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Experimental and modeling study of calcium carbonate precipitation and its effects on the degradation of oil well cement during carbonated brine exposure

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ABSTRACT

Decalcification of cement in solutions of carbonated brine is important to a host of engineering applications, especially in subsurface service environments where cementitious materials are frequently utilized as engineered barriers for wellbore seals, as well as shaft and drift seals and waste forms for nuclear waste disposal. Analysis of leaching simulations and experiments shows that, depending on solution compositions (dissolved CO₂ concentration, pH, Ca ion concentration), calcite precipitation occurring during leaching of cement in contact with carbonated brine can have a significant impact on cement reactivity, in some instances leading to complete arrest of reactivity via calcium carbonate “pore-clogging”. We present modeling and experimental results that examine the range of solution conditions that can lead to pore-clogging. Analysis of the results shows that distinct regimes of leaching behavior, based on pH and pCO₂, can be used to form a framework to better understand the occurrence of pore-clogging.

1. Introduction

1.1. Overview

Many subsurface engineering applications including oil and gas development, geologic storage of carbon dioxide, and nuclear waste storage have introduced the necessity of understanding decalcification of cement under a variety of fluid compositions. Predicting the chemical and mechanical evolution of cement in subsurface service environments is important to protect capital investments (e.g. an oil, gas, or a geothermal wellbore) and can be required to cover long timescales (e.g. nuclear waste containment). Interactions between oil well cement and carbon dioxide saturated brines are of particular interest for the aforementioned applications and are unique in that the acidic decalcification occurs in parallel to calcium carbonate formation in the degradation zone. Some studies have shown that cement/carbonated brine interactions can lead to pore clogging that greatly reduces, or completely arrests, decalcification. Others have shown that decalcification can continue indefinitely, so long as the reaction products are advected away from the reaction zone (see Section 1.4 for a more detailed summary of the relevant literature). Understanding the

regimes where “pore clogging” occurs, as well the fundamentals underlying the role of the calcium carbonate precipitation layer in the degradation zone within the cement, both have significant implications for predicting in situ chemical and mechanical evolution of cement.

We present here modeling results from a reactive transport model that show a dramatic drop in cement reactivity within a specific CO₂ concentration range (10 to 0.1 mM). We also present the results of bench-scale cement leaching experiments designed to validate whether or not the abrupt decrease in cement reactivity in this predicted range for CO₂ concentration can be attributed to pore clogging. Analysis of the leaching experiments shows that, depending on solution compositions (dissolved CO₂ concentration, pH, Ca ion concentration in solution), calcite precipitation occurring during leaching of cement in carbonated brine can have a significant impact on cement reactivity. The activity phase diagram of the CaCO₃/H₂O/CO₂/Ca(OH)₂ system shows that the stability field for calcite depends on the interplay between pH, P_{CO2}, and [Ca²⁺]. Taken with modeling and experimental results, the calcite stability field allows for an estimate of the local aqueous phase conditions needed in the cement (at the leading edge of the calcite layer) that will result in pore clogging. The applications of these findings lie in aiding prediction of seal integrity for instances where cement

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is exposed to carbonated brine, as well as improving interpretation of bench-scale cement degradation experiments.

1.2. Motivation and background

Geologic storage of CO₂ has been identified as a viable technological strategy for reducing and stabilizing carbon emissions worldwide [1,2]. Ensuring that sequestered CO₂ remains in the intended subsurface storage formation is important both to prevent CO₂ from being re-released to the atmosphere through leakage, as well as to prevent environmental damage resulting from a migrating CO₂ plume that transports subsurface contaminants into ecosystems via shallow aquifers. It is widely acknowledged that abandoned wellbores represent potential leakage pathways for migrating CO₂, allowing not only re-release to the surface, but also providing access to hydrogeological units between the CO₂ storage formation and the surface. In this context, the durability of Portland wellbore cement upon exposure to carbon dioxide-saturated brine is of principal importance in determining the permanence of carbon sequestration in any subsurface formations that are intersected by abandoned wells. As thousands of abandoned wellbores may penetrate the subsurface within the areal extent of an injected carbon dioxide plume (for example, Permian Basin in Texas, USA) [3,4], the seal integrity of each wellbore could potentially be compromised by carbonic acid-induced damage, thus creating leakage pathways that would enable the migration of CO₂ from the storage formation. The reaction of wellbore cement with carbon dioxide-saturated brine causes decalcification of the cement matrix at rates that are well documented in the literature [5,6]. A mechanism in which calcium carbonate forms at the leading edge of the reaction zone has been postulated, and it has been shown that this layer plays a role in the decalcification damage mechanism. It has also been suggested that the formation of a calcium carbonate layer can, in certain instances, lead to the self-sealing of the cement wherein calcium carbonate precipitates in the pores of the cement to the extent that the decalcification reaction is drastically reduced or even completely arrested.

