Chemical Geology 279 (2010) 106–119

Contents lists available at ScienceDirect

Chemical Geology

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

Composition effects on synthetic glass alteration mechanisms: Part 1. Experiments

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ARTICLE INFO

Article history:
Received 21 January 2010
Received in revised form 29 September 2010
Accepted 13 October 2010

Editor: J.D. Blum

Keywords:
Glass
Nuclear glass
Alteration
Dissolution
Kinetics
Gel
Passivating layer
GRAAL

ABSTRACT

Alteration of nuclear waste glasses and silicate minerals is governed by complex processes regulated by several coupled mechanisms. Among these processes is reactive mass transfer through the amorphous gel layer (known as the *passivating reactive interphase* (PRI) in case of a rate-limiting effect) located between the pristine glass and the bulk solution. In order to assess the influence of the glass composition and the pH on the properties of the PRI, and thus on the nuclear glass durability, an experimental leaching study was performed on borosilicate glass samples with or without Ca, Al, and Zr. Experiments were conducted to understand the influence of the pH and glass composition on the solvated cation diffusion coefficient within the PRI and to generate data for calibration of a PRI solubility model (not presented here). All the experiments were carried out at high *S*/*V* ratios so that silicon rapidly reached apparent saturated conditions and the PRI could form: in such conditions glass alteration is controlled only by diffusion of water and dissolved species through the PRI and by precipitation of crystallized secondary phases. The constituents in the PRI and the crystallized secondary phases depend to a large extent on the glass composition and pH. Alkali metal (Na) or preferentially alkaline earth (Ca) elements are retained in the PRI for charge compensation of Al and Zr. The apparent diffusion coefficient calculated from the release of boron, a good tracer, varies with the pH from less than 4×10^{-22} to 9×10^{-18} m^2 s^{-1} in the studied glasses. These very low diffusion coefficients decrease as the pH increases. Concerning the PRI composition we show that Si, Al, Ca and Zr have strong interactions and thus major consequences on the glass durability. Our findings indicate that the SiO_2aq activity is relatively constant and independent of the pH below pH 9, followed by a drop at pH 10. In addition, the activity of SiO_2aq is affected by the glass composition, and especially by aluminum and zirconium. As soon as dissolved silicon reaches steady state in solution the aluminum and zirconium concentrations start to decrease, probably due to silicon, aluminum and zirconium interactions with retention in the PRI. The formation of crystallized secondary phases is observed at pH 10 for aluminum-free glasses, which diminishes the saturation state of amorphous silica in solution. In these glasses the saturation index indicates that the solution is oversaturated with respect to calcium silicate hydrates (ex: tobermorite, gyrolite). Moreover, the formation of crystallized secondary phases causes dissolution of the PRI and the glass, which sustains renewed alteration. This study leads to the conclusion that modeling nuclear glass dissolution kinetics over a wide pH range (typically from pH 7 to pH 10) must take into account (1) PRI composition variations and relations between the PRI composition and properties (solubility, diffusion coefficient); and (2) crystallized secondary phases that can consume elements from the PRI. Applying PRI modeling concepts to other kinds of natural glasses or even multi-oxide minerals might prove useful for enhancing our understanding of alteration mechanisms.

1. Introduction

Many fields of research are concerned by water–rock interactions ranging from global cycling of elements to the transport of groundwater nutrients and contaminants. Mineral surface descriptions are required to understand the mechanisms involved. In France, one reference option for the management of vitrified high-level waste packages is deep geological disposal (waste management act of June 28, 2006). The current disposal concept studied by ANDRA (French National Radioactive Waste Management Agency) is based on three containment barriers: the glass package (inside its stainless steel canister), a 55 mm thick carbon steel overpack, and finally the host rock which is a 130 m thick Callovo-Oxfordian argillite layer (ANDRA, 2005). Based on the calculations for the safety assessment of a geological repository, the most important phenomena that must be thoroughly investigated concern radionuclide release from the glass matrix due to alteration by groundwater and migration through the host rock. In either normal or accident scenarios, these phenomena will take hundreds of thousands of years before the radionuclides reach near-surface aquifers. This is why a comprehensive methodology is required, including laboratory experiments to investigate chemical processes at different scales, a mechanistic model to predict

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doi:10.1016/j.chemgeo.2010.10.010

the radionuclide source term, and model validation using natural or archeological analogs, integrated mockups or in situ tests.

