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Cement CO_2-alteration propagation at the well–caprock–reservoir interface and influence of diffusion

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ABSTRACT

A geochemical model of wellbore cement–caprock–reservoir interfaces is developed. The model predicts the mechanisms of chemical alteration of cement due to interaction with the acid brine obtained after the injection of supercritical CO_2 into the reservoir rock. Numerical outputs indicate that, at the well–reservoir interface, intrusion into the cement phase of acid brine accompanied by aqueous CO_2 quasi-instantaneously transforms Portlandite and CSH into Calcite and hydrated Si-gel, leading to a slight but moderate porosity decrease, from 28% to ~20%. Conversely, at the well–caprock interface, Portlandite first leaches and the Ca^{2+} ions released from it migrate towards the caprock, where they eventually combine with slowly diffusing aqueous CO_2 to form Calcite, up to the porosity collapse of the interface. This can significantly affect the sealing behaviour of the geological storage. We can finally deduce a time-space characterisation of the system enhancing the main chemical mechanisms in view of a future export to a geomechanical model.

1. Introduction

The long-term safety of a CO_2 geological storage (CCS) relies on the stability of the reservoir and on proper assessment of CO_2 leakage and fluid displacement. Particular attention must be paid to the injection wellbore, as a man-made discontinuity in the geological medium, especially the caprock. In addition, the chemical and mechanical integrity of the well–reservoir–caprock cement sealing must be ensured throughout the lifetime of the CCS project.

CO_2 geological storage has been intensively investigated in recent years, using experimental, analytical or numerical approaches. For example, within the SACROC unit in Texas, Carey et al. (2007) studied Portland cement cores of a 55-year old oil well exposed to CO_2 flow for ~30 years. Although the integrity and the structure of the cement had survived, casing-cement and cement–shale interfaces were heavily carbonated and even the caprock showed a disturbed zone called the “shale-fragment-zone” (SFZ). Though the SFZ is likely due to mechanical factors during drilling and completion, there are signs of high reactivity at the cement edges, where decalcification of the C—S—H phases occurs. Calcite precipitates and even amorphous silica may be mobilised into the SFZ. Kutchko et al. (2007) conducted laboratory experiments of well cement degradation by CO_2-rich brine under geological (P, T) conditions and proposed a degradation mechanism for Portlandite. Indeed, CO_2-rich acid brine dissolves Portlandite $Ca(OH)_2$ and precipitates Calcite $CaCO_3$. The fully carbonated zone is eventually dissolved by the un-buffered brine (pH ~ 2.9), leading to a very porous silica material. Huet et al. (2010) confirmed these mechanisms by a benchmarked model of class-H-cement in CO_2-saturated water (pH ~ 3.7). However, they identified the need for a better porosity–diffusivity retroaction law.

Rimmelé et al. (2008) analysed samples of Portland cement immersed in wet supercritical CO_2 or in CO_2 saturated water. A cracked carbonate layer forms around the cylinders, composed of different $CaCO_3$ polymorphs, mainly Calcite and Aragonite. The thickness of this layer increases over time (up to 5–6 mm after 3 weeks). While the edges carbonate in less than half a day, after 3 months, sample cores saw all their Portlandite and Calcium-Silica gels transformed into Carbonates and possibly remaining amorphous Silicates. In addition to Calcite and Aragonite polymorphs, a precipitation of Vaterite has been observed by Corvisier et al. (2010) at the carbonation front. As discussed by Corvisier et al. (2010), the co-existence of this Calcite polymorph underlines the fact that local equilibrium cannot be assumed in order to simulate properly the carbonation of Portland cement.

Investigating the experiments of crushed cement in contact with H_2S–CO_2 (supercritical or dissolved in brine) by Jacquemet et al. (2008), it appears that H_2S is only responsible for ferrite

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sulphidation, CO_2 mainly affecting the initial cement phases: Portlandite, CSH, and aluminates. Besides, carbonation is complete and leads to amorphous silicates when minerals are in contact with dry H_2S–CO_2, but only partial when in contact with brine and dissolved H_2S–CO_2.

Gherardi et al. proposed in 2012 a quasi-exhaustive geochemical model of the very long-term evolution of well cement at the caprock–reservoir interface, taking into account most of the different phases bearing usual cement elements (Ca, Si, Al, S, Mg, Fe, C, Na, K). Because of the timescale involved, mainly crystallised phases were involved in their calculations. In addition to the previous investigations, the present work aims to establish the main degradation mechanisms at the very thin interface between the well and caprock for short space and time scales. Numerical simulations have been performed in order to simulate the short-term degradation of a newly built class-G-cement injection well, by CO_2-acidified brine, at the well–reservoir and well–caprock interfaces. Indeed, we aim at modelling the upward propagation of the CO_2-disturbed cement zone from the reservoir to the caprock interface.

The idea is to reproduce and scale up on a 3D well geometry the cement degradation processes observed by Jobard (2012) in laboratory experiments. Indeed, batch reactions of cement-surrounded shales in CO_2 solution over 30 and 60 days showed a highly carbonated interface between the cement and the shales. The cement even cracks sometimes due to the shale volume increase. Diffusion is the only transport process considered here. A sensitivity analysis is performed concerning the influence of this particular factor with respect to kinetic rates, since these two processes are competing to govern cement degradation propagation. Mineral dissolution and precipitation, as well as pH are carefully checked in order to characterise the main cement alteration mechanisms.

