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An experimental study of the effect of CO_2 rich brine on artificially fractured well-cement

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ABSTRACT

The performance of structural seals overlying reservoirs targeted for CO_2 storage relies upon the integrity of well-bore cements, which will be affected by interactions with CO_2. Microfractures within the well-bore cement may lead to seepage of CO_2 to the surface and/or fresh water aquifers. Thus, understanding CO_2-rich brine induced changes to the imperfections in cement matrix is vital for safe and effective implementation of this new technology named Carbon Capture Utilization and Storage (CCUS).

This paper presents an experimental study that depicts the changes of the cement internal structure due to interaction with acidic brine through a system of artificial fractures within the cement matrix during 100 days flow through experiments. Helical computerized axial tomography and high resolution micro-computed tomography were used to visualize several sub-volumes of flow-through cores. Furthermore, a complementary high-resolution surface profilometry allowed quantification of changes of the roughness of fracture walls and their impact on the fracture aperture.

1. Introduction

CCUS projects require capturing carbon dioxide from large point sources such as fossil fuel power plants and other manufacturing processes that produce CO_2 and storing it in the subsurface for hundreds of years. Although CO_2 has been injected into geological formations by the oil and gas industry for enhanced oil recovery (EOR), the permanent storage of CO_2 is a relatively new concept. The long-term containment of injected gas is a critical component for effective CCUS, requiring that potential pathways for leakage be identified, investigated and risk assessment performed. CCUS technology may involve injection without offsetting production of fluids leading to potentially large pressure perturbations, particularly during the injection phase [1].

The resulting vertical pressure gradients favor leakage into overlying freshwater aquifers and/or the atmosphere. Existing wellbores with a history of wellbore integrity problems and/or sustained casing pressure have been identified as one of the most likely pathway for such leakage [2].

Investigations of the long-term interactions of acidic brine (resulting from equilibration of formation waters with injected CO_2) and wellbore cement are fundamental to understanding the integrity of existing wellbores and their long-term durability during CCUS operations. In the post injection stage, acidic brine with pH $\sim$ 3–5 will interact with wellbore cements whose equilibrated pore fluids have pH $\sim$ 13.5. This significant pH change will lead to changes in the cement matrix properties since most of the hydrated and unhydrated cement minerals are in equilibrium at pH > 7. The primary objective of this experimental study is to quantify mineralogical and microstructural changes of cements containing fractures after they have been subjected to a flow through regime of CO_2 rich brine for an extended time of 100 days and establish the impact of these changes on hydraulic conductivity of cements when compared to 30 days exposure previously reported by Yalcinkaya et al. [3].

1.1. Fractured wellbore cement

Cement has been used to provide zonal isolation (i.e., minimize the potential for flow through wellbores that intersect important structural seals as well as flow between different formations) in oil, gas and geothermal wells for decades. In addition, its mechanical strength enhances the geomechanical stability of the wellbore and its low permeability provides protection for metal casings against corrosive formation waters rich in salts and often CO_2 and/or H_2S. Oil, gas and geothermal wells are designed to last a few decades; conversely, CCUS projects will require wellbore cements to perform zonal isolation for hundreds of years. The second major difference between CCUS and traditional subsurface injection of CO_2 in EOR is the volume and injection pressure, both of which will be much higher and without any production of fluids

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to offset the potential pressure buildup, especially during the injection – early stages of CCUS.

The zonal isolation provided by wellbore cements aims to prevent fluid entry into wellbores except in the perforated sections within production and injection zones. However Sustained Casing Pressure (SCP), defined as the casing pressure caused by trapped gas or liquid in the annulus, is recorded in the field as a direct manifestation of inadequate cementing. This causes major technical and economic problems during plugging and abandonment (P&A). However, CCUS technology is based on injection of large volumes of fluid therefore pressure buildup is likely to occur during injection period and can potentially cause faster SCP manifestation, resulting potentially in a rapid gas release.

Wellbore cement failures can take place both during and/or after cementing operations. Inappropriate cement slurry design or inadequate mud removal prior to cementing may result in weak bonding at cement/casing and/or cement/formation interfaces. Such conditions may result in the formation of gas channels within cement column. The set cement is further subjected to unsteady loads as a result of continuous pressure and temperature cycles during production and injection operations as well as various wellbore testing procedures [4].

The cement matrix has different thermal expansion and elasticity coefficients than the casing and adjacent rock formations. Variable expansion rates of the above materials may lead to formation of a microannulus between the casing/rock and the cement as well as create fracture networks within set cement [5].

