



Experimental and geochemical modelling study of cement degradation by CO₂

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In the context of geological CO₂ storage, integrity of wellbores is a topic of major importance. This study is focussed on CO₂ migration due to geochemical cement degradation.

Experiments were performed in a high pressure reaction vessel, using cores of Portland class G cement recovered from a well of an ECBM pilot in Poland. To our knowledge, it is the first time that cement from an actual well, with long curing times, is used. The experiments are performed in (1) excess CO₂-saturated brine, (2) water-saturated (wet), supercritical CO₂ and (3) limited, more realistic amount of CO₂-saturated brine. Also, a 1D kinetic transport model is developed in PHREEQC which is tuned to the experimental results to be able to systematically study the (long-term) geochemical effects at varying downhole conditions.

The cement samples from the performed experiments show similar reaction zones as the ones reported in literature (e.g. Kutchko et al., 2007). They comprise an altered, orange, outer zone, a thin carbonation zone (calcium enriched) and a grey core (partially depleted in portlandite). Differences are observed for the three experimental methods. After reaction in excess CO₂-saturated brine (1), the orange zone is highly depleted in calcium due to re-dissolution of carbonate, while this is not observed after reaction in wet scCO₂ (2). In addition, the carbonation zone is not as pronounced in the latter. Furthermore, the reaction zones are concentric after reaction in excess brine (1) while they occur in patches when wet scCO₂ (2) or a limited amount of brine (3) is used. The cement is highly heterogeneous and limited amounts of water will first infiltrate into more permeable areas, causing a stained pattern of alteration. The experimental results indicate that the presence of water is an important factor since it facilitates reactions and diffusion of aqueous species. Experiments with CO₂ in a limited and more realistic brine:cement ratio are on-going. It is expected that the progress of geochemical alteration will cease after all brine is consumed in the reactions.

The model results show portlandite dissolution to be directly related to CO₂ ingress and lowering of the pH. Geochemical reactions result in the formation of three distinct zones in the cement which are very similar to the reaction zones observed in the experiments. It is predicted that calcite, formed in the carbonation front, is not re-dissolved when the fronts move inward. This is probably due to the calcium saturation of the brine in contact with the cement and therefore simulates similar conditions as the experiments performed in limited brine, representing realistic, downhole conditions. These results suggest that if excess brine is not present, calcite dissolution in the outer zone of the cement will be limited. Since calcite dissolution is thought to be the main cause of porosity increase of the cement, wellbore integrity might be better than previously thought. The model will be used in future studies to simulate long-term effects at varying conditions.

Kutchko et al. (2007) *Environ. Sci. Technol.* 13 (41), 4787–4792.