Dissolution of silicate glasses is a complex process controlled by several mechanisms (Conradt, 2008; Frugier et al., 2008; Frizon et al., 2009). The alteration kinetics of silicate glasses determined from laboratory studies involve several characteristic process steps that are detailed below (Advocat et al., 1991; Berger et al., 1987; Byers et al., 1985; Crovisier et al., 1985, 1989, 1992; Guy, 1989; Vernaz and Dussossoy, 1992; Verney-Carron et al., 2007; Van Iseghem et al., 2007). Recently, Frugier et al. (2008) proposed a new mechanistic model called GRAAL (Glass Reactivity with Allowance for the Alteration Layer), which highlights the key mechanisms in the glass alteration process. This model has been applied successfully to SON68 glass (i.e. the French inactive reference glass) altered in various conditions (Frugier et al., 2009). In the GRAAL paradigm, the glass alteration process is a combination of the following steps: (1) exchange and hydrolysis reactions first involve mobile glass components (alkali metals, boron, etc.) (Geneste et al., 2006; Rebiscoul et al., 2007); (2) hydrolysis, especially of silicon, results in the existence of an initial glass dissolution rate; (3) the difference between these two kinetics causes an amorphous alteration layer to form at the glass/solution interface regardless of the alteration conditions; (4) the amorphous alteration layer progressively creates a barrier limiting the transport of water toward the glass and of solvated glass ions into solution; (5) some glass constituents precipitate as crystallized secondary phases which are present on the external surface or dispersed in solution. Depending on their composition, the formation of these crystallized secondary phases may accelerate or maintain a pseudo-constant glass alteration rate. The "final" or "residual" alteration rate can be attributed to the mechanisms of steps (4) and (5). Overall, glass alteration produces an amorphous alteration layer (often called the "gel") as well as crystallized secondary phases, and these two phenomena are of a completely different nature (Thomassin, 1984; Jercinovic et al., 1990, Advocat et al., 1991, Vernaz and Dussossoy, 1992; Verney-Carron et al., 2007).

According to basic thermodynamics, the amorphous layer is stable only when the solution is saturated with respect to its constituent elements such as silicon, zirconium, aluminum, calcium, etc. Furthermore, the transport-inhibiting effect of the amorphous layer between the glass and solution controls glass alteration (i.e. the release of glass alteration tracers like boron or alkalis). The amorphous layer is therefore termed a "passivating reactive interphase" (PRI) in accordance with its properties (Chave et al., 2007; Frugier et al., 2008). However, a low-density amorphous layer can form far from saturation thanks to low-solubility elements such as Zr. Under these conditions, it has no or negligible passivating properties compared with the PRI that is eventually formed at saturation. It is then called a depleted gel. The nature of the amorphous layer varies with the reaction conditions (glass-surface-area-to-solution-volume (S/V) ratio, flow rate, pH, temperature, etc.) and with the reaction progress (forward rate, rate drop or residual rate regimes). At high S/V ratios the system reaches saturation very rapidly, hence only the PRI is observable and the depleted gel is not significant (<1 nm) (Frugier et al., 2008). Moreover, Rebiscoul et al. (2005) carried out a detailed investigation of the amorphous layer and its properties in different reaction conditions, reporting that the amorphous layer has two different parts: a porous layer in contact with water and a dense layer at the gel-glass interface. Furthermore, the dense zone is identified as the one controlling the residual rate, which is expected to be the most important regime in a geological repository.

