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Investigation of gel porosity clogging during glass leaching

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ABSTRACT

A 5-oxide glass (62.5SiO_2, 16.6B_2O_3, 13.1Na_2O, 6.0CaO, 1.8ZrO_2) was leached at 90 °C at a high glass-surface-area-to-solution-volume ratio ($SA/V = 80\ cm^{-1}$). Its dissolution rate diminished over time until it became unmeasurable. The alteration layer was characterized by ^{29}Si isotopic tracing in the leaching solution. ToF-SIMS elemental profiles showed that glass dissolution ceased due to clogging of the gel porosity at the gel/solution interface. One of the hypotheses proposed to account for the rate drop observed during borosilicate glass alteration is based on morphological changes in the alteration gel over time. Monte Carlo modeling of glass alteration, especially with simple glasses, indicates a clogging of the porosity on the external portion of the gel (near the solution/gel interface) after densification of the layer by silicon precipitation, but this phenomenon had never previously been directly observed experimentally. The initial results obtained by isotopic tracing provide new data that appears to confirm this hypothesis.

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1. Introduction

France has opted to reprocess spent fuel from its nuclear power plants. The resulting wastes (fission products and minor actinides) are immobilized in a borosilicate matrix known as R7T7 glass. Radionuclides are released from the glass matrix when water comes into contact with the package. The long-term behavior of R7T7 glass has been investigated under various types of leaching conditions with a view to geological disposal [1], and the kinetics and mechanisms of glass alteration have been studied in aqueous media [2]. Leaching of nuclear glass begins by water diffusion into the glass, resulting in an interdiffusion process between protons supplied by the water and alkalis in the glass. As long as the solution remains sufficiently dilute the glass dissolution kinetics are controlled by hydrolysis of the covalent bonds of glass network-forming elements and the glass alteration rate remains constant at a maximum value known as the initial rate, r_0. The rate then gradually diminishes by several orders of magnitude as the solution tends toward saturation, especially with respect to silicon.

Leaching of high-level waste containment glass forms an altered layer on the glass surface. This layer, called gel, includes a large number of radionuclides and exhibits diffusion barrier properties [3,4] that vary according to the leaching conditions and the glass composition [5]. Taking into account the high number of chemical elements constituting the R7T7 glass, the leaching behavior of simplified glasses was studied [5] in the aim to understand the influence of a specific element (Al, Ca, Zr, REE) on the kinetics dissolution of glass. The glass composition was based on a ternary glass (SiO_2, B_2O_3, Na_2O) from which the specific elements were added to obtain more and more complex glasses made of 4-, 5-, 6- and 7-oxides. Leach tests on an R7T7 glass formulation simplified to only 5-oxides showed that the glass dissolution rate not only diminished over time but ultimately dropped to zero [6]. The onset of a zero glass alteration rate is classically attributed to the solution reaching saturation with respect to silicon, or more specifically silicic acid, H_4SiO_4 [7]. Recent work has shown that the morphology of the gel differs significantly according to the alteration conditions [8]. The structure could also directly affect the glass alteration kinetics. This effect was revealed by Monte Carlo simulations of simple glass alteration [9,10] showing that, under certain leaching conditions, the dissolution rate of 5-oxide glass samples dropped to zero following silicon recondensation that resulted in clogging of the gel porosity [11]. Exchanges between the pristine glass and the leaching solution were no longer possible and glass dissolution stopped. Previous experiments have been done using ^{29}Si tracing [12] to study the glass dissolution reactions and the silicon recondensation during gel forming. The ^{29}Si profiles measured by ionic microprobe (SIMS) had been used to determine the silicon distribution in two successive layers of altered glass. The isotopic analysis of altered glass layers showed that phyllosilicates were formed by precipitation while the gel was formed by

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hydrolysis/condensation reactions at the gel/pristine glass interface. Other experiments showed the silicon transfer from the solution to the gel under isotopic gradient. They were used to determine the silicon apparent diffusion coefficients in the pores of different gels.

Our objective here was to check clogging in the gel porosity experimentally by isotopic tracing of ^{29}Si in the leaching solution.

2. Experimental

2.1. Glass composition

The material used for this study was a 5-oxide glass (SiO_2, B_2O_3, Na_2O, CaO, ZrO_2), with the chemical composition indicated in Table 1. The elemental molar ratios were identical with those of the major elements in the R7T7 glass except for aluminum (this last element is not present in the studied glass). The glass was chemically analyzed by alkaline fusion ($NaOH + KNO_3$ and $Li_2B_4O_7 \cdot 5H_2O$) of glass powder, then recovered in HNO_3 for ICP-AES (inductively coupled plasma-atomic emission spectroscopy) analysis. The glass was heated for 3 h at 1350 °C in a platinum crucible and annealed for 1 h at 570 °C in a graphite crucible. The glass density determined using a hydrostatic balance was 2.547 ± 0.005 g cm^{-3}.

