Impact of Temperature and Cement Formulation on CO₂ Induced Changes in Oilwell Cements Under Downhole Conditions

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Context and objectives
The development of geological storage solutions to reduce CO₂ release and mitigate climate change requires improvements of several technological and scientific issues. One of the major issues regarding efficiency and long-term confinement of CO₂ in a depleted geological reservoir is the proper assessment of the sealing performance of the wells that connect reservoir to the surface. This is achieved using cement-based materials, which are placed between the steel casings and the geological formations to provide complete isolation of each geological zone (reservoir, caprock, aquifers...), support the casing and finally protect casing strings from corrosion.

After CO₂ injection, when water is present, the CO₂ will chemically react with the cement based materials.

How the CO₂ enriched formation fluids may change cement chemistry and properties? Could the sealing performance of the wells be affected by these changes?

The objectives of this study are to experimentally assess the phenomenology (chemical and mechanical), the kinetics of the changes occurring in different class G Portland cements (neat and with silica flour) exposed to CO₂ enriched aqueous fluids at 8 MPa and two different temperature conditions.

Experimental program
The experimental program for this study consists of:

- A first carbonation test using neat class G cement, at a temperature of 90°C (194°F) and a pressure (supercritical CO₂ above water) of 8 MPa (1160 psi);
- A second carbonation test using class G cement with silica flour (to prevent strength retrogression), at a temperature of 140°C (284°F) and at the same CO₂ pressure of 8 MPa.

The samples are exposed to either CO₂-saturated water or wet CO₂, without forced flow through the samples (static tests). These static experiments are considered as relevant of the conditions at the formation/cement sheath interface.
Cement specimens experimented various CO$_2$ exposure time periods and were characterized using advanced methods for chemical and mineralogical analysis (X-ray tomography, SEM, XRD, TGA-TDA…) and mechanical testing (micro hardness).

Finally, coupled chemo-mechanical tests (dynamic tests) are underway on similar class G cement and similar CO$_2$-rich water. Dynamic experiments were developed to simulate downhole pressure conditions in the injection zone, where high pressure gradients will drive CO$_2$ flow in the geology and also in the cement sheaths. During the tests, a sample confined under triaxial stress is subjected to controlled pressure gradients of CO$_2$-saturated water and other fluids. Axial strain, flow rate are measured and permeability is calculated over time.

**Detailed results**

- **Static experiments:**
  The static carbonation tests on neat class G cement at 90°C and class G cement with silica flour at 140°C resulted in partial or total carbonation of the samples. Class G oilwell cement is thus reactive when exposed to carbonic acid under these conditions. However, the behavior is different for each material: the carbonated front moves faster (and deeper) at 140°C than at 90°C: the carbonation front progression is controlled by diffusion for neat class G cement (the front evolves linearly with the square root of time), while it is limited by reaction kinetics for class G cement + silica flour (the carbonation front evolves linearly with time).

  Chemical and Mechanical characterization show:
  - A higher decrease in porosity for neat class G cement, compared to class G cement + silica flour;
  - The Young’s modulus decreases in class G cement + silica flour, while lower evolution is observed for neat class G cement.

  As the initial connected porosity exhibits a similar value for both materials (about 30%), and the CO$_2$ solubility is similar in pure water at 90°C and 140°C, the difference may stem from the mineralogical nature of the hydrates, their proportion and microstructural assemblage of the cement formulations. The differences induce different invasion rate (i.e. carbonation rate), different chemical reactions, and finally different evolution of the mechanical properties.

- **Dynamic experiments:**
  It appears from the main results, with neat class G cement, that adding CO$_2$ to the water injected throughout the mechanically stressed cement has no significant impact on deformation of the cement (no change in the strain rate is observed). Simply, compaction was observed, as expected due to the increase in deviatoric stress. No change in the cement’s mechanical properties was measured during CO$_2$-rich water injection. The permeability values decrease rapidly, finally resulting in cement samples plugging.

**Conclusions:**

From the preliminary results, the cement matrix reaction in CO$_2$ environments does not appear to be the driving phenomenon for loss of well integrity, even for cement with silica flour that exhibits greater carbonation rate; mechanically induced damage to the cement sheaths (hydro frac, micro-annulus, etc.) may give greater cause of concern.