1.3. Summary of work

Geochemical modeling [7] has been used to identify key aspects of the reaction mechanism involving CO₂-bearing solution and Portland cement. Previous experimental work has demonstrated that the calcium carbonate layer enhances cement reactivity and that, in general, the concentration of aqueous species at the solution/solid interface exerts a strong influence on cement decalcification rate [8].

In this paper, we test a theoretical model that suggests that the carbonate layer increases the Ca²⁺ gradient and thereby enhances the rate of attack on the cement, and which predicts that high concentrations of CO₂ (~30 mM) result in rates of attack on cement greater than those at a lower CO_{2(aq)} concentration at the same pH (pH can be controlled via HCl or CO_{2(aq)} concentration in solution). A first set of bench-top leaching experiments at ambient conditions (22 °C, 1 atm) was performed at high and low CO₂ concentrations and confirms that this phenomenon is observable at both pH 2 and pH 3. The CO₂ enhancement effect was more pronounced at the higher pH 3.

A second set of bench-top leaching experiments was performed (see sections 2.2 and 2.3) to explore the effect of aqueous fluid compositions (i.e., pH, P_{CO₂}, and Ca²⁺) on the phenomenon of “pore-clogging”, where an impermeable layer of calcium carbonate forms in the cement matrix that slows or arrests degradation of the cement matrix.

1.4. Context

Both field studies and laboratory studies have reported the formation of a calcium carbonate reaction layer in wellbore cement upon exposure to carbonic acid. Relatively fast reaction rates were reported in studies by Barlet-Gouédard et al. [9] and Rimmelé et al. [10], where

exposure to CO₂-saturated brine resulted in a mobile calcium carbonate front. Rimmelé et al. conclude that calcium carbonate precipitates and dissolves at or near the leading edge of the reaction front, which leads to progressive and significant reactivity of the cement matrix. Duguid and Scherer [5] also report faster reaction rates for CO₂-saturated brine in flow-through laboratory experiments (1 bar of CO₂, pH 2.4 and 3.7), where the calcium carbonate layer appears between a layer of amorphous silica gel and a layer of calcium hydroxide depleted cement. Duguid et al. [11] also observe fast reaction rates and no evidence of pore clogging in the presence of a sandstone barrier (1 bar of CO₂, pH 3.0, 4.0 and 5.0). These studies present evidence of a carbonate layer that is clearly part of the calcium leaching process.

Kutchko et al. [6,12] attribute a pronounced retardation of the rate of attack to the formation of a calcium carbonate layer in quasi-batch experiments, where CO₂ was continuously recharged, while leachate accumulated in the reservoir. Similar average rates and reaction patterns were found in examination of core samples taken from a wellbore exposed to a natural source of CO₂ for 30 years [13]. While the flow rate was not quantified for this field sample, the authors speculate that the reaction depths may indicate static conditions similar to the Kutchko laboratory study. A follow-up laboratory study by Wigand et al. [14] simulated a CO₂/brine leak through a fractured wellbore, and concluded that precipitation of a layer of CaCO₃ – in the form of calcite, aragonite, and vaterite – led to a decrease in porosity that, in turn, blocked pores and decreased the flux of products and reactants. Again, the flow rates were slow, implying a potential pattern in the literature of static and slow-flow reaction leading to “pore-clogging” by precipitation of calcium carbonate. Similarly, Luquot et al. [15] investigated cement reactivity via flow through fractured cement interfaces, and like Wigand et al. [14], reported the formation of a protective calcite layer that, once formed, prevented reaction of cement beyond the reaction front. Huerta et al. [16] also used an experimental setup that incorporates flow through a fractured cement interface, and concluded that calcium ion concentration and pH, in addition to residence time, can result in sealing of a leaky wellbore. The model of Brunet et al. [17], based on the experimental results of Kutchko et al. [12], identifies the ratio of initial portlandite to initial porosity (vol%) as a key parameter that determines the pore-clogging potential of calcite formation.

The aim of this work is to collect experimental evidence that will contribute towards refining, confirming or denying the above proposed mechanisms. A second companion paper using reactive transport modeling [18] further expands the analysis of governing processes by investigating not only the contributions of water composition, but also the initial cement composition and the mass transfer properties of each layer.

2. Methods

2.1. Reactive transport model

The reactive transport code used for calculations herein consists of a geochemistry module and a transport module. The geochemistry module is implemented similarly to other geochemical codes (e.g. EQ3/6 and Geochemist's Workbench), using the SUPRCRT92 thermodynamic database for most minerals, with the addition of cement-specific hydrate minerals culled from the literature. The transport module implements Dynflow™[35], which is used to solve the system of non-linear partial differential equations presented by the fluid flow and mass transfer calculations. A finite volume discretization was implemented for the mesh and implicit backward finite difference time stepping was used for transport equations. The code was validated against the experimental results of Duguid et al. [5]. The diffusion coefficients for the degradation layers were calculated using a modified Archie's Law expression. Further details of the reactive transport calculation methods, cement composition, thermodynamic properties, and mass transfer

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