Chemical Geology xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

Coupled reactive transport model study of pore size effects on solubility during cement-bicarbonate water interaction

Sanheng Liu*, Diederik Jacques

Belgian Nuclear Research Centre (SCK·CEN), Belgium

ARTICLE INFO

Keywords:
Pore size controlled solubility
Reactive transport modelling
Porosity change
Concrete
Dissolution
Precipitation

ABSTRACT

We investigate the interaction between Ca rich cementitious materials and bicarbonate rich clay pore water with the primary focus on pore size effect on the dissolution of the main hydration products, portlandite and calcium silicate hydrates (C-S-H), and the precipitation of the secondary mineral, calcite, in a coupled reactive transport modelling framework. The concept of pore-size dependent solubility is extended to reactive transport modelling within cementitious materials. For the two pore sizes 1e-6 and 1e-8 m considered here the effect of pore size on the solubility of portlandite, C-S-H and calcite is different, with portlandite and calcite less affected and C-S-H more affected due to a higher water/C-S-H interfacial tension. This difference leads to a different evolution of porosity at the interface of a cementitious material and bicarbonate-enriched pore water between systems with large or small pores. In systems with mixed large and small pores, if diffusion through large pores is much faster than through small pores, precipitation will only occur in large pores because the pore solution diffused into small pores has already become under-saturated with respect to calcite due to precipitation in large pores first. These results might also explain why cementation of porous rocks occurs preferentially in large pores relative to small pores observed in nature.

1. Introduction

Cementitious materials in geological disposal systems of high-level waste either have a pure geotechnical reason or, for the Belgian reference concept, provide a pH buffer in the so-called supercontainer concept (ONDRAF/NIRAS, 2004). In the supercontainer design, a thick layer of cementitious materials surrounds a carbon steel overpack with waste forms (vitrified high-level radioactive waste or spent fuel) inside. Outside of the cementitious materials is a stainless steel envelope. This whole container will be placed in disposal galleries in the host material; Boom Clay is the host material currently considered as the reference material in the Belgian waste management program. The high pH condition, exerted by the buffering cementitious materials, is favorable for the formation of a passive oxide film on the outer surface of the carbon steel, which results in very low and almost negligible uniform corrosion rate of the carbon steel (Kursten et al., 2013).

The pore water of the reference formation Boom Clay is HCO_3^- rich water (De Craen et al., 2004). It is foreseen that after perforation or failure of the stainless steel envelop, the HCO_3^- rich Boom Clay pore water will eventually come into contact with the Ca^{2+} and OH^- rich cementitious materials, which may significantly decrease the pH in the pore water of the cementitious materials and neutralize the buffering capacity. The decrease of the pH is controlled by the transfer of Ca^{2+} and OH^- from the cementitious materials and HCO_3^- from the Boom Clay to the reaction front, which is further controlled by the porosity of the cementitious materials, more precisely, the porosity at the interface with the Boom Clay.

An important chemical alteration process is carbonation; Ca^{2+} and OH^- released during dissolution of portlandite from the cementitious materials will react with HCO_3^- to precipitate $CaCO_3$. During carbonation, vaterite and aragonite may initially form, but these polymorphs of $CaCO_3$ ultimately revert to calcite (Fernandez Bertos et al., 2004). Since the molar volume of calcite is slightly higher than the molar volume of portlandite, 3.31×10^{-5} m^3/mol versus 3.69×10^{-5} m^3/mol (Matschei et al., 2007), a stoichiometric conversion of portlandite into calcite will result in a decrease of the porosity. Theoretically, this can be beneficial, because a decrease of porosity will slow down the mass transfer of solutes and thus elongate the lifetime of the buffering materials. On the other hand, if precipitation of calcite is slow compared to portlandite dissolution, then an increase of porosity is expected.

