Influence of zeolite precipitation on borosilicate glass alteration under hyperalkaline conditions

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HIGHLIGHTS

- Mechanisms responsible for zeolite precipitation during glass alteration are proposed.
- Two types of glass alteration kinetics are obtained depending on the S/V.
- S/V has a major influence on the time needed to form stable zeolite nuclei.
- S/V and pH are keys parameters controlling zeolite precipitation and glass dissolution kinetics.

ARTICLE INFO

ABSTRACT

This study enables a better understanding of how nucleation-growth of zeolites affects glass dissolution kinetics in hyperalkaline solutions characteristic of cement waters. A 20-oxide borosilicate glass, an inactive surrogate of a typical intermediate level waste glass, was altered in static mode at 50 °C in a hyperalkaline solution rich in Na^+, K^+ and Ca^{2+} and at an initial $pH_{50°C}$ of 12.6. Experiments were performed at four glass-surface-area-to-solution-volume (S/V) ratios to investigate various reaction progresses. Two types of glass alteration kinetics were obtained: *(i)* at low S/V, a sharp alteration resumption occurred after a rate drop regime, *(ii)* at high S/V, a high dissolution rate was maintained throughout the test duration with a slight progressive slow-down. In all the experiments, zeolites precipitated but the time taken to form stable zeolite nuclei varied dramatically depending on the S/V. Resulting changes in pH affected zeolite composition, morphology, solubility and growth rate. A change in a critical parameter such as S/V affected all the processes controlling glass dissolution.

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1. Introduction

In France, the high level and some of the long-lived intermediate-level nuclear wastes (ILW) are vitrified. According to the French 2006 Act related to nuclear waste management, these wastes are to be stored in a deep geological repository. Under such disposal conditions, ground water is considered to be the main cause of glass package degradation, and therefore will be responsible for the release and migration of radionuclides. It is thus of primary importance to elucidate the mechanisms controlling long term glass dissolution rates [1].

The leaching of borosilicate glass has been extensively studied and arises from several coupled reactions: hydration due to water

diffusion through the glass structure [2], exchanges between alkali ions and positively charged hydrogen species, also called *interdiffusion* [3,4], and hydrolysis of the covalent bonds forming the borosilicate network. When controlled solely by these types of reactions, the glass dissolves under the *initial rate* regime, which is characteristic of low reaction progress. At a high reaction progress, parts of the hydrolysed species recondense to form a low-porosity amorphous hydrated layer called a *gel layer*, which can be passivating and transport-limiting for aqueous species [5–8]. Both passivation by surface layers and the diminishing affinity of the hydrolysis reaction of the silicate network contribute to the drop of the glass dissolution kinetics. The corresponding kinetic regime is generally called the *rate drop* regime. The main components of the alteration layer network (mostly Si and Al) can be consumed by the precipitation of secondary crystalline phases [9,10]. Depending on the type of secondary phases that precipitate, two regimes can be observed: *(i)* a *residual rate* regime when a quasi-steady state is

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reached between the formation of phases (mainly clay-type minerals) and the destabilization of the passivating layer [11–14], or (ii) an *alteration resumption* regime due to massive precipitation of secondary phases, mainly zeolites and, to a lesser extent, calcium silicate hydrates (C-S-H), which destabilize the passivating layer [12,14–16].

In the disposal concept, intermediate-level vitrified waste packages could be disposed of in concrete containers. Over the long term, the environment will be buffered by different cement pore water compositions corresponding to the different stages of cement aging. The first stage corresponds to leaching of alkalis, leading to the most alkaline solution, since the $pH_{25°C}$ of the leachates of Ordinary Portland Cement varies between 14 and 13 [17]. The hyperalkaline stage could last from hundreds to tens of thousands of years depending on the amount of cement and the diffusivity and reactivity of the host rock. It is thought that in such chemical conditions, zeolite precipitation could destabilize the formation of the gel layer.

Natural zeolites are mainly formed by the hydrothermal alteration of volcanic rocks with a large glass fraction [18]. Zeolites also crystallize in post-depositional environments over periods ranging from thousands to millions of years in shallow marine basins. In the field of nuclear waste management, archaeological and natural glass analogues have been used to validate the mechanistic models developed from observations at the laboratory scale over a short period of time [19,20]. In basaltic glass samples older than one Ma, the presence of zeolites has been observed in alteration layers [21]. Another study revealed the presence of zeolites between the 3 Ma Icelandic glass grains [22]. Zeolites could also result from the short-term alteration of aluminosilicate minerals in contact with alkaline solutions. Depending on the geological repository design, engineered barriers of bentonite or the Callovo-Oxfordian host rock clay considered in the French disposal project may be in direct contact with concrete or cement, leading to major changes in the mineralogy, including the precipitation of zeolites [23–27].

