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Leach testing at 50 °C of α-doped SON68 glass alteration gels

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Abstract

Gels formed by altering α-doped (Np, Pu, Am) SON68 glass at 300 °C were leached during 1 year at 44 cm^{-1} and 50 °C under oxidizing conditions ($Eh_{/NHE} \approx +150$ mV) and under reducing conditions ($Eh_{/NHE} \approx -250$ mV). After 3 days of leaching the gel dissolution was highly incongruent. The gel dissolution rate calculated from the silicon concentrations was 4.4×10^{-5} g m^{-2} d^{-1}, except for the Am-doped gel, for which the rate was two times higher. During leaching, Np is weakly retained in the gel (35% under oxidizing conditions and 50% under reducing conditions) whereas Pu and Am are strongly retained (over 90%). The three lanthanides La, Ce, and Nd exhibit exactly the same leaching behavior, but different from that of actinides. Speciation and complexation calculations for neodymium showed that its solubility could be controlled by $Nd(OH)_3$ for periods beyond 3 months. Conversely, no simple chemical compound appears to control the solubility of the actinides.

1. Introduction

Radionuclides are retained in various degrees in the gels that form during SON68 glass alteration. In the case of the rare earth elements and actinides, retention in the gels can significantly diminish the glass source term. The radioelement containment stability in the gels must be assessed in order to take radionuclide retention into account in glass package performance calculations. Radionuclide retention depends on the conditions in which the gels are formed. The main objectives of this study were to assess the influence of the oxidation–reduction potential Eh of the solution on the release of the multivalent actinides Np and Pu, to determine the influence of α and βγ self-irradiation in the gel pores on the gel dissolution rate and to check if the long term actinides concentrations in solution were controlled by simple phases. The gels were obtained by complete alteration at 300 °C of SON68 glass specimens doped with NpO_2, PuO_2 and Am_2O_3. The three gels were then leached at 50 °C under oxidizing conditions to determine their stability under self-irradiation. The Np- and Pu-doped gels were also leached under reducing conditions to investigate actinide release versus the oxidation–reduction potential in solution.

2. Gel fabrication and characterization

Four gels were obtained by altering glass under static hydrothermal conditions in stainless steel reactors with gold seals. An inactive SON68 glass coupon and three SON68 glass coupons doped with α-emitters (^{237}Np,

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^{239}Pu and ^{241}Am) were altered at 300 °C under 100 bars. Three glass monoliths ($25 \times 25 \times 3$ mm^3) representing a surface area of 45 cm^2 were placed in each reactor in a solution volume of 40 cm^3 to obtain an SA/V ratio of 1.1 cm^{-1}. The glass monoliths were completely altered within 72 days. After alteration, the glass monoliths had doubled in volume and were extensively cracked. The gels were oven-dried for 1 day at 90 °C, then manually ground with a mortar and a pestle. The specific surface area of an inactive gel sample measured by krypton adsorption using the BET method was 4.4 m^2 g^{-1}. The specific surface areas of the α-doped gels were not measured; the value obtained for the inactive gel was used, as all four gels were ground in the same way.

SEM observation of the inactive gel revealed secondary phases consisting of needles and sheets mixed with the gel itself, as shown in Fig. 1. Afterwards, the word gel will refer to the amorphous material including the crystallized phases. The X-ray diffraction pattern (Fig. 2) shows that the Np-doped gel was mainly amorphous (bump between 10° and 40°) and contained crystallized phases. The X-ray diffraction patterns of inactive, Np-, Pu-, Am-doped gels were identical. The following phases were identified:

