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Modelling acid attack of oilwell cement exposed to carbonated brine



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ABSTRACT

A diffusion-reaction model for the carbonation process of oilwell cement exposed to carbonated brine under CO₂ geological storage conditions is presented. The formulation consists of two main diffusion/reaction field equations for the concentrations of aqueous calcium and carbon species in the pore solution of the hardened cement paste, complemented by two diffusion-only field equations for chloride and alkalis concentrations, and by a number of chemical kinetics and chemical equilibrium equations. The volume fraction distribution of the solid constituents of the hardened cement paste and the reaction products evolve with the progress of the reaction, determining the diffusivity properties of the material. The model is used to simulate experimental tests performed by Duguid and Scherer (2010), leading to promising results indicating that the fundamental aspects of the phenomenon are captured.

1. Introduction

Capture and geological storage of CO₂ are intended to avoid emitting CO₂ into the atmosphere, by capturing CO₂ from major stationary sources (thermal power plants, cement factories, etc.), transporting it usually by pipeline and injecting it into suitable deep rock formations (IPCC, 2005). Among other possibilities (e.g. saline formations, coal formations), CO₂ storage in depleted oil and gas reservoirs is very promising, first, because the oil and gas that originally accumulated in traps did not escape (in some cases for many millions of years), demonstrating their integrity and safety, and second, because these structures are well known and significant infrastructures are already in place. However, a major source of concern arises when the security of many mature oil fields for CO₂ storage is assessed: the presence of abandoned wells that perforate the cap rock of the reservoir and which may potentially constitute CO2 leakage pathways. In many cases plugging of abandoned wells began decades ago when CO₂ storage was not under consideration and, so, the primary cement used for the casing, and/or the plug cement used in the well were regular Portland cements. If the resulting hydrated cement pastes (HCP) in the abandoned well gets in contact with the injected CO₂, two possible outcomes can be expected (Duguid and Scherer, 2010): (1) if the HCP is not submerged in water, a process similar to the carbonation of concrete in normal conditions will take place, with resulting slight increase of HCP strength and decrease of its permeability (Kutchko et al., 2008, 2007; Rimmelé et al., 2008); (2) if the HCP is submerged in water or brine, which is the most likely condition in an abandoned well in the long-

term, it will suffer a progressive decalcification process, the so-called 'acid attack', which leads to a drastic loss of mechanical strength and increase of permeability (Carey et al., 2007; Duguid et al., 2011; Duguid and Scherer, 2010; Kutchko et al., 2008, 2007; Rimmelé et al., 2008; Walsh et al., 2013).

Potentially, acid attack may create leakage pathways through the well cement and worsen existing ones. Since redoing the abandoned wells cementation with acid resistant cements (e.g. calcium aluminate cements), even if possible at all, would be extremely expensive, one idea is clear: the acid attack can make more difficult, more expensive or even jeopardize the technical and economic feasibility of storing CO2 in abandoned reservoir sites.

In this context, the potential benefits are evident of numerical models that make possible an accurate assessment of the long term performance of abandoned well cements when exposed to the injected CO₂.

In recent years, some models have been proposed. A detailed simulation of the cement paste degradation requires considering a large number of chemical species and reactions, as it has been proposed by Huet et al. (2010). However, for engineering purposes, satisfactory results can be obtained with simpler chemistry by omitting aluminium, iron and sulphur (solid and aqueous) species (Brunet et al., 2013; Fabbri et al., 2012; Raoof et al., 2012; Shen et al., 2013). One key aspect of the degradation process that due to its complexity is subject to simplification is the dissolution of C-S-H. It is well known that C-S-H presents an incongruent behaviour, i.e. the dissolution rate of the ions composing C-S-H is not proportional to the stoichiometric coefficient,

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and consequently, the composition of the C-S-H varies as the dissolution progresses. This incongruent behaviour is neglected by Huet et al. (2010) by emulating C-S-H gel as the crystalline mineral jennite and by Raoof et al. (2012) by directly omitting C-S-H dissolution. Shen et al. (2013) proposed an approach based on thermodynamics which leads to generalization of the mass action law for C-S-H with variable C/S ratio. This approach allows reproducing the incongruent dissolution of silicate and calcium ions. Other authors appealed to a less complex approach by simulating C-S-H dissolution as a multi-step process of decalcification passing from initial calcium-rich C-S-H (C/S = 1.6-1.8) to intermediate C-S-H with lower calcium (Fabbri et al., 2012) or directly to amorphous silica (Brunet et al., 2013). Each of these intermediate compositions C-S-H is treated as a distinct mineral with fixed stoichiometry and solubility product constant. This approach allows those authors to approximate the incongruent dissolution behaviour without introducing any special treatment of C-S-H in comparison with the other solid species considered (e.g. portlandite or calcite).

The chemical model needs to be coupled to a transport model in order to simulate the ingress of carbon species and the egress of calcium. This coupling can be done via a monolithic formulation (fully coupled) (Brunet et al., 2013; Shen et al., 2013) or via an uncoupled formulation combined with an iterative procedure (staggered implementation) (Fabbri et al., 2012; Huet et al., 2010; Raoof et al., 2012). Staggered implementations allow easily combining pre-existent geochemical and transport codes, but exhibit the disadvantage of being only conditionally convergent, i.e. requiring small time steps to converge. On the other hand, fully coupled implementations converge much better but require important coding efforts.