Numerous studies have reported the role of the amorphous layer and its protective properties on the alteration of glass or silicate minerals (Angeli et al., 2001; Ledieu et al., 2005; Hellmann et al., 2003, 2004; Lee et al., 2007; Rebiscoul et al., 2005). Some studies investigated the amorphous layer characteristics and its structural rearrangement during alteration, porosity, diffusion properties, retention of elements in the amorphous layer, etc. (Arab et al., 2008; Jollivet et al., 2008; Houston et al., 2008; Angeli et al., 2001b, 2008; Chave et al., 2007). Nevertheless, the composition of the amorphous layer has still not been fully defined. Generally, the amorphous layer is depleted in highly soluble elements and enriched in sparingly soluble elements. The constituents of the amorphous layer vary with glass composition, pH, temperature, etc. (Angeli et al., 2006, 2008). However, silicon, aluminum and zirconium are the predominant elements in the amorphous layer when SON68-type nuclear waste glasses undergo alteration. Element interactions within the amorphous layer are also an important factor; for example, in aluminosilicate glasses, silicon and aluminum strongly interact in the amorphous layer. Houston et al. (2008) studied the interaction between aluminum and amorphous silica using bulk solution chemistry experiments with NMR techniques. They reported three reaction pathways for aluminum–silica interactions such as adsorption of Al at surface silanol sites, surface-enhanced precipitation of aluminum hydroxides and aluminosilicate secondary phases. Several researchers have documented the role of dissolved aluminum on aluminosilicate mineral dissolution reactions (Oelkers and Schott, 1994; Bickmore et al., 2006; Chou and Wollast, 1985; Samson et al., 2005; Jones and Handreck, 1963; Hingston and Raupach, 1967; Ballou et al., 1973; Iler, 1973; Van Bennekom et al., 1991; Van Cappellen and Qiu, 1997). They concluded that Al species diminish the silica or silicate mineral dissolution rates in different reaction conditions.

Because the time scale considered for geological disposal is inaccessible to laboratory experimentation, modeling is the principal method used to assess the overall glass alteration behavior. Geochemical models are widely employed to simulate crystallized secondary phase formation during glass alteration (Advocat et al., 2001; Berger et al., 1987, 1994; Crovisier et al., 1985, 1989, 1992; Gislason et al., 1993; Gong et al., 1998; Grambow et al., 1985; Michaux et al., 1992,). These studies examined and simulated the dissolution kinetics and the formation of crystallized secondary phases, but the simulation did not take into account the formation of an amorphous layer at the glass/solution interface. Munier et al. (2004) modeled the amorphous layer composition of simple borosilicate glasses by the precipitation of an ideal solid solution. They considered three types of solid solutions: oxides, hydroxides and metasilicates. The major limitation of this work concerns the phases considered for the amorphous layer. Except for amorphous silica, silicates cannot form an amorphous layer. Furthermore, the present work will show that sodium is not retained as sodium oxide or hydroxide or silicates, but only as a charge compensator of Al and Zr in the amorphous layer. Moreover, if calcium is present in the glass constituents, most of the sodium will not remain in the amorphous layer. In addition, the chemical interactions between elements such as Si, Al, Ca, Zr within the amorphous layer were not considered in this study. Likewise, in the GRAAL model (Frugier et al., 2009), the amorphous layer (PRI) consists of simple phases which represent its forming elements such as Si, Al, Ca and Zr, and does not take into account the chemical interactions between these elements.

Hence, the present study was carried out to model the PRI composition of French nuclear waste glasses (stoichiometry similar to SON68) using simple and complex phases which represent PRI-forming elements and their chemical interactions. This study focuses on the main PRI-forming constituents of SON68 type glass: Si, Al, Zr and Ca. The study combines experiments and modeling. Experiments were carried out to understand the influence of the pH and glass composition on the diffusion coefficient and glass alteration phenomena, and to generate data for model calibration and validation. The pH range was chosen to cover alteration conditions imposed by the groundwater (pH near neutrality in most cases) up to conditions imposed by the glass dissolution (pH around 9.5). As the PRI is by definition (Frugier et al., 2008) the most passivating amorphous layer eventually formed in silicon-saturated condition, all the experiments were carried out at a high S/V ratio (2000 m^{-1}) and at 90 °C. In these conditions, saturation is achieved in a few hours; consequently, the