



The fate of silicon during glass corrosion under alkaline conditions: A mechanistic and kinetic study with the International Simple Glass

Stéphane Gin^{a,*}, Patrick Jollivet^a, Maxime Fournier^a, Claude Berthon^b,
Zhaoying Wang^c, Alexandre Mitroshkov^d, Zihua Zhu^c, Joseph V. Ryan^d

^a CEA, DEN, DTCD, SECM, F-30207 Bagnols-sur-Ceze, France

^b CEA, DEN, DRCP, SMCS, F-30207 Bagnols-sur-Ceze, France

^c W.R. Wiley Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA 99354, USA

^d Pacific Northwest National Laboratory, Richland, WA 99354, USA

Received 24 May 2014; accepted in revised form 10 December 2014; available online 20 December 2014

Abstract

International Simple Glass – a six oxide borosilicate glass selected by the international nuclear glass community to improve the understanding of glass corrosion mechanisms and kinetics – was altered at 90 °C in a solution initially saturated with respect to amorphous ²⁹SiO₂. The pH_{90°C} was fixed at 9 at the start of the experiment and raised to 11.5 after 209 d by the addition of KOH. Isotope sensitive analytical techniques were used to analyze the solution and altered glass samples, helping to understand the driving forces and rate limiting processes controlling long-term glass alteration. At pH 9, the corrosion rate continuously drops and the glass slowly transforms into a uniform, homogeneous amorphous alteration layer. The mechanisms responsible for this transformation are water penetration through the growing alteration layer and ion exchange. We demonstrate that this amorphous alteration layer is not a precipitate resulting from the hydrolysis of the silicate network; it is mostly inherited from the glass structure from which the most weakly bonded cations (Na, Ca and B) have been released. At pH 11.5, the alteration process is very different: the high solubility of glass network formers (Si, Al, Zr) triggers the rapid and complete dissolution of the glass (dissolution becomes congruent) and precipitation of amorphous and crystalline phases. Unlike at pH 9 where glass corrosion rate decreased by 3 orders of magnitude likely due to the retroaction of the alteration layer on water dynamics/reactivity at the reaction front, the rate at pH 11.5 is maintained at a value close to the forward rate due to both the hydrolysis of the silicate network promoted by OH⁻ and the precipitation of CSH and zeolites. This study provides key information for a unified model for glass dissolution.

© 2014 Elsevier Ltd. All rights reserved.

1. INTRODUCTION

1.1. Context

For decades, borosilicate glass has been produced in several countries to confine fission products and minor actin-

ides remaining after the reprocessing of spent nuclear fuels (Ojovan and Lee, 2011). Such high-level radioactive wastes are intended to be stored in deep geological repositories. The question of how fast the radionuclides (RN) confined in the glass are released to the geosphere has mobilized a broad scientific community since the beginning of the 1980s and continues to be challenging because of the high complexity of the system (Grambow, 2006; Van Iseghem et al., 2009; Jantzen et al., 2010; Gin et al., 2013a; Gin, 2014). Glass undergoes both dissolution and the irreversible

* Corresponding author. Tel.: +33 466791465; fax: +33 466796620.

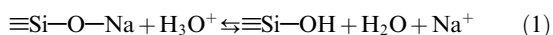
E-mail address: stephane.gin@cea.fr (S. Gin).

transformation into more stable phases but the rate of this transformation strongly depends on the geochemical boundary conditions (T, pH, solution composition, flow rate, etc). Moreover, from a safety standpoint, the glass and RN behavior must be calculated to be below regulatory limits for geological timescales (typically a million years in certain countries). Only a robust methodology can meet such an objective. This methodology must be a science-based understanding of the chemical and physical processes associated with the dissolution of the glass and the transport of the RN to the near- and far-field environment. This understanding forms the basis for a multi-scale modeling effort (ASTM, 1997; Poinssot and Gin, 2012). Historic, archeological and natural glasses are used to test the model for a wide range of environmental conditions and long time periods (Ewing, 1979; Lutze et al., 1985; Libourel et al., 2011).