A few long-term experiments studied the interaction between cement and clay in the context of geological disposal including experiments with Boom Clay (Read et al., 2001), argillaceous or

---

* Corresponding author.
E-mail addresses: sliu@sckcen.be (S. Liu), djacques@sckcen.be (D. Jacques).

http://dx.doi.org/10.1016/j.chemgeo.2017.07.008
Received 7 April 2017; Received in revised form 28 June 2017; Accepted 6 July 2017

Please cite this article as: Liu, S., Chemical Geology (2017), http://dx.doi.org/10.1016/j.chemgeo.2017.07.008

Callovian–Oxfordian clay (Dauzères et al., 2010; Gaboreau et al., 2012) and Opalinus Clay (Jenni et al., 2014). These experiments have shown a different evolution of porosity changes at the interface. The in situ test conducted at the HADES underground laboratory Mol (Belgium), has clearly indicated an increased porosity in the zone of portlandite dissolution after 18 months, with some calcium within the calcium depleted cement zone present as calcite (Read et al., 2001). In Opalinus clay, a potential host-rock for disposal of high level waste in Switzerland, calcite formation and pore space clogging has been observed after 2.2 years of interaction between Opalinus Clay, and ordinary Portlandite cement (OPC) emplaced at the Mont Terri Underground Laboratory (St. Ursanne, Switzerland) (Jenni et al., 2014). Experiments in the Underground Research Laboratory near Bure, France have shown that, depending on the availability of CO_2 or bicarbonate and the chemical composition of cementitious materials, porosity in cement could both increase as a result of decalcification of portlandite and calcium silicate hydrates (C-S-H) and decrease as a result of calcite precipitation (Dauzères et al., 2010; Gaboreau et al., 2012). Note that not only carbonation reaction, but also reaction of cement with e.g., sulfate and chloride can cause porosity change (Glasser and Matschei, 2007). Because it is unknown whether the systems mentioned above had reached steady state at the time of samplings as a result of e.g., complete clogging, and also there are only limited experimental data, it is difficult to evaluate the impact of carbonation on the long-term evolution of the porosity for a given system, and thus coupled reactive transport models are often sought to provide additional information. Coupled reactive transport modelling has been used to describe fluid/rock and rock/rock interaction for > 20 years (Steefel and Lichtner, 1994). A recent study has benchmarked a number of reactive transport codes for modelling cement-clay interactions (Marty et al., 2015). This approach has been applied for almost each potential clay rock for geological disposal, such as Callovo-Oxfordian (COX) Clay in France (Trotignon et al., 2007; Marty et al., 2009, 2015), Opalinus Clay in Switzerland (Kosakowski and Berner, 2013) and Boom Clay in Belgium (Wang et al., 2010; Liu et al., 2014). Typically, those models treat cementitious materials as porous media with one lumped porosity capturing gel and capillary porosity. During equilibrium or kinetic-controlled dissolution and precipitation reactions, porosity alters which is sometimes linked to changes in diffusivity. When the porosity for a certain grid cell, usually the cell at the interface, drops below a threshold value, solutes transfer becomes extremely slow and the system is assumed to be totally clogged. Depending on the geochemical conceptual model, including the composition of cement and clay and the choice of secondary phases, different minerals cause the clogging such as calcite (Liu et al., 2014) and zeolites (Trotignon et al., 2007; Marty et al., 2009). Even more, clogging could occur at different locations near the interface (e.g., Liu et al., 2014; Trotignon et al., 2007). Despite extensive modelling work done for cement/clay interaction in the past two decades, there is at least one unexplored aspect within this context, which is the interplay between pore size and geochemical processes, such as pore size controlled solubility of mineral.

