Geochemical, mineralogical and geomechanical effects of impure CO_2 on reservoir sandstones during the injection and geological storage: an experimental approach

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Within the German national project COORAL* the behaviour of reservoir rocks from deep saline aquifers during the injection and geological storage of CO_2 with inherent impurities such as SO_X and NO_X is studied in laboratory experiments. Samples are taken from sandstone outcrops of possible reservoir formations of Rotliegend and Bunter Sandstones from the North German Basin. A combination of geochemical/mineralogical alteration experiments and geomechanical tests was carried out on these rocks to study the potential effects of the impurities within the CO_2 pore fluid. Mineralogical alterations were observed within the sandstones after the exposure to supercritical (sc)CO_2 with SO_X/NO_X and brine, mainly of the carbonatic, but also of the silicatic cements, as well as of single minerals. Besides the partial solution effects, secondary mineral precipitations of carbonates and subsidiary silicates were observed within the pore space of the treated sandstones. The evaluation of the chemical composition of the reaction fluid during the course of the autoclave experiments also indicate that dissolution and precipitation processes occur in the system fluid/rock/gas. The alterations affect the porosity and permeability of the treated sandstones and also weaken their grain structure. Results of geomechanical experiments on untreated samples indicate that the rock strength as well as the amount of injected scCO_2 is influenced by the chemical composition of the pore pressure fluid (scCO_2 + SO_X/NO_X). After long-term autoclave treatment with impure scCO_2, sandstone samples exhibit reduced strength parameters and modified deformation behaviour compared to untreated samples.

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Systematics of biodegradation of sulfur compounds in heavy oil reservoirs

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The growing trend of producing and refining large volumes of high-sulfur content petroleum leads to a need for exploring new ways of meeting environmental regulations regarding the allowable sulfur emissions and sulfur content of petroleum derivatives. Biodesulfurization is one of the new technologies currently being considered [1,2]. In this study, we use a natural biodegradation site to examine the systematics of biodegradation of sulfur compounds in oil at reservoir conditions. The biodegradation of alkylbenzothiophenes (alkylBT) and alkyldibenzothiophenes (alkylDBT) were investigated in oil columns with progressively biodegraded oil from top to bottom, using gas chromatography mass spectrometry and sulfur isotopic compositions of bulk oil and oil fractions. The concentrations of alkylBT and alyklDBT decrease from hundreds of ppm to almost complete removal in biodegraded oil columns with different ranges of biodegradation levels. The order of sensitivity to biodegradation was found to be generally dibenzothiophene (DBT), dimethylBT (DMBT) > trimethylBT (TMBT) > methylDBT (MDBT) > dimethylDBT (DMDBT). The preferential removal or preservation of some of the isomers gives insights into reaction mechanisms. Changes are also seen in alkylated high molecular weight S and mixed SNO species observed using Fourier Transform Mass Spectrometry (FTICRMS), providing evidence for dealkylation of even very high molecular weight S bearing species. Despite multiple changes at the molecular level in the thioaromatic and NSO fractions, the bulk sulfur content of the oil did not change significantly in the studied oil columns. The $\delta^{34}S$ values of bulk oil also did not change systematically with increasing biodegradation of sulfur compounds, while slight variations in the oil thioaromatic and asphaltene fractions may be related to the microbial alteration process. We propose a route forward for studying the natural and industrial scale sulfur systematics of biologically altered crude oils.

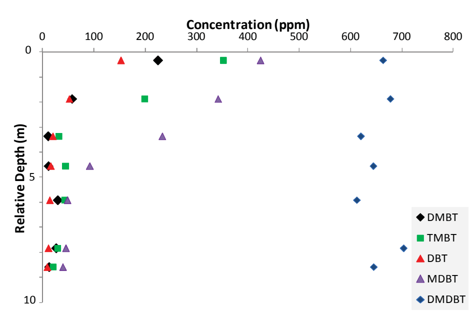

Figure 1: Progressive biodegradation of sulfur compounds in progressively biodegraded oil towards the reservoir base.

[1] Marcelis et al. (2003) *Biodegradation* **14 (3)**, 173-182.
[2] Mohebali and Ball (2008) *Microbiology* **154**, 2169-2183.