Zeolites are known to be responsible for the alteration resumption of nuclear glasses [28], especially at $pH_{20°C} > 10.5$ at 90 °C [29]. It has been established that several parameters impact the alteration resumption regime, such as glass compositions [29–32], solution composition [33–35], temperature [34,36], pH [28,29,37] and S/V ratio [38,39].

To better understand the mechanisms responsible for zeolite precipitation and the subsequent alteration resumption, a set of four static experiments run at different high S/V ratios were carried out with a typical inactive ILW nuclear glass surrogate, called Complex Glass or CG thereafter, in a simplified synthetic leaching solution corresponding to the first stage of cement aging fairly close to the *young cement water* (YCWCa) used by Liu et al. [40]. Experiments were performed at 50 °C in order to accelerate the degradation process without dramatically changing the cement pore solution chemistry. Lothenbach et al. have shown that after 150 days, the composition of the pore solution is similar for most elements from 5 up to 50 °C [41]. In this study, the experiments were designed to investigate various reaction progresses, with a special focus on high reaction progress in order to consider the consequence of zeolite precipitation on glass alteration over long periods of time. A complementary experiment was performed on a Simplified Glass (SG) consisting of the seven main CG glass oxides to see whether or not the alteration resumption regime would be sensitive to the presence of minor elements.

Note that the terminology *alteration resumption* (also called Stage III) has historically been adopted in the literature to describe a phenomenon corresponding to a sudden increase in the glass dissolution rate, occurring after the rate has significantly dropped, and indicating that a passivating layer has formed on the glass surface before being destabilized by secondary phase precipitation. In this study, it was observed that zeolites can precipitate in the very first moments of alteration, so that no initial rate or rate drop regimes were observed. Therefore this restrictive term is expanded here, and we refer to the *alteration resumption* regime when zeolites precipitate and control glass dissolution. We also refer to (i) the *plateau stage*, the period during which the dissolution rate is nearly constant before the alteration resumption, and (ii) the *gel layer*, i.e. the glass alteration layer.

2. Materials & methods

2.1. Glasses

The compositions of the two glasses (CG and SG) are given in Table 1. Analyses were performed by X-ray fluorescence (XRF) for all the elements excepted for B and Li which were analysed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and atomic absorption spectroscopy (AAS) respectively. The compositions were within the stated specifications under 1% of the nominal compositions. The glasses were melted for 3 h at 1250 °C in a platinum crucible. A part of the melted glass was poured into graphite molds to form glass bars, and the other part was quenched on a metallic support. The glass bars were annealed at 530 °C for 1 h. Glass homogeneity was checked by SEM and TEM characterization, and no non-homogeneity was detected at the micrometer and nanometer scales, respectively. The glass samples were ground and sieved to recover different particle size fractions, and the resulting powder was cleaned ultrasonically in acetone followed by absolute ethanol. It was dried and stored in a desiccator. Specific surface areas were determined by the BET method (Kr adsorption) (Table 2). A recent study by Fournier et al. [42] showed that the reactive surface area of a glass powder measured by the BET method (S_{BET}) is overestimated compared to a monolith. The authors determined a 1.9 corrective factor (due to the grain shape and surface irregularities) which the S_{BET} must be divided by in order to be compared with the geometric surface area of a polished monolith. The determination of the dissolution rates was based on this reactive surface area, given in Table 2.

Monolithic test coupons measuring 25 mm × 25 mm × 4 mm were prepared by cutting the annealed glass bars. Each face was polished with SiC papers up to grade 1000 and with diamond pastes (9, 3, and 1 μm) to obtain an optical polishing. The samples were then cleaned in the same way as the powder specimens.

2.2. Leaching solution

The leaching solution used was representative of cement pore water at the first stage of Ordinary Portland Cement degradation. Its composition was $6.55 \cdot 10^{-2}$ mol L^{-1} of Na^+, $1.61 \cdot 10^{-1}$ mol L^{-1} of K^+ and $1.2 \cdot 10^{-3}$ mol L^{-1} of Ca^{2+} for a $pH_{50°C}$ of 12.6 ± 0.1. The

Table 1
Molar compositions of the CG and SG glasses (mol.%).

Oxide	CG	SG	Oxide	CG	SG
SiO_2	55.0	56.7	P_2O_5	0.2	–
B_2O_3	13.6	14.0	BaO	0.2	–
Na_2O	13.3	13.7	Ce_2O_3	0.2	–
Al_2O_3	5.6	5.8	MnO_2	0.1	–
Li_2O	4.8	4.9	SO_3	0.1	–
CaO	3.6	3.7	Nd_2O_3	0.08	–
Fe_2O_3	1.2	–	La_2O_3	0.06	–
ZrO_2	1.1	1.1	CoO	0.03	–
MoO_3	0.3	–	Cr_2O_3	0.03	–
NiO	0.3	–	RuO_2	0.01	–