Transport models may be divided in those which only consider transport of aqueous species through Fick's diffusion (Brunet et al., 2013; Huet et al., 2010), and those which also consider advective transport (Fabbri et al., 2012; Raoof et al., 2012; Shen, 2011). Since flow velocities through bulk cement paste is expected to be typically very slow under deep subsurface conditions, the effect of advective transport may be neglected in sound cements. However, in the case of cracked cements, the convective transport becomes dominant and needs to be considered in order to reproduce phenomena such the cracks widening or healing depending on flow rate of carbonated water (Huerta et al., 2016).

Besides the sink/source terms, coupling between chemical reactions and transport of aqueous species is also caused by the evolution of transport parameters such as porosity and effective diffusivity. The first is readily obtained from the volumetric balance of the solid species. Estimation of the effective diffusivity of the degraded HCP, in contrast, is not trivial. One usual approach is to consider the effective diffusivity to be a function of the porosity and one or more empirical parameters which remain constant (e.g. a power law in Huet et al. (2010) and Brunet et al. (2013) or an exponential law in Chen et al. (2013)). It must be noted that the parameters used with these laws were calibrated using cement pastes with different porosities due to different w/c ratios or age, but not with degraded pastes.

In the model presented in this paper, the emphasis has been made on keeping the formulation and the numerical implementation as simple as possible while reproducing the main aspects of the phenomenon, in particular those related with the degradation of the mechanical and transport properties.

2. The model

2.1. Reaction mechanism

The proposed reaction mechanism is schematically summarized in Fig. 1, which represents the interfacial zone between the HCP and the carbonated brine. The HCP is considered to be composed by four volumetric fractions: calcium silicate hydrates (C-S-H), free portlandite, inert cement hydrates, namely aluminate and sulphate compounds, and



Fig. 1. Scheme of proposed carbonation mechanism. Note: CH = portlandite; $C\overline{C}$ = calcite.

capillary pores. The HCP pores are assumed to be fully saturated with water with concentrations of alkalis (sodium and potassium) and chloride resultant from the cement hydration and from the exchange with the surrounding medium. These conditions, as well as the system pressure and temperature, are assumed to remain constant at all times during the reaction.

C-S-H is an amorphous gel with variable stoichiometry with averaged calcium to silica molar ratio around 1.70 for regular Portland cement. When exposed to an acid solution, degradation tends to lower the Ca/Si ratio, due to preferential release of Ca over Si (incongruent dissolution). A usual approach to model this incongruent dissolution behaviour is considering C-S-H as a solid solution of pure fixed-stoichiometry phases (components or end-members, with activity equal to 1) with defined saturation product constants (Börjesson et al., 1997; Rahman et al., 1999). In a similar way, we have considered C-S-H as a solid solution of hydrated silica gel and two fractions of portlandite, i.e.

$$(CaO)_{1.7}(SiO_2)(H_2O)_{3.2} \equiv \underbrace{ [Ca(OH)_2]_{0.7}}_{A} \\ \underbrace{ [Ca(OH)_2]}_{B} \\ [(SiO_2)(H_2O)_{1.5}] \end{bmatrix}$$

Fraction A of portlandite is assumed to have the same solubility of free portlandite, and for all purposes it will be included in the free portlandite fraction considered in the model. In contrast, solubility of fraction B is assumed to be somewhat lower than that of free portlandite. Finally, for the sake of simplicity, silica gel is considered to be insoluble. Summarising, for modelling purposes, the C-S-H ($C_{1.7}SH_{3.2}$ in cement chemistry notation) is decomposed in two parts, on one hand, the 'free' portlandite (CH in cement chemistry notation) and, on the other, C-S-H with lower Ca/Si ratio (CSH_{2.5} in cement chemistry notation), i.e. $C_{1.7}SH_{3.2} = 0.7CH + CSH_{2.5}$. Then, the C-S-H dissolution process can be represented in a simplified fashion by means of the reactions given in Eqs. (1) and (2). Note that C-S-H with different Ca/Si may also be considered just by modifying the amount of free portlandite (fraction A) present in the C-S-H.

When CO_2 is dissolved in brine, carbonic acid (H_2CO_3) is formed, which is subsequently dissociated into bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions. This process is summarized in two reactions (Eqs. (3) and (4)), where the intermediate formation of H_2CO_3 is omitted since its concentration is usually negligible. Consequently, the molar fraction of each species in relation to the total moles of carbon species depends on the pH of the solution, through the self-ionization reaction of water (Eq. (5)), as it can be appreciated in Fig. 2 which is discussed in Section 2.2.4.

The concentration gradient of aqueous carbon species causes a diffusion process from the brine towards the HCP, which is followed by a decrease of the pH of the pore solution in the HCP.

As pH lowers, the free portlandite in contact with the pore solution

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