1.2. State of the art

Knowledge about nuclear glass durability and the remaining open questions have been discussed in recent papers (Van Iseghem et al., 2009; Vienna et al., 2013; Gin, 2014; Pierce et al., 2014; Fournier et al., 2014b). Briefly, when placed in static or slightly renewed solution, nuclear glass corrosion generally follows 3 behavioral stages:

- I. The *initial* or *forward rate*, denoted as r_0 , that is characterized by hydration (diffusion of water molecules into the glass), ion exchange (interdiffusion) (Eq. 1) and the hydrolysis of the silicate network (Eq. 2) in relatively dilute conditions that do not hinder the forward hydrolysis reactions and preclude the formation of effective barrier layers.



- II. As the concentration of silica in solution increases, the corrosion rate decreases as it begins to be affected by the diminishing of the affinity for reaction (2) accompanied by the formation of a passivating layer. This eventually leads to the *residual rate*, denoted as r_r , a relatively constant or slowly decreasing rate much slower than the forward rate. It is suggested that the residual rate could correspond to a steady-state between the formation and the dissolution of the passivating layer (Frugier et al., 2008). However there is not yet a broad consensus on the mechanisms that control this particular regime (Van Iseghem et al., 2009; Vienna et al., 2013).
- III. The potential sudden *resumption of alteration* that is coincident with the rapid precipitation of certain silica-bearing alteration products. This increase in dissolution rate for some glasses appears to occur only under specific conditions, typically high temperature and/or high pH (Fournier et al., 2014b).

In geological disposal, glass packages only have the potential to last hundreds of thousands years to few million

years if glass reaches and stays in the residual rate regime (Gin et al., 2004). Thus, it is of primary importance to better understand and model the mechanism(s) responsible for the residual rate and understand when and why glass alteration can suddenly resume. The pH is a first order parameter in this regard. The presence of B in nuclear glasses contributes to buffer the pH of most leaching solutions at around 9, but in some cases (e.g., cement-type waters) hyperalkaline pH values are expected.

There is a strong consensus on the fact that dissolved Si ($\text{SiO}_2(\text{aq})$ or H_4SiO_4 (Icenhower and Steefel, 2013) and the ionized forms) plays a major role in the different processes involved in the regimes listed above. Aqueous Si affects the ΔG (i.e., the affinity) of reaction (2) (Advocat et al., 1998; Abraitis et al., 2000; Pierce et al., 2008; Neeway et al., 2011), the passivating layer is mainly composed of Si (Grambow and Muller, 2001; Frugier et al., 2008; Rajmohan et al., 2010), and secondary phases acknowledged to affect the rate are mostly silicates (Abrajano et al., 1990; Caurel et al., 1990; Ebert and Bates, 1991; Gong et al., 1998; Pierce et al., 2006, 2007; Valle et al., 2010; Debure et al., 2012; Michelin et al., 2013; Gin et al., 2013b).

1.3. Objectives

In this paper, we focus on the fate of Si during glass corrosion in the residual rate (II above) and alteration resumption (III above) stages. The two regimes are investigated in a single experiment carried out on the International Simple Glass (ISG), a six-component glass selected by the international community to build a consensus on the understanding of glass corrosion processes because it has the same cation ratios as the major components in the SON68 glass, a more representative material of actual nuclear glasses (Gin et al., 2013a). Moreover it has been shown that both ISG and SON68 glass have similar initial and residual release rates (Gin et al., 2012). The experiment discussed in this paper was started with a solution initially saturated with respect to $^{29}\text{SiO}_2(\text{am})$ at 90 °C and a $\text{pH}_{90^\circ\text{C}}$ value of 9. The monitoring of Si isotopes with isotope-sensitive analytical techniques provides information about the dynamics of exchanges between aqueous species and solid species during glass corrosion and therefore about the solubility of the silicate network. Since $\text{SiO}_2(\text{am})$ is the silica polymorph with the highest solubility, glass alteration occurred in the presence of the highest possible concentration of H_4SiO_4 at pH 9 (Iler, 1979). Moreover, these starting conditions enabled us to dramatically reduce the time associated with regime I above (initial dissolution rate) and rate drop and thus focus on the residual rate.

After 209 days at $\text{pH}_{90^\circ\text{C}}$ 9, the solution pH was raised to 11.5 by the addition of KOH and maintained at this value. The results of this second stage of the experiment improve the understanding of how the slow residual rate observed at pH 9 can suddenly increase.

1.4. Terminology

As a result of the complex suite of corrosion processes listed above (hydration, interdiffusion, hydrolysis,

Download English Version:

<https://daneshyari.com/en/article/4701909>

Download Persian Version:

<https://daneshyari.com/article/4701909>

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