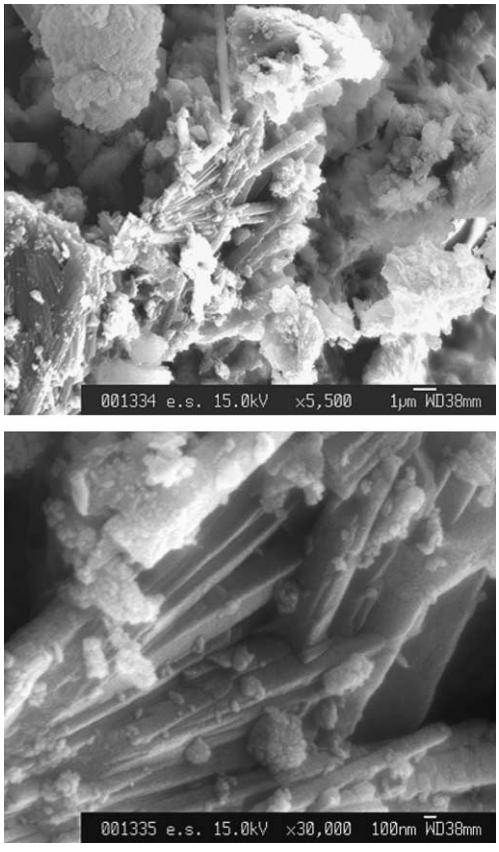

Fig. 1. SEM image of inactive gel.

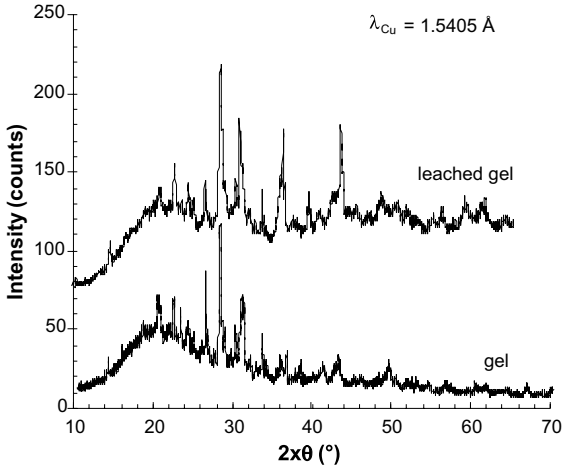

Fig. 2. X-ray diffraction pattern of Np-doped gel before and after leaching.

- analcime $Na_{14.80}Al_{14.24}Si_{33.76}O_{96}(H_2O)_{16}$,
- intermediate albite $NaAlSi_3O_8$,
- low calcian albite $Na_{0.84}Ca_{0.16}Al_{1.16}Si_{2.84}O_8$,
- labradorite $Ca_{0.64}Na_{0.35}Al_{1.63}Si_{2.37}O_8$,
- $Ca_{8.25}Na_{1.5}Al_6O_{18}$,
- acmite $NaFeSi_2O_6$.

The crystallized phases could not be quantified by XRD analysis for lack of calibration but SEM observations showed that these crystallized phases were very few (in quantity) compared to amorphous material. The diffraction pattern of the leached Np-doped gel (Fig. 2) includes additional peaks at 36.42°, 39.67° and 43.69° ($2 \times \theta$) not found in unleached gel, indicating the presence of rare earth phosphates after leaching.

The chemical composition of the inactive gel (amorphous material and crystallized phases) was very near that of SON68 glass (Table 1), with only a lower boron and sodium content in the gel than in the glass and the presence of an appreciable quantity of water (≈6 mol%) in the gel. The measured silicon retention in the gel was 81%. The chemical compositions of the α-doped gels could not be analyzed, but were assumed to have the same composition as the inactive gel, considering that all four gels were obtained under the same conditions with the exception of the actinide content. The actinide content of the α-doped gels was calculated from the material balance as the difference between the quantity of actinide in the glass and the quantity found in solution. The actinide weight percentages in the gel samples are indicated in Table 2.

In the same time, another gel was obtained by complete alteration of inactive SON68 glass powder (granulometric size ranged from 3 to 25 μm) in pseudo-dynamic mode (renewal rate of 0.25 d^{-1}) at 30 cm^{-1} and 90 °C during about 1 year. The silicon