Journal of Nuclear Materials 486 (2017) 70–85

Contents lists available at ScienceDirect

Journal of Nuclear Materials

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

A mechanistic model for long-term nuclear waste glass dissolution integrating chemical affinity and interfacial diffusion barrier

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ARTICLE INFO

Article history:
Received 14 November 2015
Received in revised form
26 November 2016
Accepted 2 January 2017
Available online 3 January 2017

Keywords:
Nuclear waste glasses
Long-term dissolution
Mechanisms
Modelling

ABSTRACT

Understanding the alteration of nuclear waste glass in geological repository conditions is critical element of the analysis of repository retention function. Experimental observations of glass alterations provide a general agreement on the following regimes: inter-diffusion, hydrolysis process, rate drop, residual rate and, under very particular conditions, resumption of alteration. Of these, the mechanisms controlling the rate drop and the residual rate remain a subject of dispute. This paper offers a critical review of the two most competitive models related to these regimes: affinity–limited dissolution and diffusion barrier. The limitations of these models are highlighted by comparison of their predictions with available experimental evidence. Based on the comprehensive discussion of the existing models, a new mechanistic model is proposed as a combination of the chemical affinity and diffusion barrier concepts. It is demonstrated how the model can explain experimental phenomena and data, for which the existing models are shown to be not fully adequate.

1. Introduction

Radioactivity wastes are generated at all stages of the nuclear fuel cycle, including the decommissioning of nuclear facilities, as well as from military applications. Of particular concern for the storage/disposal of radioactivity wastes are those containing long-lived radionuclides [1]. The current plan (countries such as Belgium, Finland, Sweden, France etc.)for long-term management of such wastes is to store them in deep, stable and low-permeable geological formations [2]. The storage design is based on the so-called multi-barrier concept, where several barriers prevent for a period of time, or slow down the release and migration of radionuclides through the geosphere [3,4]. Within this concept, hazardous nuclides are immobilized into solidified bodies. The wasteform selection is difficult, since durability is not the sole criterion [5]. Currently, vitrification is regarded as the best solution for immobilizing radionuclides. This technology has been progressively developed over the last half-century, has matured and has become industrially robust.

Data collected to date suggest that glass waste forms offer the advantages that they can accommodate a wide range of waste streams, are resistant to radiation damage, and are relatively inert to both chemical and thermal perturbations [6]. The use of natural and archeological analogues supported further the durability argument of glass as waste forms [7–11]. Except for the alumino-phosphate glass used in Russia, the borosilicate glass has been universally selected by all other nations [12].

In order to make scientifically-underpinned safety cases, the long-term behaviour of glassy wasteforms requires further understanding and assessment. Half-lives of some radionuclides extend to millions of years, requiring isolation for geological periods, while the period of investigation possible in the field and the laboratory is relatively short. The development of reliable performance assessment models must be based on a rational consensus on the mechanisms controlling the long-term dissolution of glass.

Experimental observation is that the dissolution rate of nuclear waste glass decreases with increasing time of exposure, only if the Si concentration in solution increases or an alteration layer is formed. The interpretations of this currently relate either to a

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http://dx.doi.org/10.1016/j.jnucmat.2017.01.001
0022-3115/

thermodynamically (chemical affinity) or to a kinetically controlled dissolution behaviour (diffusion barrier). However, models based on these concepts yield quite different long-term predictions, even though they fit equally well particular sets of experimental data [13–15].

This work presents a new model, which combines the two previous approaches. Firstly, the aqueous alteration regimes of nuclear waste glass and related dominant mechanisms are reviewed briefly. This is followed by a discussion on the rate drop and residual rate controlling mechanisms, leading to the new model. It is used to interpret the key experimental observations found in the literature.

2. Mechanisms and models of long-term glass dissolution: consensus and arguments

The vitrification process creates chemical bonds between radionuclides and the nuclear waste glass network. Consequently, the radionuclides cannot be released if the glass remains undissolved. For the purpose of “source term” estimation, it is essential to clarify the long-term dissolution behaviour of nuclear waste glasses.

The dissolution of glass is a complex process that depends on both the intrinsic properties of the glass and the leaching conditions. When glass comes into contact with water, processes of interdiffusion, ion exchange, reaction diffusion and hydrolysis occur. These processes and their interactions of nuclear glass alteration generally involving five rate regimes, as shown in Fig. 1 [12,16,17]): I. Initial diffusion or interdiffusion; II. Hydrolysis process; III. Rate drop; IV. Residual rate; and V. Possible resumption of alteration in particular conditions.

These observations of the alteration kinetics, determined from concentration variations of the mobile elements (boron, alkali metals, Si etc.)in solution, as well as solid phase observations which were determined by modern experimental techniques such as SEM, TEM, Raman etc., can be related to the nature of the underlying mechanisms.

