Alteration of nuclear glass in contact with iron and claystone at 90 °C under anoxic conditions: Characterization of the alteration products after two years of interaction

Michel L. Schlegel [a,b,*], Christelle Martin [c], Florence Brucker [a,d], Christian Bataillon [e], Cécile Blanc [a], Matthieu Chorro [f], Patrick Jollivet [g]

[a] CEA, DEN, DPC/SEARS/LISL, Bât. 391, 91191 Gif-sur-Yvette, France
[b] University of Evry, LAMBE, 91025 Evry, France
[c] Andra, Direction Recherche et Développement, 1-7 rue Jean Monnet, 92298 Châtenay-Malabry Cedex, France
[d] Ecole de Chimie, Polymères et Matériaux, 67087 Strasbourg, France
[e] CEA, DEN, DPC/SCCME/LECA, Bât. 458, 91191 Gif-sur-Yvette, France
[f] LUCIA Beamline, Synchrotron SOLEIL, L'Orme des Merisiers, 91190 Saint Aubin, France
[g] CEA, DEN, DTCD/SECM/LCLT, 30207 Bagnols-sur-Cèze, France

ABSTRACT

The present study investigates the alteration of a fractured glass block in contact with iron and Callovo-Oxfordian claystone at 90 °C under anoxic and water-saturated conditions. The alteration rates and the nature of glass alteration products at the different compact interfaces (glass-clay, glass-iron) and in cracks were assessed by solution chemistry and microscopic-scale techniques (scanning electron microscopy coupled with energy-dispersive X-ray microscopy, microRaman spectroscopy, and X-ray absorption fine structure spectroscopy). A significant but modest (two-fold) increase in glass alteration in contact with steel was observed, leading to an average alteration rate over the experiment of about 0.007 −0.014 g/m^2/d. This rate is significantly lower than forward rate r$_0$ in clay-equilibrated groundwater (1.7 g/m^2/d), indicating that a decrease of the alteration rate was not hindered by the steel presence. The corrosion−alteration interface was made up of successive layers of corrosion products in contact with iron, a layer of Fe silicates, and an altered glass layer enriched in Fe. Characterization of the glass block in direct contact with claystone revealed that the thickness of altered glass was much more important than at the glass-iron interface. The altered glass layer in contact with clay was slightly enriched in Fe and Mg, and depleted in alkali cations. Altered glass layers in cracks were usually limited to fringes thinner than 2 μm, with a thickness decreasing from the crack mouth, indicating that alteration is controlled by transport in the cracks. The fractures were partially filled with calcite and lanthanide hydroxocarbonate precipitates. These results contribute to the understanding of nuclear vitrified waste-iron-corrosion products interactions in a deep geological repository.

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1. Introduction

Reprocessing of spent nuclear fuel and recovery of fissile materials for military and civilian purposes has generated large amounts of acidic solutions concentrated in fission and activation products. Vitrification of this waste in a glass matrix greatly reduces the risk associated to dispersion of radiocontaminants either from leaking tanks (Streicher, 1999) or by overheating reservoir explosion (Novikov et al., 2006; Trabalka et al., 1980). Therefore, glass has become a selected matrix for stable and relatively safe storage of high-level radioactive waste (HLW) in oxic, air-cooled facilities at the Earth surface. After this temporary storage, disposal of nuclear waste in deep geologic repositories is considered as the safest and most sustainable solution to shield future civilizations from radiotoxic elements (De Marsily et al., 1977; Krauskopf, 1986; Sawiki, 2011). Hence, it is essential to assess whether glass can be a suitable matrix for long-term confinement of HLW under these

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geologic conditions (Gin et al., 2013).

Repository projects for HLW disposal usually rely on long-term confinement in metallic canisters surrounded by clay, bentonite, or concrete barriers (King, 2012, 2013). For example, in early designs by the French radioactive waste management agency (Andra), HLW disposed as a nuclear glass in stainless steel containers would be enclosed in low-alloy steel overpacks inserted in the claystone of the repository (Andra, 2005). The HLW packages will be exposed to conditions changing from an initially vapour-saturated and slightly oxic environment to a high-temperature (up to 90 °C), clay porewater-saturated anoxic medium, and eventually to saturated, anoxic conditions at moderate temperature (~25 °C) (King, 2012). These shifting conditions will result in complex interactions between engineering materials and geologic medium (Schumacher et al., 2015). These interactions must be fully identified for a reliable prediction of the long-term safety of such repositories.

