CHEMICAL ALTERATION OF OIL WELL CEMENT WITH BASALT ADDITIVE DURING CARBON STORAGE APPLICATION

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Abstract

Capturing and storing carbon dioxide (CO₂) underground for thousands of years is one way to reduce atmospheric greenhouse gases, often associated with global warming. Leakage of CO₂ through wells is one of the major concerns when storing CO_2 in depleted oil and gas reservoirs. CO₂-injection candidates could be new wells, or old wells that are active, closed or abandoned. To prevent the leakage, the possible leakage paths and the mechanisms triggering these paths must be examined and identified. It is known that the leakage paths can occur due to CO_2 -rock interaction and CO_2 water-cement interaction. Interaction between well cement and carbon dioxide has attracted much renewed interest because of its implication in geological storage of carbon dioxide. The diffusion of CO₂-water through well cement is a longterm phenomenon which can take many thousand years. Partial pressure, porosity, permeability, cement type, moisture content and temperature are the factors that affect the carbonation of well cement. The objective of this research is to investigate the chemical reactions of the dissolved CO₂ in the synthetic formation water with the plugs of well cement. Cement specimens were left in contact with CO₂ saturated brine at 1100 psi and 65 °C for three months. The 1100 psi pressure and 65 °C temperature are the points where CO_2 is in the state of CO₂ saturated brine. The four cement plugs studied differed in their basalt content from 0%, 6%, 9%, and 13 % by weight. The effects of basalt content studied are change in porosity, permeability and compressive strength. The scanning electron microscope images were obtained to observe the depth of penetration of CO_2 brine solution into cement plugs after three months of contact. The results indicate that presence of basalt increased the compressive strength of plugs and decreased porosity and permeability. As a conclusion the use of basalt as an additive to well cement can be beneficial in CO₂ storage wells.

Chemical reactions due to Cement-CO₂-brine interaction

First step: Carbonic acid formation $CO_2(g) \leftrightarrow CO_2(aq)$ $CO_2(aq) + H_2O \leftrightarrow H_2CO_3(aq)$



Second step: Portlandite carbonation or cement hydrates $H_2CO_3 + Ca (OH)_2(s) \rightarrow CaCO_3(s) + 2H_2O$ $H_2CO_3 + C-S-H (Calcium Silicate Hydrate) \rightarrow CaCO_3 + SiO_2$ (gel) + H_2O

Third step :Calcium Carbonate Dissolution $H_2CO_3 + CaCO_3 \rightarrow Ca (HCO_3)_2$

In-situ mineral carbonation in basaltic rocks

Mineral carbonation requires divalent metallic cations, like Fe⁺², Ca⁺² and Mg⁺² for the carbonation process. When CO₂ reacts with Fe, Ca and Mg oxides, the corresponding carbonate is formed and heat is released. These oxides are prevalent in silicate minerals. Given the concentration of the oxides and their reactivity, focus on in-situ mineral carbonation has been on rocks rich in olivine, serpentine, pyroxene, plagioclase feldspar and basaltic glass. Crystalline basalt is rich in plagioclase feldspar, pyroxene and olivine and basalt, glassy and crystalline, contains 7-10 wt% Ca, 5-6 wt% Mg, and 7-13 wt% Fe. After injection of CO₂ in deep aquifers in basaltic rocks following exothermic chemical reactions are taking place:

Result and Discussion

The four cement plugs before and after experiment



- SEM analyses of the cores were carried out to investigate any mineralogical changes on the core surfaces.
- Near to surface are more loose than the inner part of the core, which shows the CO₂ diffusion into the core.by

Objectives

Underground CO_2 storage may have some effect on wellbore integrity and wellbore cement has been identified as the risk contributing to leakage of CO_2 from geologic carbon storage. The purpose of this thesis work is to investigate the chemical reactions that occurs between the CO_2 saturated brine and cement + additive mix and as additive basalt was added to cement mix.

The cement mix to be prepared by adding basalt in 0,10,20,30 weight percent of cement in 4 cement plugs will be tested for physical properties and change in these properties to be studied on similar cement plugs subjected to CO_2 -brine saturated under 1100 psi pressure and 65°C temperature. The change of cement plug properties after 3 months duration is to be tested. SEM photographs will visually show alteration in microscopic scale.

 $(Mg^{+2}, Ca^{+2}) + CO_2 + H_2O = (Ca, Mg) CO_3 + 2H^+$

Experimental Procedure

Before starting the experiment, the four core holders were pressurized up to 1000 psi by air and placed into the water bath to test for leakage. The parts of set up were assembled and the mixing cylinder and core holders vacuumed.266.38 ml synthetic formation water was filled into the cylinder of ISCO pump. The experiment was carried out under 1100 psi pressure and 65°C temperature. Firstly CO₂ was conducted to the mixing cylinder by opening at a pressure of 300 psia. Secondly, synthetic water formation from ISCO pump was sent to the mixing cylinder at a constant pressure of 1500 psia, then, in mixing cylinder, water and CO₂ was allowed to equilibrate for 4 hours and the pressure transducer recorded the pressure of mixing cylinder at around 1500 psi but since CO₂ is dissolving in synthetic water, the pressure started to decrease but after some hours leveled off at 1100 psi. After CO₂ completely dissolved in synthetic water, the prepared carbonic acid sent to the four core holders simultaneously and the whole system kept in constant pressure and temperature.

SEM analysis the invaded zone (color change) can be observed in samples # 1,2,3 while in sample # 4 the invaded part was negligible.

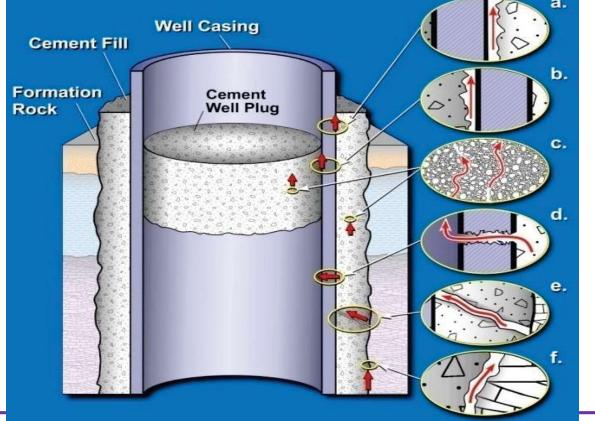
- It can interpreted from SEM photos that three distinct zones formed . First zone is the porous zone where $Ca(OH)_2$ is dissolved, the dissolution of Ca $(OH)_2$ increased the porosity of the sample. The second zone is less porous zone and is the zone where $CaCO_3$ precipitated. The formation of $CaCO_3$ decreased the sample permeability and increased its compressive strength. The third zone is unaltered zone, where the CO_2 saturated brine did not diffuse through zone.
- compressive strength and porosity and permeability measurement has done for four cement plugs before and after the carbonic acid invasion.

Conclusion

■Cement plugs compressive strength has been increased significantly with regard to basalt content of 0, 6, 9 and 13 weight percent. Cement plugs containing basalt ultimately show improved durability to acid attack and increased the strength of the cement. Since the acid attack in cement and basalt mix cause carbonation so the carbonated part shows more uniform microstructure containing CaCO₃ and Mg, Fe (CO₃).

Possible pathways of CO_2

leakage



Change in depth of penetration (movement of carbonation front) from cement plugs 1~4 indicate that increasing basalt amount create CO₂ resistance of cement to carbonic acid.

Carbonation of cement blends (cement +basalt) improved structural performance in that it reduces porosity and permeability and increases the mechanical strength of the cement matrix