Effect of Very Low pH on Degradation of Class G Cement: Implications for CO₂ Geological Storage

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Abstract

Identification and mitigation of CO₂ leakage through well cement, particularly for abandoned wells, is currently considered one of the major technical challenges associated with ensuring security of CO₂ storage. Any potential leakage pathways in a typical abandoned well would likely be along the well cement, and would arise due to the interactions between CO₂, brine and the well cement that affect mineral stability and lead to carbonation [1-3]. Any resultant degradation, together with a general increase of porosity and permeability, could lead to the loss of cement structural integrity. Despite the importance of pH in identifying the rates of chemical reactions, very few studies have been performed in brine-CO₂ mixtures at high pressure [4], and more specifically the effect of low pH on cement wellbore has received little attention. Therefore, the aim of this work is to understand the effect of low pH on wellbore integrity under geological CO₂ storage conditions and to assess whether or not the interactions between CO₂, brine and the well cement can cause a noticeable change in the cement’s microstructure.

This paper presents the results of a series of laboratory experiments using Class G cement, reacted at pH 1.3 in batch reactors for periods of up to 9 months at specific pressure and temperature conditions ($P_{CO₂}$=150-250-265 bar and $T$=50-80-90°C), which are representative of different depths along a typical wellbore. The prepared brine composition mimics that of North Sea seawater, but sodium hydrogen sulphate (NaHSO₄) was used instead of a neutral salt like sodium sulphate (Na₂SO₄) in order to decrease the pH of the brine to a very low value, thereby stress testing the system in extremis. As a result, the brine used for this work has a pH of 1.3, while typical North Sea seawater has a pH of 8.1 [5]. Following the hydrothermal batch reactor studies, it was clear that the cement samples had undergone chemical reactions, as they showed significant colour change. In the case of the samples that were under $P_{CO₂}$=150 bar and $T$=50°C conditions, the outermost region
presented an orange-brown ring. By contrast, cement samples that have been subjected at higher pressure and temperature ($P_{\text{CO}_2}=250-265$ bar and $T=80-90^\circ\text{C}$) showed a pale green colour in the outermost region with some crystals covering that area.

The cement and brine samples have subsequently been analysed using a number of techniques, including ICP-OES, XRD and SEM-EDX. The ICP-OES analyses showed variations in the abundance of $\text{Na}^+$, $\text{Ca}^{2+}$, $\text{K}^+$, $\text{Mg}^{2+}$, $\text{S}^{2-}$, $\text{Sr}^{2+}$, $\text{Li}^+$, and $\text{Si}^{4-}$. The concentrations of $\text{Ca}^{2+}$, $\text{S}^{2-}$ and $\text{Sr}^{2+}$ have dropped throughout the experiment for the cement samples exposed at $P_{\text{CO}_2}=150$ bar and $T=50^\circ\text{C}$ conditions, whereas $\text{K}^+$, $\text{Si}^{4-}$, $\text{Mg}^{2+}$ and $\text{Li}^+$ were leached from the sample. Cement samples exposed at higher pressure and temperature conditions ($P_{\text{CO}_2}=250-265$ bar and $T=80-90^\circ\text{C}$) showed a slightly different behaviour. The concentrations of $\text{Ca}^{2+}$, $\text{K}^+$, $\text{Mg}^{2+}$, $\text{Si}^{4-}$ and $\text{Li}^+$ increased in the brine sample as a result of the experiment and, conversely, $\text{S}^{2-}$ and $\text{Sr}^{2+}$ decreased slightly.

The results obtained thus far indicate that the cement samples may have chemically reacted and this degradation is expected to change the petrophysical properties of the cement. If porosity and permeability were increased, that change would affect the long-term performance of the cement, and could in an extreme case lead to well failure. This paper will present a comprehensive characterization of the reacted cement and brine samples, including ICP-OES, XRD and SEM-EDX measurements, to improve our understanding of the effect of very low pH on degradation of Class G cement at downhole conditions, as a reference point for understanding wellbore CO$_2$ storage security.

References