



Rock alteration in alkaline cement waters over 15 years and its relevance to the geological disposal of nuclear waste



Elizabeth B.A. Moyce^a, Christopher Rochelle^c, Katherine Morris^b, Antoni E. Milodowski^c, Xiaohui Chen^d, Steve Thornton^d, Joe S. Small^e, Samuel Shaw^{b,*}

^a Earth Surface Science Institute, School of Earth and Environment, University of Leeds, Leeds LS2 9JT, UK

^b Research Centre for Radwaste Disposal, School of Earth, Atmospheric and Environmental Sciences, The University of Manchester, Manchester M13 9PL, UK

^c British Geological Survey, Nicker Hill, Keyworth, Nottingham NG12 5GG, UK

^d Kroto Research Institute, University of Sheffield, Sheffield S10 2TN, UK

^e National Nuclear Laboratory, Birchwood Park, Warrington WA3 6AE, UK

ARTICLE INFO

Article history:

Available online 7 September 2014

Editorial handling by M. Kersten

ABSTRACT

The interaction of groundwater with cement in a geological disposal facility (GDF) for intermediate level radioactive waste will produce a high pH leachate plume. Such a plume may alter the physical and chemical properties of the GDF host rock. However, the geochemical and mineralogical processes which may occur in such systems over timescales relevant for geological disposal remain unclear. This study has extended the timescale for laboratory experiments and shown that, after 15 years two distinct phases of reaction may occur during alteration of a dolomite-rich rock at high pH. In these experiments the dissolution of primary silicate minerals and the formation of secondary calcium silicate hydrate (C–S–H) phases containing varying amounts of aluminium and potassium (C–(A)–(K)–S–H) during the early stages of reaction (up to 15 months) have been superseded as the systems have evolved. After 15 years significant dedolomitisation ($\text{MgCa}(\text{CO}_3)_2 + 2\text{OH}^- \rightarrow \text{Mg}(\text{OH})_2 + \text{CaCO}_3 + \text{CO}_3^{2-}(\text{aq})$) has led to the formation of magnesium silicates, such as saponite and talc, containing variable amounts of aluminium and potassium (Mg–(Al)–(K)–silicates), and calcite at the expense of the early-formed C–(A)–(K)–S–H phases. This occurred in high pH solutions representative of two different periods of cement leachate evolution with little difference in the alteration processes in either a KOH and NaOH or a $\text{Ca}(\text{OH})_2$ dominated solution but a greater extent of alteration in the higher pH KOH/NaOH leachate. The high pH alteration of the rock over 15 years also increased the rock's sorption capacity for U(VI). The results of this study provide a detailed insight into the longer term reactions occurring during the interaction of cement leachate and dolomite-rich rock in the geosphere. These processes have the potential to impact on radionuclide transport from a geodisposal facility and are therefore important in underpinning any safety case for geological disposal.

© 2014 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/3.0/>).

1. Introduction

A widely recognised concept for the disposal of radioactive waste, which will remain hazardous for hundreds of thousands of years, is emplacement in a geological disposal facility (GDF). Many proposed GDF concepts for Intermediate Level Waste (ILW), such as those in the UK, France, Canada and Switzerland (NDA, 2010a; Andra, 2012; Nuclear Waste Management Organisation, 2010; Nagra, 2014), involve cement e.g. as a waste-form, backfill and construction material. Post-closure, groundwater will saturate the facilities and cement dissolution will produce a

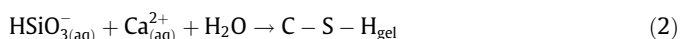
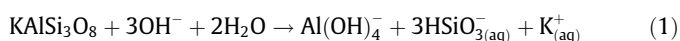
high pH leachate which will evolve in composition and pH over the lifetime of the GDF (Atkinson, 1985; Berner, 1992). Initially, dissolution of KOH and NaOH within the cement will form a leachate of pH ~13. The leachate pH will then decrease to ~12.5 where it will be buffered by equilibration with portlandite ($\text{Ca}(\text{OH})_2$). The leachate will remain at this pH until all the $\text{Ca}(\text{OH})_2$ has dissolved, after which, pH will be controlled by equilibrium with calcium silicate hydrate (C–S–H) gel and will decrease to ~10.5. The leachate will form a chemically disturbed zone (CDZ) in the geosphere surrounding the GDF, also known as an alkaline disturbed zone (ADZ; NDA, 2010b). Previous studies have shown that in the CDZ high pH leachates could cause the dissolution of aluminosilicate minerals and formation of secondary mineral phases (e.g. C–S–H phases, Gaucher and Blanc, 2006 and references therein). This could

