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Resumption of alteration at high temperature and pH: rates measurements and comparison with initial rates

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Abstract

Resumption of alteration – corresponding to a sharp increase of glass aqueous corrosion rate – is observed under specific experimental conditions of high pH and temperature. This phenomenon may occur with long duration time, making very difficult to foresee its appearance time and rate. In this study, leach tests performed with the International Simple Glass (ISG) at high buffered pH and 90°C show that the lower is the pH, the later is the resumption of alteration and the lower is the dissolution rate. Under the experimental conditions of this study, the resumption of alteration rate is an order of magnitude lower than the initial dissolution rate and two orders of magnitude higher than the rate of the "plateau stage" preceding the sharp increase of the corrosion rate.

1. Introduction

It is now well known that borosilicate glasses alteration by water follows several stages corresponding to different rate limiting steps (Ojovan and Lee, 2011, Gin et al., 2013): initial rate (or Stage 1 in the American literature) controlled by dissolution of the glass network followed by a rate drop as the solution approaches

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saturation with respect to the siliceous amorphous layer. After establishment of the residual rate (Stage 2) characterized by an incongruent dissolution of glass, a resumption of alteration (Stage 3) – i.e. a sudden acceleration of the glass corrosion rate – can occur (Vienna et al., 2013, Fournier et al., 2014). Resumptions of alteration have been observed in laboratory experiments under very specific conditions such as high alkali-content glasses, $pH_{measured\ at\ 20°C}$ > 10.7 for experiments performed at 90°C (Ribet et al., 2004) and/or $T \geq 90°C$. This phenomenon is associated with the precipitation of alumino-silicate minerals, mainly from the zeolite family (Bates and Steindler, 1982, Van Iseghem et al., 1985, Ebert et al., 1996, Ribet and Gin, 2004).

The point in time at which a resumption of alteration occurs is difficult to determine accurately (Fournier et al., 2014). Indeed, this phenomenon may happen after several years of leaching, a time after which samplings are usually spaced several tens or even hundreds of days. Moreover, the number of samples taken during the resumption of alteration is rarely sufficient to allow a precise measurement of the corrosion rate because this phenomenon quickly leads to high alteration levels.   In addition, accuracy of shrinking core model weakens when glass alteration becomes important.

In this study, static leach tests were performed on the International Simple Glass (ISG) to characterize precisely the effect of pH on resumption of alteration by a precise determination of the onset of this kinetic regime and the corresponding rate in order to make comparisons, especially with the initial rate which is the maximum dissolution rate under given pH and temperature conditions. To achieve this goal, a model system was built to accelerate zeolite precipitation kinetics: it is based in particular on the selection of experimental conditions very favorable to resumption of alteration.

2. Material and methods

All experiments were performed on the International Simple Glass, an alumino-borosilicate glass composed of six oxides (Table 1) chosen to be a reference glass for international studies on waste glass corrosion (Gin et al., 2013). After crushing and sieving, the different size fractions extracted were washed by an iterative decantation process in acetone and ethanol to remove fine particles. A measurement of specific surface area (SSA) was performed by the BET method to measure the glass-surface-area-to-solution-volume-ratio (S/V ratio) of leaching experiments. Tests described in section 2.1 were carried out with the 63-125 μm size fraction (SSA = 720 $cm^2 \cdot g^{-1}$). For tests described in section 2.2, the 125-250 μm size fraction (SSA = 465 $cm^2 \cdot g^{-1}$) was used.

Table 1. ISG composition expressed in oxide weight percent.

Oxide	SiO_2	B_2O_3	Na_2O	Al_2O_3	CaO	ZrO_2
wt%	56.2	17.3	12.2	6.1	5.0	3.3

2.1. Static leach tests dedicated to resumption of alteration characterization

Leaching experiments were performed in PFA reactors. Experimental conditions were chosen so as to favor occurrence of resumption of alteration: high S/V ratio of 40 cm^{-1} in order to quickly reach "saturation" conditions, relatively high temperature of 90°C, and highly alkaline environments obtained with sodium hydroxide solutions of different molarities: $2.5 \cdot 10^{-1}$, $7.9 \cdot 10^{-2}$ and $2.5 \cdot 10^{-2}$ M (Table 2). During all experiments, pH was buffered at its initial value by appropriate additions of 5 N sodium hydroxide solution. Note that to overcome difficulties linked to pH measurements at high temperature in alkaline medium, the comparison to a control reactor having the same initial NaOH concentration was systematically performed.

Table 2. Sodium hydroxide concentrations used in leach tests and calculated or measured pH at 90°C and 25°C.