Cementitious materials have a pore size distribution typically extending from about 10 µm to as small as 0.5 nm or less in diameter (Jennings et al., 2002). Nanometer-scale pores represent a substantial proportion of the cement porosity due to the presence of a large volume of C-S-H, sometimes refer to as gel porosity (Taylor, 1990). According to the Powers-Brownyard model, gel porosity is a function of water to cement ratio (w/c) and accounts for more than half of the total porosity in hydrated cement paste. In the nano- to micron-scale pores, interfacial energy can play a critical role in determining the stability and solubility of solid phases (Adamson, 1960; Stumm and Morgan, 1996; Scherer, 1999) with the effective solubility of a mineral phase inversely proportional to pore size (Rijniers et al., 2005; Emmanuel and Berkowitz, 2007; Emmanuel et al., 2010). Several studies (Emmanuel and Berkowitz, 2007; Espinoza-Marzal and Scherer, 2010) have identified pore size controlled solubility (PCS) as an important process in the evolution of porosity during dissolution and precipitation of minerals in porous media in pores smaller than 0.1 µm. PCS typically results in preferential precipitation of minerals in large pores because of lower solubility in these pores compared to the smaller pores. A number of experimental studies have supported this PCS theory. For example, halite tends to fill the larger pores than the smaller pores in cemented sandstones (Putnis and Mauthe, 2001). The solubility of hydrated Na_2CO_3 in 10 nm pores is more than twice that of the bulk solubility (Rijniers et al., 2005). Emmanuel and Berkowitz (2007) implemented pore size controlled solubility into a reactive transport model. The one dimensional model domain comprises of only one single mineral type (calcite) with two different pore sizes, 10^{-8} m (small pores) and 2×10^{-3} m (large pores). The boundary solution is at chemical equilibrium with the small-pore matrix. Thus when fluid enters the modelling domain, there is no change of small pore porosity, but a decrease of large pore porosity due to calcite precipitation.

The coupled reactive transport models for cement/clay interaction mentioned above never considered PCS, rather these models calculated dissolution and precipitation of minerals based on the bulk solubility, i.e., solubility of minerals in sufficient large pores. This might be a possible reason for the fast clogging of the cement in these models when applied to simulating the interaction between cement and clay host rocks, especially in the case of Boom Clay with a high bicarbonate concentration of the pore water. The reference bicarbonate concentration in the Boom Clay pore water (De Craen et al., 2004) is about 4 to 8 times higher than the reference concentrations for COX (Marty et al., 2009) and Opalinus Clay (Pearson et al., 2011). Due to the high bicarbonate gradient between Boom Clay and cement, coupled reactive transport modelling always resulted in a large amount of calcite precipitation and extremely fast clogging based on both equilibrium and kinetic reaction models (Wang et al., 2010; Liu et al., 2014). It is hypothesized here that given the presence of nano- and micro-scale pores in cementitious material, PCS results in faster dissolution of the hydration products and slower calcite precipitation, and therefore a slower decrease of porosity near the interface. Furthermore, if precipitation preferentially occurs in larger pores, small pores can still act as transport conduit after clogging of the large pores.

The objectives of this study is to investigate the effect of pore size on both dissolution of cementitious materials and precipitation of calcite, and further on the evolution of the porosity near the interface between the cement and the host rock; the study used Boom Clay pore water as a case study. We focused on the cement-side of the interface, neglecting pore clogging and other processes on the clay side, as well as the influence of anion exclusion on the transport across the interface (Jenni et al., 2017). We extended the model approach by including both precipitation of calcite and dissolution of cementitious materials, as those two processes will occur simultaneously in the cement-bicarbonate pore water system. Thus, the implementation of the PCS is not limited to a single mineral as is the case in Emmanuel and Berkowitz (2007). In addition, we considered both pore radii and lengths updates resulted from minerals dissolution and precipitation.

2. Materials and methods

2.1. Theoretical backgrounds of pore size controlled solubility

The Kelvin equation which describes the change in vapor pressure due to a curved liquid–vapor interface, may also be applied to describe the solubility of crystal particles by means of relating vapor pressure to solubility (Adamson, 1960). For example, for the case of a spherical surface of radii of curvature r, by replacing P/P_0 in the Eq. (1) with S/S_0

$$ln\frac{P}{P_0} = \frac{2\gamma\nu}{RTr} \tag{1}$$

the Kelvin equation relates the solubility of an isotropic and spherical particle to its radius r