* Corresponding author.

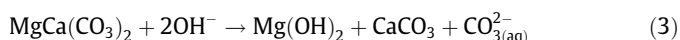
E-mail address: sam.shaw@manchester.ac.uk (S. Shaw).

change the physical (e.g. porosity and permeability) and chemical (e.g. reactive surface area and sorption capacity) properties of the host rock thereby affecting radionuclide transport. For example, mineral dissolution could increase rock permeability and promote radionuclide transport, or the formation of secondary solid phases could block flow paths and have the opposite effect. The formation of secondary phases will also change the nature of the surfaces with which radionuclides could interact e.g. any increased sorption capacity of secondary phases could retard contaminant transport. The potential for cement leachates to alter host rock properties shows that understanding the chemical and mineralogical changes which occur will be key to developing a long term safety case for any cementitious GDF. However, there is a lack of long-term (>10 years) experimental studies which investigate these processes.

Overall, it has been suggested that CDZ alteration can be divided into two regions (Savage, 2011). Firstly, a zone closest to the cement/rock interface (zone 1) where extensive mineral alteration occurs, including dissolution of primary silicate minerals and precipitation of secondary solid phases. Secondly, a zone further from the interface (zone 2) where fluid chemistry is perturbed and ion exchange reactions are important, but rock alteration is significantly diminished. Many short term laboratory and underground rock laboratory experimental studies have investigated rock and mineral alteration in high pH cement leachates (zone 1; e.g. Gaucher and Blanc, 2006; Bateman et al., 1999; and references therein; Braney et al., 1993; Cuevas, 2004; Mäder et al., 2006). Generally, these studies have found that reaction in high pH, Ca-bearing cement-type leachates results in the dissolution of silicate minerals (Eq. (1)) followed predominantly by the precipitation of secondary C–S–H phases (Eq. (2)) of varying Ca:Si ratio (e.g. 0.5–1.5 (Gaucher and Blanc, 2006)), morphology and crystallinity e.g. C–S–H gel (Savage and Rochelle, 1993; Hodgkinson and Hughes, 1999).



where aluminium (e.g., from primary mineral dissolution) and potassium (e.g. dissolved in cement leachate) are present, secondary aluminium and potassium bearing C–S–H (C–(A)–(K)–S–H) phases have also been identified (e.g. Braney et al., 1993; Savage et al., 1992). Studies of clay alteration (e.g. bentonite) at high pH found the formation of a number of Na/K/Ca bearing silicate phases including zeolites (e.g. phillipsite (K,Na,Ca)_{1–2}(Si,Al)₈O₁₆·6H₂O, analcime NaAlSi₂O₆·H₂O) and apophyllite (KCa₄Si₈O₂₀(OH)·8H₂O) (Gaucher and Blanc, 2006; Ramirez, 2005). Carbonate may also be released into solution during high pH rock alteration. For example, cement pore water can promote the breakdown of dolomite (CaMg(CO₃)₂) according to the reaction shown in Eq. (3) (Poole and Sotiropoulos, 1980; Bérubé et al., 1990; Braithwaite and Heath, 2013 and references therein) releasing carbonate to solution leading to the formation of calcium carbonate minerals e.g. calcite. However, these processes have not been studied in the context of the CDZ.