Special attention is paid to porosity evolution since it can evolve either up to complete sealing (risk of mechanical failure and loss of cement tightness, Fabbri et al., 2009) or to a high increase (leading to a permeability increase?) depending on time and location in the model. The present work begins with a description of the system concerning its different chemical domains (well, reservoir, caprock). Then, the modelling scenarios are presented, including the different hypotheses concerning the effective cement diffusion. The results presented support a vertical and lateral mechanism of cement degradation propagation that is discussed in light of the sensitivity analysis undertaken.

2. Geochemical background

In this paper, we consider a newly built CO_2 injection well that starts to operate in a carbonated reservoir, capped by shales, similar to the Dogger and Callovo-Oxfordian formations of the Paris basin (Rojas et al., 1989). According to previously reported works, the injected supercritical CO_2 will partially dissolve and acidify the brine. Before the well surroundings have completely dried up, CO_2-rich brine has already reacted with hydrated cement minerals and modified the well–reservoir interface. This degradation scheme then propagates along the well–caprock interface. The present work reports some year-long 3D-centimetre-scale simulations that aim to parameterise the chemical intensity and spatial propagation of the cement degradation, with respect to the cement diffusivity parameter. It is based on laboratory experiments undertaken by Jobard (2012) and aims at illustrating scaling up effects.

2.1. Solution composition

The geochemical calculations were performed in the complex chemical system SiO_2–Al_2O_3–Fe_2O_3–FeO–MgO–CaO–K_2O–Na_2O–SrO–CO_2–SO_3–H_2O, which includes mineral phases, aqueous phases and gases. Different initial conditions were retained, depending on the geochemical domains. The pore solution of the caprock was assumed to be in equilibrium with its constituent minerals (Illite, Quartz, Calcite, Montmorillonite, Chamosite, Dolomite and Celestite), following the approach of Gaucher et al. (2009). Similarly, the Dogger Reservoir pore solution composition was generated by considering equilibrium with the minerals Illite, Montmorillonite, Kaolinite, Quartz, Calcite, Dolomite and Magnesite, according to mineralogical analyses provided by André et al. (2007). The solution was then acidified with gaseous CO_2 at 180 bars pressure, but still buffered by carbonates. After initial geochemical equilibrium, the respective pH values were 7 for the caprock and 5.1 for the initially CO_2-acidified reservoir solutions. The cement initial pore solution was eventually calculated by assuming equilibrium with the main minerals: Portlandite, CSH, Katoite, Ettringite, C3FH6, Hydrotalcite and Calcite, leading to an initial geochemical equilibrium at pH 11 (normal at the temperature of 75 °C). The resulting solution compositions are reported in Table 1.

Table 1
initial water compositions before speciation.

Primary element	Cement (mol/kg)	Caprock (mol/kg)	Reservoir (mol/kg)
pH	11[a]	7	5.1
Ca^{2+}	0.27E−01	0.54E−01	0.10E+01
Mg^{2+}	0.57E−07	0.18E−01	0.10E−01
Na^{+}	0.40E+00	0.10E+00	0.38E−02
K^{+}	0.29E−01	0.80E−03	0.15E+00
Fe^{2+}	0.19E−07	0.90E−06	0.18E−01
H_4SiO_4(aq)	0.32E−04	0.19E−03	0.11E−03
Al^{3+}	0.36E−04	0.41E−06	0.29E−02
Cl^{-}	0.43E+00	0.24E+00	0.35E−08
$HCO_3{}^{-}$	0.35E−04	0.23E−03	0.23E+00
$SO_4{}^{2-}$	0.90E−02	0.45E−02	0.11E+01
Sr^{2+}	1.00E−10	0.14E−02	0.30E−05

[a] Value at 75 °C.

2.2. Cement material

Class-G cement contains different mineral phases bearing various elements (Ca, Si, Al, S, Mg, Fe, C, Na, K). Its mineral composition is described by Marty et al. (2009). Mineral proportions are fixed by the experimental setup of Jobard (2012) and are similar to other cement pastes from the above cited literature. The main chemical constituents of the cement clinker are: CaO, SiO_2, Al_2O_3, SO_3, MgO, Fe_2O_3, Na_2O, K_2O. We suppose 100% hydration, with a water/cement ratio of 0.4. This corresponds to an ideal case. Taylor (1997) actually indicates 5–10% of unhydrated grains after 6 months of hydration for Oil Well Portland Cement (W/C = 0.4). This approximation may lead to slightly delay the propagation of the cement degradation front. After hydration, these elements should form, according to thermodynamic equilibrium (Marty et al., 2009): Portlandite, CSH, Katoite-Si, Ettringite, Hydrotalcite, C3FH6 (Fe hydrogarnet) and Calcite. This leads to an initial pH = 11 in the cement. Table 2 summarises these proportions.

Table 2
Cement mineral composition.

Class-G cement	Formula	Composition (vol%)
CSH1.6	$Ca_{1.6}SiO_{3.6}{:}2.58H_2O$	38.1%
Portlandite	$Ca(OH)_2$	26.1%
Ettringite	$Ca_6Al_2(SO_4)_3(OH)_{12}{:}26H_2O$	13.8%
Katoite-Si	$Ca_3Al_2SiO_4(OH)_8$	10.5%
C3FH6	$Ca_3Fe_2(OH)_{12}$	5.5%
Hydrotalcite	$Mg_4Al_2O_7{:}10H_2O$	5.4%
Calcite	$CaCO_3$	0.6%