Test	Initial NaOH concentration	Calculated pH (Chess code)	Measured pH
T1	$2.5 \cdot 10^{-1}$ M	11.7 (90°C) – 13.3 (25°C)	11.3 (90°C) – 13.1 (25°C)
T2	$7.9 \cdot 10^{-2}$ M	11.2 (90°C) – 12.8 (25°C)	11.0 (90°C) – 12.7 (25°C)
T3	$2.5 \cdot 10^{-2}$ M	10.8 (90°C) – 12.3 (25°C)	10.7 (90°C) – 12.3 (25°C)

Altered glass percentage (*AG*%), equivalent alteration thickness (*e*, nm) and normalized mass loss (*NL*, g·m^{-2}) are calculated by mass balance from boron solution analysis, taking into account *S/V* variations with time due to solution sampling and grains shrinking (Chave et al., 2011). Boron is chosen for rate calculations because it is known to be a tracer element (Jantzen et al., 2010), not being retained in secondary phases once released from glass.

During leach tests, regular samplings were taken, filtered (10 kDa) and analyzed by ICP-AES. The uncertainty was 3% for boron concentration measurement, allowing quite precise rate calculations. At the end of experiments, secondary phases were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM).

2.2. Initial dissolution rate measurements

Initial dissolution rates r_0 of ISG were measured by static leach tests with identical alteration conditions as experiments presented above (2.5·10^{-1}, 7.9·10^{-2} and 2.5·10^{-2} M NaOH solutions at 90°C) and *S/V* ratios close to 0.05 cm^{-1} in order to ensure a sufficient experimentation duration to achieve samplings. An additional test was performed at [NaOH] = 2.5·10^{-3} M, 90°C. ISG was dissolved with vigorous stirring and regular samplings were taken while [Si] < 1 mg·L^{-1} to avoid a retroactive effect of silica on alteration rate. Because Si is the major glass matrix constituent, silicon concentration in samples was measured by spectrometry. Initial dissolution rates were calculated by linear regression from silicon concentrations versus time data. At the end of experiments, congruence of dissolution (ensuring that glass dissolves in initial rate) was checked by ICP-AES; invariance of pH during measurements was also tested. All tests were performed at least twice with the same powder batch to check leaching reproducibility.

3. Results and discussion

3.1. Resumption of alteration characterization

Resumption of alteration occurs in the interval 1.0-2.2 days in test T1, 15-21 days in T2 and 29-40 days in T3 (Fig. 1). It follows a "plateau stage" during which corrosion rate is pseudo-constant and whose duration is pH-dependent. The onset and rate of the resumption of alteration is positively correlated with pH.
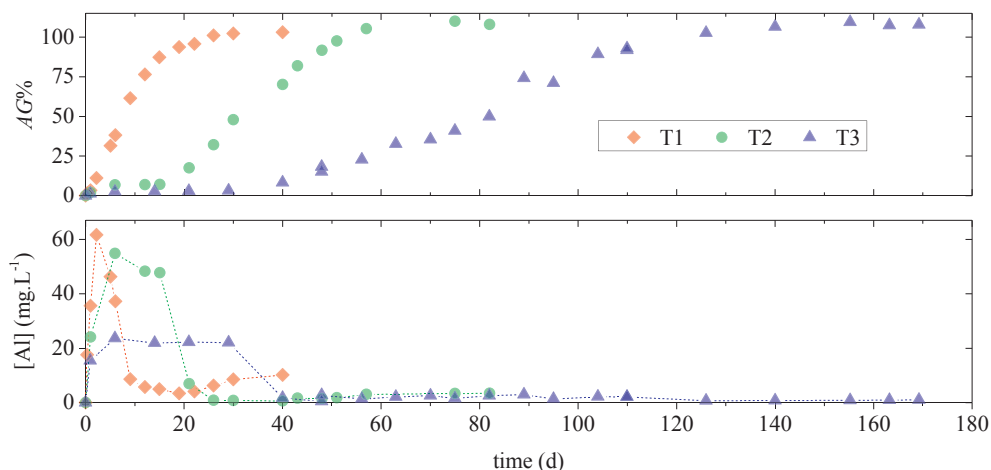

Fig. 1. Altered glass percentages and aluminum concentrations versus time for ISG at 90°C, 40 cm^{-1}.

