

15th Water-Rock Interaction International Symposium, WRI-15

Modeling resumption of glass alteration due to zeolites precipitation

Pierre Frugier^{a,*}, Maxime Fournier^a, Stéphane Gin^a

^aCEA, DEN, DTCD, SECM, F-30207 Bagnols sur Cèze, France

Abstract

Under hyper-alkaline pH or relatively high temperatures, a resumption of glass alteration can occur. This sudden acceleration of the glass corrosion rate is almost always associated with zeolites precipitation. Zeolites precipitation consumes silica and aluminum, key elements of the glass surface layer controlling its dissolution. A better understanding and quantification of this mechanism is crucial for predicting glass long-term behavior. Geochemical modeling applied to experimental data is a useful tool to reach that goal. However, it has never been applied successfully so far for modeling the kinetics of that reaction. Within the framework of the GRAAL glass dissolution model, and with simple zeolite precipitation kinetic assumptions, a simulation of glass resumption of alteration is attempted. Concentrations in solution and element mass balance between amorphous and crystallized phases are reproduced. Key parameters are revealed. Better understanding is now achievable through sensitivity studies on minerals stoichiometry and on the respective weight of dissolution and precipitation kinetics in the control of the whole reaction rate.

© 2017 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Peer-review under responsibility of the organizing committee of WRI-15

Keywords: glass; alteration; zeolite precipitation; nucleation; growth; geochemical modeling.

1. Introduction

In natural systems, zeolites are classical secondary products of aqueous alteration of basaltic glasses. Within laboratory time scales, zeolites precipitate at the expense of industrial glasses¹. How their precipitation drives glass dissolution rate is a real concern when it comes to prediction of the long term behavior of nuclear wastes confinement glasses: sudden increases in the alteration rate could be observed after many years of experiment for some alkali rich glasses².

Thermodynamic models were proposed in the past in order to predict the occurrence of zeolite precipitation and glass resumption of alteration^{3,4}. These models have two limitations:

* Corresponding author. Tel.: +33 466797724.

E-mail address: pierre.frugier@cea.fr

- None are kinetic models: time is not a parameter, therefore neither the extent nor the kinetics of the resumption of alteration could be forecasted.
- During zeolite precipitation, an increase in silica activities is measured in solution. This experimental fact is at odds with the use of an affinity term based only on silica, which has been the reference for describing the drop in glass alteration rate close to saturation⁵.

Since the 90's, geochemical modeling codes and understanding of the glass dissolution mechanisms have been improved. New experiments especially designed for the purpose of modeling have become available. Time has come for a new attempt to model glass alteration. We hope such a modeling exercise can be a useful tool for identification of the predominant mechanisms and to highlight future experimental work design.

2. Methods and modelling tools

2.1. Experiments

The glass alteration experiments chosen for applying the model are described elsewhere^{6,7}. These are chosen because pH is buffered at a constant value during the whole experiment. That way, the pH dependence of many modeling parameters, such as precipitation and dissolution kinetics, does not have to be known beforehand: constant parameters can be used for a given pH. Leaching experiments are carried out at 90°C in PFA reactors with glass powders in the 63-125 µm size fraction ($SSA_{BET} = 0,072 \text{ m}^2 \cdot \text{g}^{-1}$) of the International Simple Glass. This is an aluminoborosilicate glass composed of six oxides: SiO₂ (56.2 wt%), B₂O₃ (17.3), Na₂O (12.2), Al₂O₃ (6.1), CaO (5.0), ZrO₂ (3.3), chosen to be a reference glass for international studies on waste glass corrosion⁸. Surface area to solution volume ratio is $4\,000 \text{ m}^{-1}$. The fluid initial composition is sodium hydroxide at $2.5 \cdot 10^{-2} \text{ M}$ for which $\text{pH}_{90^\circ\text{C}}$ is measured at 10.7. pH is buffered at ± 0.2 unit by appropriate additions of 5 M sodium hydroxide.

In order to assess the role of the zeolite surface on zeolite precipitation kinetics and glass dissolution, a seeded experiment was performed: seeds were synthesized for that purpose⁶. These have the same crystalline structure as the zeolites formed during glass alteration. The seeds' external surface, supporting the growth of new crystals, was measured by laser diffraction to $0.25 \text{ m}^2 \cdot \text{g}^{-1}$. In the test, the ratio between zeolite and glass surfaces was equal to 3.

2.2. Glass alteration model

The framework of the GRAAL model⁹ has been chosen to model glass dissolution kinetics. GRAAL relies on:

- the formation of a non-passivating (depleted) gel layer: the model describes the composition and solubility of the glass amorphous layer thanks to end-member compositions, splitting it in two parts: a depleted gel with no passivation properties and a Passivating Reactive Interphase (PRI). The PRI is silica rich to account for the fact that high silica retention is required for achieving passivation. A strong effect of Al on silica apparent solubility has been experimentally observed¹⁰. Therefore, PRI contains not only silica but also Al. With this approach, modeling the increase of silica activities in solution in response to Al consumption due to zeolites precipitation might be achievable.
- the formation of a passivation layer (PRI). Equation (1) describes how the glass dissolution rate decreases with the increasing thickness of the PRI. Variation of PRI thickness x is written in equation (1) as a function of diffusion coefficient D_{PRI} , glass initial dissolution rate r_0 , PRI ionic product Q_{PRI} and solubility K_{PRI} .

$$\frac{dx}{dt} = D_{\text{PRI}}/x - r_0 \cdot (1 - Q_{\text{PRI}}/K_{\text{PRI}}) \quad (1)$$

2.3. Zeolites precipitation model

The simplest model is chosen to account for zeolite precipitation: given that pH is buffered, the assumption is made that the rate of zeolite nucleation on the amorphous external surface of glass is constant. Zeolites are also assumed to grow at a constant rate and in a single direction, perpendicular to the surface. Therefore, equations (2)

Download English Version:

<https://daneshyari.com/en/article/5779304>

Download Persian Version:

<https://daneshyari.com/article/5779304>

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