2.1. Initial diffusion or interdiffusion

The term interdiffusion refers to the exchange between glass network-modifier cations and protons in solution. At the very beginning of corrosion, water species penetrate into glass, protons in the solution undergo diffusional ion exchange with mobile alkali modifier ions such as Li^+, Na^+, leaving an alkali-depleted zone at the glass surface, called diffusion zone. This reaction can be divided into two parallel processes: water penetration into glass [18–22] and alkali ions release into solution [23,24]. The mechanism has been identified experimentally during leaching of many minerals and natural glasses, especially in acidic media [17].

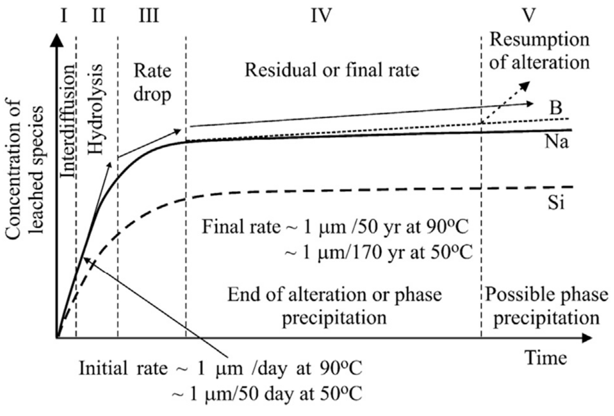

Fig. 1. Time sequence of different rate regimes with sodium, boron and silicon concentrations in solution [16].

If only alkali ions were released into solution through the ion exchange reaction, the glass would remain in its glassy state. However, works with borosilicate glass have shown that the release of boron is practically congruent to those of alkali ions [15,24], and B is the network former element. Geneste [25] investigated hydrogen–sodium interdiffusion in borosilicate glasses from first principles, using density functional calculations. They found that the substitution of the Na^+ network modifiers does not alter the glass covalent network, whereas a bridging bond is systematically broken when the substitution involves Na^+ ions bonded to BO_4 tetrahedra. The systematic dissociation of hydronium into water suggests that this chemical species probably has a short lifetime in the glass, due to the capability of anionic sites to trap the protons very strongly. That is to say, the substitution of Na^+ ions would lead to the collapse of BO_4 tetrahedra, and result in the rapid release of boron into solution.

Water diffusion and glass modifier diffusion, including B and alkali ions, are two parallel processes, and the slower of the two is rate limiting. It's reasonable to consider water diffusion as rate limiting, because in the opposite case one would expect large difference in the release properties of alkali ions and of B. In fact congruent release of alkali ions and B is often observed during leaching experiment [13].

2.2. The hydrolysis process

The initial stage, where the corrosion rate is relatively constant and at a maximum, is also referred to as the forward rate stage. This occurs before the solution reaches saturation with the silica phases occurring in the time of the experiments, such as chalcedony or amorphous silica, at which point the corrosion has been observed to decrease markedly. It also occurs before any significant development of a leached layer can form. Initial rate involves the hydrolysis of covalent and iono-covalent Si–O–M bonds (M = Si, Al, Zr, Fe, Zn,etc.), which constitute the net structure of a glass [12,17,21]. Hydrolysis modifies the silicate network by attacking bridging bonds (Si–O–Si, Si–O–Al, Si–O–Zr, etc.) in the interphase created by the release of mobile elements. Water molecules thus act on the glass by directly affecting network connectivity, leading to matrix dissolution according to the reaction: $\equiv Si{-}O{-}Si\equiv + H_2O \rightarrow 2\equiv Si{-}OH$. The rupture of all bridging bonds (1–4) around a silicon atom in the glass, leads to the release of an orthosilicic acid molecule, H_4SiO_4. The hydrolysis reaction has been observed to accelerate in both acid and basic conditions, with a lowest rate in neutral environment [26,27]. Based on the first principles, it has been found [28–33] that the activation energy of the hydrolysis of $T^m{-}O{-}T^n$ (where T = Si, Al; m, n = number of bridge oxygen atoms and $0 < m, n < 4$) bonds can be rather variable: lower in acid and basic conditions but higher in neutral conditions.

In dilute solution with low Si concentration, the initial dissolution rate depends essentially on the temperature, pH and glass composition. Some ions, such as aluminium and iron, can catalyze or inhibit these kinetics [33]. For borosilicate glasses, the initial dissolution rate, r^0, was determined as a function of the pH and the temperature according to [34]:

$$r^0 = k_+ \left[H^+\right]^n exp\left(\frac{-E_a}{RT}\right) \tag{1}$$

where k_+ is the pre-exponential factor ($g.m^{-2}.\ d^{-1}$); n is the pH dependence coefficient, E_a is the activation energy of hydrolysis of Si–O–M bonds ($kJ.mol^{-1}$). Notably, the E_a does not relate to a