Generally, experimental studies have limited timescales, with few longer than 1–2 years (e.g. a 540 day experiment is the longest study reviewed by Gaucher and Blanc, 2006) and no longer-term experimental studies examine the stability of the secondary phases formed. However, GDFs will evolve over tens to hundreds of thousands of years. To investigate the effect of high pH alteration at timescales more comparable to GDF scenarios, natural and anthropogenic analogue sites have been studied. At natural analogue sites such as Maqarin, Jordan (Milodowski et al., 1998; Alexander, 1992;

Alexander et al., 2012; Linklater, 1998; Savage, 2011) and Troodos, Cyprus (Alexander et al., 2011), alkaline groundwaters have interacted with rock at timescales extending beyond 1 million years. Whereas anthropogenic analogue sites (e.g. the Tournemire Tunnel; Tinseau et al., 2006; Techer et al., 2012) bridge the gap between laboratory experiments and natural analogues. A review of many such sites representing timescales of alteration from ~30 years to >1 million years is provided by Savage (2011). Overall, these studies indicate that over time a variety of secondary phases can form, predominantly alkali-silica gels (e.g. C–S–H gel), which can crystallise with time to zeolites, C–S–H minerals e.g. okenite (CaSi₂O₅·2H₂O), and feldspars. The key factors controlling which phases form are primarily solution composition (e.g. pH) and reaction time. Modelling has also been used to predict the chemical and physical evolution within the CDZ (e.g. Savage et al., 1992; Savage and Rochelle, 1993; Braney et al., 1993; Bateman et al., 1999; Pflingsten et al., 2006; Soler and Mäder, 2007; Fernandez et al., 2010; Alexander et al., 1992). These studies generally support the experimental findings that silicate mineral dissolution is followed by secondary solid phase (e.g. C–S–H) formation, with subsequent transformation of C–S–H to feldspar and zeolite over time, as found at analogue sites. However, modelling predictions are limited by the ability to constrain which solids will form due to slow reaction rates, and a lack of reliable thermodynamic data for some phases (e.g. C–S–H gel).

The secondary solid phases produced during high pH rock alteration may affect radionuclide migration through the CDZ by changing the sorption properties of the material. A key radionuclide of concern is U(VI) which is highly mobile and hazardous over the long timescales relevant to geological disposal (NDA, 2010c). As C–S–H has been found to be the predominant secondary phase produced by high pH rock alteration and is also the most abundant phase in hardened cement paste (Taylor, 1990), which is used as an ILW wastefrom, the interaction of U(VI) with these phases has been studied in some detail (Harfouche et al., 2006; Tits et al., 2011; Gaona et al., 2012; Atkins and Glasser, 1992). However, few experimental studies have looked at the interaction of U(VI) with secondary phases in-situ following high pH mineral/rock alteration and these have generally been limited to investigation after only several months of high pH reaction (e.g. Berry et al., 1999). Continued evolution of altered material over decades may further change surface properties and so affect U(VI) interactions. Therefore experimental investigation of these interactions with rock after extended periods of alteration could help fill this knowledge gap.

1.1. Review of alteration experiment up to 15 months

In this study rock alteration by high pH cement waters has been characterised in unique experiments lasting over 15 years, providing new insight into longer-term rock alteration. These experiments were originally part of the Nirex Safety Assessment Research Programme (NSARP) run by the British Geological Survey (BGS). The experiments were started in 1995 and the rock type and solution compositions used reflect the focus of NSARP at that time (Rochelle et al., 1997; details of how to access this report are provided in Supporting Information). However, as the rock contains many common rock-forming minerals the long-term alteration processes which have occurred will be representative of many rock types. The experiments investigate reaction of disaggregated dolomite-rich fracture fill rock (Borrowdale Volcanic Group (BVG), UK) with fluids representative of young (pH 13, Young Near Field Pore-water (YNFP) and intermediate (pH 12, Evolved Near Field Groundwater (ENFG)) cement leachates. The products of these experiments (fluid and solid phases) were initially investigated up to 15 months of reaction, and a full description of the results

Download English Version:

<https://daneshyari.com/en/article/6335181>

Download Persian Version:

<https://daneshyari.com/article/6335181>

[Daneshyari.com](https://daneshyari.com)