Innovative Leaching Tests of an Oilwell Cement paste for CO_2 Storage: Effect of the Pressure at 80°C

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In the case of CO_2 geological storage, well integrity is of utmost importance to guaranty the safety of future industrial operations. One of the main challenges is the long-term behavior of the cemented annular. In the recent years, several published studies dealing with the alteration of Portland cement by CO_2-rich fluids have been performed on sound cement-based materials. However, in downhole conditions, the cement sheath might have been altered due to the exposure to geological formation fluids for several decades. Consequently, the initial state considered in the published literature on oilwell cement integrity is likely not to be representative of the cement annulus in the well.

The key issue to predict the long term behavior of cement paste is to improve the knowledge of its evolution when contacted by CO_2-rich fluids; this is the case in particular for the old wells which have been exposed to severe environment before being in contact with CO_2. Indeed, some studies indicate that significant modification of the well cement can be expected in older wells, and this should be taken into account in modeling the chemical durability of cements exposed to geosequestered CO_2. Moreover, it is known that pressure has an impact on the kinetics of the chemical reactions involved during cement hydration and thus on the microstructure of the cement paste. Therefore, pressure is also expected to modify the kinetics of degradation and the associated changes of the microstructures leading to different degradation patterns.
This study reports the characterization of an oilwell cement paste exposed at high pressure and high temperature, to a formation fluid with low carbonates content (representative of some sedimentary basins) in order to improve the knowledge of the long-term behavior of oilwell cement in downhole conditions.

Materials and Methods

The Class G (Cemoil®) Portland cement used in this work was obtained from Italcementi company. The cement powder was mixed with distilled water with a water/cement ratio (w/c) of 0.44 (prepared according to ISO/API specifications). Specimens were hardened for 1 month at 80°C in pressurized curing chambers (70 bar and 200 bar). The pressurized curing chambers were filled with water saturated with $Ca(OH)_2$, NaOH and KOH to prevent pre-alteration during the curing period.

A specific leaching experimental set-up was developed, making it possible to carry out innovative degradation tests on cement pastes at high temperature and high pressure, with a continuous renewal of the aggressive fluid corresponding here to a brine containing carbonates. The degradation tests were carried out at 80°C-1 bar, 80°C-70 bar and 80°C-200 bar on the cement paste samples previously cured. These specimens were exposed to the running brine for one month and then were characterized using advanced methods for chemical and mineralogical analysis (MIP, SEM, XRD, TGA-TDA and $^{29}Si/^{27}Al$ NMR).

Main Results

The main results at atmospheric pressure indicated that cement leached exhibited a classical degradation pattern: the degraded thickness matched with the portlandite total dissolution front.

The tests carried out at 80°C-70 bar and 80°C-200 bar, highlighted a strong effect of the pressure leading to a mechanism of deterioration different from that observed at atmospheric pressure. Cement samples leached respectively at 70 and 200 bar showed a different behavior: the degraded thickness was greater and the portlandite total dissolution front was thicker. This was due to the presence of an inner zone where portlandite was partially dissolved. Secondary precipitations, leading to a succession of fronts of dissolution/precipitation (including carbonation due to the presence of carbonate in the aggressive fluid), were observed in this zone. The alteration mechanism at high pressure appears to be more complex than the one observed at atmospheric pressure.

This study showed that pressure had a strong impact on the phenomenology and the kinetics of oilwell cement paste degradation in downhole conditions. Degradation tests with saline water illustrated that significant modifications of the well cement (in the mineralogy and microstructure) can be expected in older wells.

The initial material used to carry out degradation tests under CO_2 environments should account for these modifications. Advanced characterization of retrieved cementitious materials might be required, because it is unknown how these significant alterations will ultimately affect the integrity of the cement under CO_2 injection scenarios.

Based on these new considerations, predictive models will have to simulate the sealing ability of cement annular, for long-term safety demonstration of CO_2 geological storage projects.