A major safety element of HLW disposal is the carbon steel overpack, which should prevent water from reaching the vitrified HLW at least during the thermal phase (>50 °C) lasting about a thousand years (Andra, 2005). During this period, steel corrosion would rapidly promote local reducing conditions at the clay–steel interface, in addition to water resaturation and localized heating resulting from radioactive decay (King, 2012). At the end of this thermal phase, the overpack and the primary container are expected to finally breach due to corrosion processes and mechanical overload (King et al., 2014; Schumacher et al., 2015). As a result, nuclear glass will contact clay porewater possibly equilibrated with corrosion products (CPs) of steel. Several studies have focused on elucidating the influence of clay material such as bentonite (Gin et al., 2001a; Godon et al., 1989; Godon and Vernaz, 1990; Poinssot and Toulhoat, 1998; Pozo et al., 2007; Werme et al., 1990), clay, or clayey water (Bosbach et al., 2008; Frugier et al., 2008; Jollivet et al., 2012a, 2012b; Neeway et al., 2015) on glass alteration (initial rate, rate drop regime, residual rate, and full alteration). However, it is also essential to determine how the CPs and the continuous overpack corrosion can influence the alteration kinetics of nuclear glass under repository conditions. For example, processes such as sorption of dissolved silicic acid on CPs and precipitation of silicate phases are believed to favour glass dissolution by delaying the saturation of the aqueous solution required for the formation of a protective gel (de Combarieu et al., 2011; Godon et al., 2013; Grambow et al., 1987; Mayant et al., 2008; Michelin et al., 2013b; Philippini et al., 2006; Rebiscoul et al., 2015; Werme et al., 1990). This possible complexity is compounded by the preliminary exposure of CPs to substantial amounts of dissolved silicic acid originating from clay porewater. Thus, CPs would already have partially reacted with high concentrations of dissolved silicic acid, resulting in the formation of (meta)stable silicate solids (Rivard, 2011; Schlegel et al., 2008, 2010, 2014). It thus appears that laboratory-scale experiments can provide some insight into these complex interactions. Such experiments allow one, for example, to understand steel corrosion and clay transformation under water-saturated, relatively high temperature conditions (Bataillon et al., 2001; Bourdelle et al., 2014; Carlson et al., 2007; Charpentier et al., 2006; El Mendili et al., 2013, 2014; 2015; Guillaume et al., 2003; Jodin-Caumon et al., 2012; Le Pape et al., 2015; Madsen, 1998; Martin et al., 2008; Pignatelli et al., 2013, 2014; Rivard et al., 2013a, 2013b; Schlegel et al., 2008, 2010, 2014; Smart et al., 2008). Comparatively, the number of integrated experiments on mutual interactions between clay, glass, and steel or Fe-containing CPs is limited (Burger et al., 2013; de Combarieu et al., 2011; Dillmann et al., 2016; Michelin et al., 2013a, 2013b; Rebiscoul et al., 2015). To our knowledge, only one study was performed at 90 °C (de Combarieu et al., 2011), and used a thin foil (10 μm) of metal iron (iron), which was corroded within 10 months,

limiting both concentration and supply of oxidized Fe. Also, CPs were in limited amount compared to clay and so their impact on glass alteration was debatable at best. Therefore, additional data are needed to better assess glass alteration in a complex (clay and steel) environment over periods of time exceeding one year.

The present study investigates the alteration of a fractured glass block in contact with iron and clay rock (claystone) at 90 °C under anoxic, water-saturated conditions. The temperature of the study is somewhat higher than the nominal conditions expected at the end of the overpack lifetime, but is relevant if earlier-than-expected loss of confinement occurs. Glass fracture, although not planned by experimental design, was an unexpected bonus, because it allows us to investigate the alteration of a fracture network similar to that in the HLW container. Time-dependent alteration rates were assessed from solution composition, and the thickness and composition of the alteration layers were investigated using microscopic and spectroscopic methods. Focus was placed on the possible incorporation and impact of Fe on the mean alteration rate and on the nature of glass alteration products. These experiments confirm the significant but limited impact of Fe$^{(II,III)}$, both in space and time, on the alteration mechanism of glass in a confined medium. The results also corroborate our previous findings and extend our understanding of long-term iron-glass-clay interactions in complex geologic environments.

2. Material and methods

2.1. Experimental setup

The experimental setup has been extensively described in a companion paper (Schlegel et al., 2014). Briefly, three probes were inserted in a brick of claystone from the Callovo-Oxfordian (COx) formation of the East of Paris Basin. Two of these probes were electrodes; the lower one was made of Armco iron (pure ferrite) and was used as a working electrode for corrosion monitoring, and the upper one was made of gold and used as a pseudo-potential reference electrode. The third probe (in the middle) was a mockup of broken overpack and was made up of a rod (diameter 12 mm, length 30 mm) of SON68 glass (the non-radioactive surrogate of French nuclear glass R7T7) partly encapsulated in two short iron pipes. The central part of the glass rod (over 12 mm width) was directly in contact with clay whereas the two end parts were geometrically shielded from direct contact by the iron pipes. Thus, the clayey porewater could percolate between the glass and the iron pipes. The claystone brick was confined in a nickel insert, and then inserted in a triaxial cell. This brick was saturated with 32 mL of a synthetic solution having the calculated composition of porewater in equilibrium with claystone at 90 °C (Gaucher et al., 2009), and heated at 90 °C for two years. Periodically, 20–30 mL of the solution inside the containment cell was sampled and replaced with a fresh input of synthetic porewater. The element concentrations in solution (Li, B, Na, Si, Mg, Ca, Fe, Ni) were determined by ICP-AES (uncertainty ~3%).

2.2. Sample preparation for microscopic characterization

At the end of the corrosion experiment, the claystone brick was extracted from the high-pressure setup. The gold electrode was removed and replaced by a polymer rod, and the whole brick was embedded in epoxy resin to ensure confinement, even during manipulation in air. The block was then analysed by X-ray tomography to non-destructively assess sample heterogeneities such as fractures affecting glass and clay, and the extent and heterogeneity of the corrosion affecting iron surfaces (Schlegel et al., 2014). All subsequent preparation steps were made in an anoxic glove box to