Table 1
Molar composition of glass and gels

Oxide	Glass	Gel 1d	Gel 86d
SiO_2	62.5 ± 1.9	86.0 ± 2.6	87.4 ± 2.6
B_2O_3	16.6 ± 0.5	0.0 ± 0.5	0.0 ± 0.5
Na_2O	13.1 ± 0.4	0.0 ± 0.4	0.0 ± 0.4
CaO	6.0 ± 0.4	10.6 ± 0.7	9.7 ± 0.7
ZrO_2	1.8 ± 0.2	3.4 ± 0.3	2.9 ± 0.3

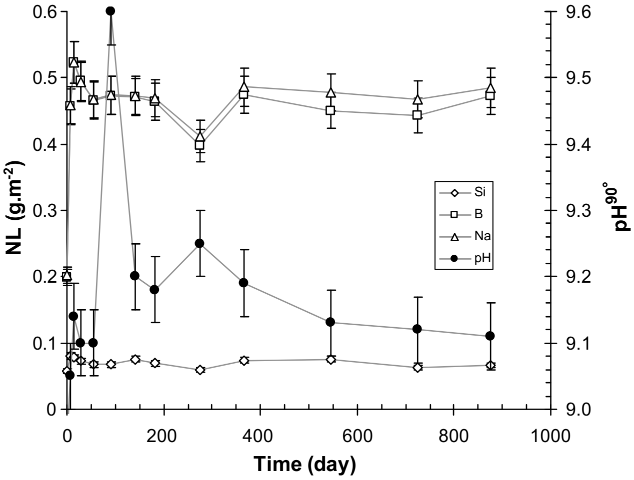

Fig. 1. Evolution versus time of pH and normalized mass losses for Si, B, Na for a previous experiment [6] at 90 °C and 173 cm^{-1}.

2.2. Description of the experiments

Two leaching experiments were carried out in PTFE (PolyTetraFluoroEthylene) reactors at a glass-surface-area-to-solution-volume (SA/V) ratio of 80 cm^{-1} in static mode at 90 ± 1 °C for durations of 1 and 86 days. One reactor was used for the 1 day experiment and another one for that of 86 days. The evolution of elements solution concentration versus time was followed up by solution samplings of about 1 mL in the reactors. The purpose was to obtain experimental data before and after the inhibition of alteration. The operating conditions were those used by Gin and Jegou [6], which resulted in the cessation of glass alteration for long time, as shown in Fig. 1. The glass surface area was obtained with the powder size fraction between 100 and 125 μm. The specific surface area of the glass powder measured by krypton adsorption using the BET method was 566 ± 28 cm^2 g^{-1} (the uncertainty on this value includes both the Kr adsorption measurement error and the uncertainty on the representativeness of the powder sample used for analysis). A 1×1 cm^2 optically polished glass monolith (roughness $\leqslant 1$ μm) was placed on the powder for ToF-SIMS (time of flight-secondary ion mass spectrometry) measurement of the elemental profiles in the gel. Like this, a side of the monolith is in contact with the glass powder and the other one with the solution, as indicated in Fig. 2. The developed surface area of the glass monolith was negligible compared with that of the powder. To avoid any abrasion of the gel formed during glass alteration, the solutions were not stirred. The 1-day leaching experiment was initiated 1 day before the end of the 86-day experiment. The ultrapure water supplied to the leaching reactors was initially at a temperature of 90 °C, and the pH values (±0.05 unit) were measured at 90 °C.

At the end of the 86-day leaching experiment, a 20 cm^3 leachate sample was taken and transferred to a PTFE reactor, together with 4 cm^3 of an 88 mg L^{-1} ^{29}Si solution (96.7% isotopic enrichment) at pH 9.2 at 20 °C. The ^{29}Si solution was obtained by alkaline fusion of a mixture $^{29}SiO_2$/KOH at 600 °C for 45 min. After fusion, the mixture was dissolved in pure water and the pH of the solution was adjusted to 9.2 with nitric acid. The glass monoliths leached for 1 and 86 days were then placed in the tracing solution. Tracing was carried out at room temperature. The natural abundance of ^{29}Si is 4.67%; the ^{29}Si isotopic enrichment of the tracing solution was thus 2.1 (final ^{29}Si/initial ^{29}Si mass ratio). In first approximation, the diffusion time t_d is given by the relation $t_d \sim e^2/D$, where e is the gel thickness and D the silicon diffusion coefficient in the gel pores. Assuming a value of 5×10^{-9} m^2 s^{-1} for D [12] and a gel thickness of 1 μm, this leads to a t_d value of 20 s. So, if porosity is open, a few seconds were sufficient for ^{29}Si to penetrate to the pristine glass/gel interface, but the contact time between the glass monoliths and ^{29}Si tracing solution was extended to 15 min to ensure the tracer reached the pristine glass. The contact time was sufficient because with the thickest gel (∼ 1 μm), ^{29}Si reached the pristine glass. The first point of gel analyzed by ToF-SIMS corre-

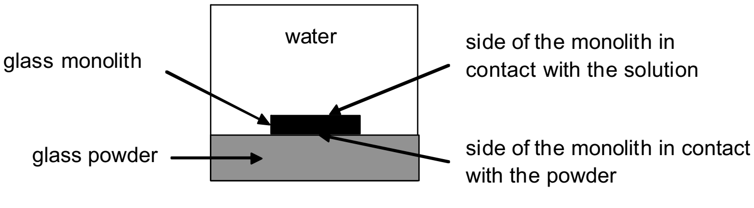

Fig. 2. Schema of glass monoliths leaching in presence of glass powder.

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