core flooding. The aging process of the rock sample is investigated for rock samples from five different reservoirs at aging times ranging from 3 days to 9 months. The chalk surfaces were analyzed by SEM-EDS before and after immersion in crude oil for the selected aging periods to show the changes in the elemental composition of the surface. The adsorption of organic material on the surface during aging is investigated by IR-enabled AFM (Bruker NanoIR3) which indicates the distribution and qualitatively the amount of polar organic material which adheres to the surface. The results indicate an enrichment in -COOH and -OH groups on the surface, and a material richer in N and S compounds than elements than the crude oil. These changes are generally most evident after aging times longer than 2 months which is longer than generally considered sufficient for aging. During displacement experiments, the geochemical processes result in a reduction of Ca after water flooding, and other elements are seen to accumulate increase, including Si, Al, Mg, Sr, Ba, and Na. The results of surface changes after flooding experiments for both organic and inorganic materials are discussed in the context of low salinity water flooding in mature carbonate reservoirs. The results are used to interpret a series of recovery experiments on North Sea chalk samples, in which the effect of injection brine composition on absolute recovery has been investigated. The effluents of the recovery experiments have been analyzed for major ions, the content of added trace compounds representing surface active organic acids, and structural changes to describe the chemical changes taking place during flooding.

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