1.2. Cement – acidic brine chemistry

Calcium and silica are the two major elements of Portland cement, which consists of four main crystalline components: Tricalcium Silicate (Ca_3SiO_5–C_3S), Dicalcium Silicate (Ca_2SiO_4–C_2S), Tricalcium Aluminate ($Ca_3Al_2O_6$–C_3A) and Tetracalcium Aluminoferrite ($Ca_4Al_2Fe_2O_{10}$–C_4AF). As a result of hydration, Calcium Silicate Hydrates (C–S–H) and Portlandite ($Ca(OH)_2$) are formed. Furthermore, the hydration process forms other minerals such as Ettringite ($(CaO)_6(Al_2O_3)(SO_3)_3{\cdot}32\ H_2O$) [6].

When the cement matrix is exposed to CO_2-saturated brine, the following chemical reactions occur [7].

$$CO_2 + H_2O \rightarrow H_2CO_3 \quad (1)$$

$$H_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 + H_2O \quad (2)$$

$$H_2CO_3 + CaCO_3 \rightarrow Ca(HCO_3)_2 \quad (3)$$

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 + 2H_2O \quad (4)$$

Once consumption of all the major Ca-containing minerals (mainly portlandite and traces of calcite) occurs, C–S–H will start leaching Ca^{2+}, leading to a formation of an amorphous silica rich gel-like material, which has a deleterious effect on the mechanical properties of the cement and more importantly an increase in porosity [6,8].

In this study we investigated stability of fully hydrated Portland cement in contact with low pH fluids under dynamic conditions. However, some of unhydrated cement clinker minerals can still exist and therefore need to be introduced, as they also can contribute for example as a source of Ca once portlandite is depleted. The second set of characteristic typical for cement that is of importance in cement-fluid interaction is porosity and permeability. Chemically unaltered cement has low permeability, primarily due to the nature of fully hydrated cement which is dominated by C–S–H and its nanoporosity. In addition porosity and permeability can be impacted by hydrostatic pressure applied to cement in the field as well as various admixtures commonly used in the field, such as fluids loss control material, weighting agents, and contaminations. Ca leaching of hydrated Portland cement is associated with an increased total porosity and expected increase in permeability [2].

2. Methodology

2.1. Flow through apparatus

The experimental set-up reported in detail by Yalcinkaya et al. [3] was used for the current study. It consisted of a Hassler cell, syringe pump, hydraulic pump, data acquisition system, filters and pressure gauges. The Hassler cell was oriented vertically to simulate the upward flow of CO_2 saturated brine through a vertically fractured cement system. To maintain continuous flow of brine, a dual syringe pump system, with a maximum capacity of 507 ml, was adjusted to single-pump auto-refill mode during the experimental period. A 100-day flow-through experiment was carried out [3].

2.2. Cement core

Class H cement, as specified by American Petroleum Institute (API) cement classification was used, as it is a most commonly used type of wellbore cement in the United States, to form the cylindrical, 1-in × 12-in (2.54 cm × 30.48 cm) cement core. Following the recommendations from API (API 10B – Recommended Practice for Testing Well Cements), a water to cement ratio of 0.38 was used for the cement slurry, utilizing deionized water. Trapped air was removed from the cement using a vacuum pump before pouring cement slurry into teflon molds. Cement slurry was poured into custom made teflon molds to cast two halves and de-molded after 24 h. The cement core halves were cured in water bath pH ∼ 13 for 30 days at room temperature.

Upon hydration and curing the cement halves were glued using epoxy along the edges to obtain a 1-in × 12-in (2.54 cm × 30.48 cm) cylindrical shape with the channel in the middle. This design provided a parallel-plate-like channel along the length of the cement core. Though this design is a somewhat simplified representation of real fractures in well-bore cements, which are likely to have rough fracture walls, it provides a controlled initial fracture geometry, which allows for unambiguous observation and quantification of fracture-surface alterations as an evidence for dissolution/precipitation. Sample preparation methods are described and documented in Yalcinkaya's master thesis [9].

2.3. Reactive fluid

The brine (2% salt solution) used for the flow-through experiment consisted of distilled water mixed with NaCl and KCl salts at concentrations of 0.3455 M and 0.0046 M, respectively. The influent brine was equilibrated with CO_2 by bubbling CO_2 through the solution. The pH of the CO_2-equilibrated brine ranged from 4.9 to 5.2 and was continuously measured daily prior to entering flow-through experiment.

2.4. Experimental conditions

The experiment was performed at atmospheric pressure (14.7 psi, 0.1 MPa) and room temperature (21 °C, 70 F) conditions. The flow-through experiment lasted for 100 days. CO_2 saturated brine flow rate was 2 ml/min. The confining stress of 600 psi (4.14 MPa) was applied to the rubber sleeve containing the cement core in order to create linear flow only through the cement fracture preventing any radial flow of reactive fluids. At the end of 100 days, the pressure was gradually reduced and the cement core was re-