Impact of CO_2 Saturated Brine on Fractures in Well Cement

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Abstract

As climate is changing an international effort is underway to identify solutions to reduce effects of global warming. Carbon capture and storage (CCS), which is storing CO_2 in subsurface, is currently being considered as a remedy for reducing CO_2 concentration in the atmosphere. For safe, sustainable CCS technology implementation, it is crucial that existing oil wells in the fields used for CO_2 storage, should not have pathways for gas to escape back to the surface. Fractures in oil well cement, formed during cementing and production operations, are the possible leakage routes. This study tested a novel approach, by creating controlled internal fractures within cement cores (without subjecting samples to external stresses), where cement-fluid interaction were monitored and characterized after 4 and 8 weeks periods, focusing on the “fracture”-slit alterations. The observed changes will enable us to make long term predictions on whether the cement-fractures in abandoned oil field wells can withstand CO_2 rich brines in a long term (minimum 500years).

The cement core samples were prepared by following API-10B, dimensions 2inch length and 1inch diameter, composed of class-H cement (density 16.5 lbm/gal; water to cement ratio: 0.388). The controlled slits were embedded within the center of each of the cores using 2 x 0.39 x 0.012 inch lubricated shim stock. The shim stocks were extracted from each of the cores after they were cured under high temperature/pressure conditions for a period of four weeks. A pressurized accumulator supplied the CO_2 saturated brine to an in-house experimental apparatus which allowed fluid displacement through six cores independently at a pressure of 50 psig. Each of the cores was held in a pressure tight core holder that has needle valves at the top and ball valves at the bottom to displace the saturated brine into the controlled channel and out to a container for pH measurements. An outlet line was also installed to determine pH before it would enter the cores. The cores were centered in the core holder by paraffin wax to ensure there was only displacement through the controlled channel. The ion chromatography (brine analysis) detected leaching of calcium out of the cement into the brine, with a constant increase of Ca over time followed by the reduction in pH of the effluent brine (Fig. 1a). The mineralogical composition of the core, both qualitative and quantitative, determined by XRD (Fig. 1b) confirmed the presence of altered zones within the fracture walls, typically depleted in $Ca(OH)_2$ and enriched in $CaCO_3$. Environmental Scanning Electron Microscopy (ESEM) and Energy Dispersive Spectroscopy (EDS) were used to characterize the sample surface without drying or any intrusive sample preparation, further supporting physical alterations at the fracture walls. Dissolution of cement and material loss was clearly visible on the surfaces of the fracture. The ESEM detected microstructural changes at the fracture walls, depicting crystal growth within the fracture/slit. Simultaneously, new micro-fractures, perpendicular and parallel to the fracture, were detected as well. (It is not certain what exactly caused these micro-fractures, possibly due to the stress applied to the fracture walls from the bridging crystal growth) (Fig.2). The EDS showed the decrease in calcium in the altered portion of the core in comparison to the unaltered (Fig.3b). Computer Automated Tomography Scanning (CAT scan), a non-destructive scanning method, evaluated each core in its as received state. CT scans primarily revealed the fracture geometry and image contrast pointed visible alterations within cement. These changes were only observed after 8weeks (static and dynamic conditions) (Fig.3a).

Being that all the alterations caused by the CO_2 saturated brine were at a microscopic level after 4weeks, we were able to detect changes in more details after 8weeks and furthermore the changes were more evident in the sample run under dynamic conditions (continuous fluid flow through the slit at 3ml/minute), best illustrated by a sequence of CT scans in Figure 3a. Early conclusion is that the chemical/physical properties of the system will determine reaction rates. This is still a work in progress and more conclusive data is being acquired needed for modeling and long term prognosis of cement durability under CO_2 sequestration conditions.

Sample Identity	Calcite	Portlandite*	Calcium Silicate**
CVX-0wks	4	87	6
CVX-4wks	2	88	8
Fracture D-1-8wks	59	3	22
No Fracture D-1-8wks	12	63	12

Fig. 1a Ion chromatography analysis of the effluent brine showed an increase of Ca concentration and pH (left), Fig1b: XRD mineralogical alteration showed an increase in carbonate and CSH near the fracture (right)

Fig. 2 – ESEM. The bridge-like feature observed within the slit suggests a self-healing possibility.

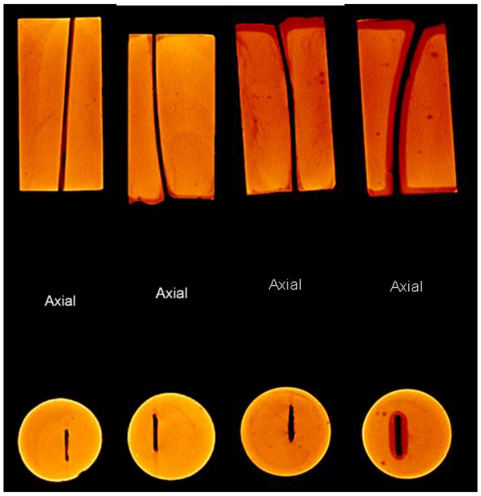

Fig. 3a: CT scans of cement cores: (1-control, 2-after 4weeks exposure, 3-after 8weeks exposure, 4-after 8weeks exposure with continuous fluid flow) (left) Fig 3b: EDS elemental analysis of unaltered and altered areas within cement core, in spot mode analysis (right)

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