Rate acceleration at the very beginning of resumption of alteration is perfectly correlated with the decrease in aluminum concentration in solution indicating the precipitation of aluminous rich phases. These were identified by XRD (Fig. 2) as mainly zeolite P2 with a small amount of analcime in tests T1 and T2, zeolite P1 in T3. The major

peaks of calcite are also visible in the test T1 XRD pattern. The morphology of the zeolite crystals is observable by SEM (Fig. 3) which also shows that the alteration layer surface is covered with phases that seems to be calcium silicate hydrates for tests T1 and T2, whose presence is confirmed by the broad reflection around 30° 2θ on XRD patterns. XRD and SEM results suggest that the assemblage of secondary phases varies with pH and/or sodium content of the medium.
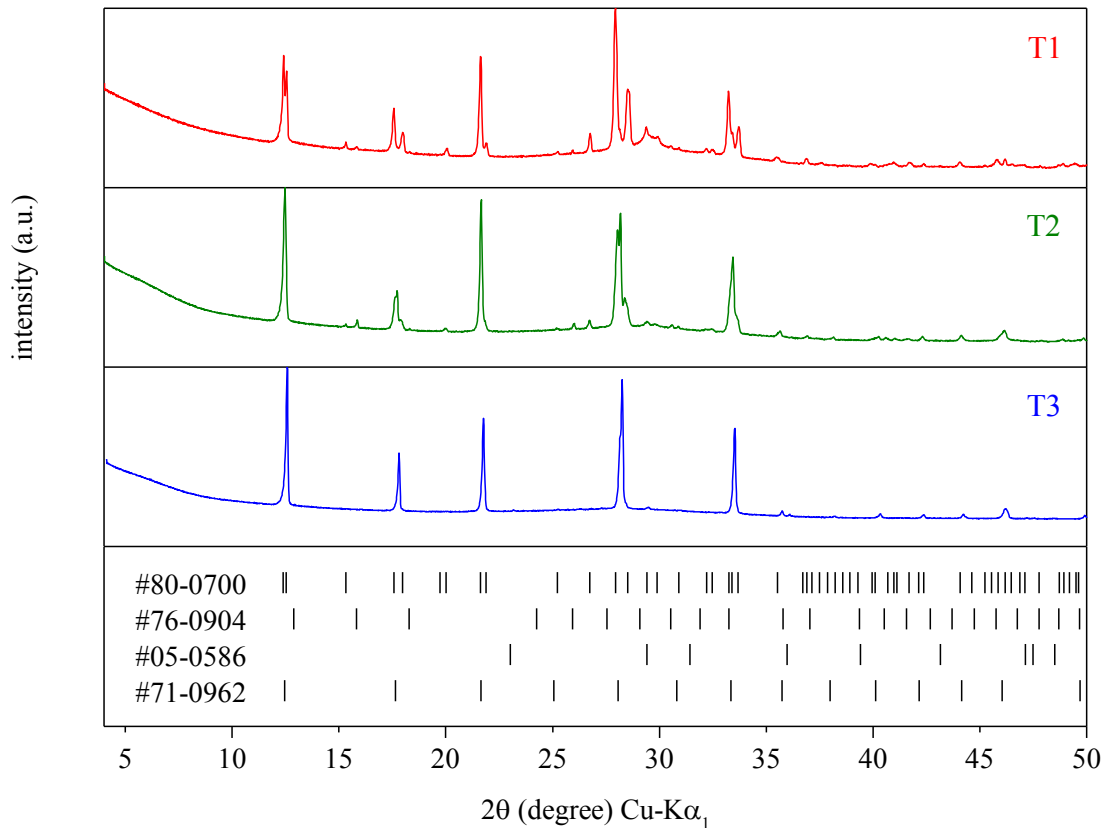

Fig. 2. XRD patterns for tests T1 (red), T2 (green) and T3 (blue). Identified crystalline phases are zeolite P2 (JCPDS #80-0700) and some analcime (JCPDS #76-0904) in tests T2 and T3; zeolite P1 (JCPDS #71-0962) and few calcite (JCPDS #05-0586) in test T1.
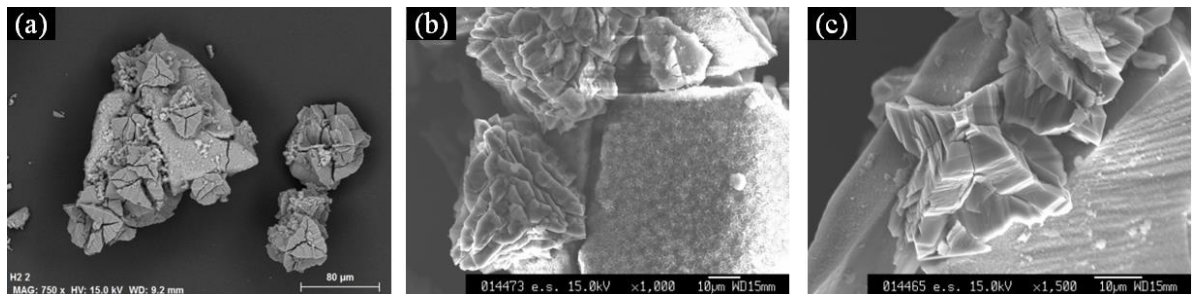

Fig. 3. Morphologies of zeolite precipitated onto glass grains in tests (a) T1, (b) T2 and (c) T3; zeolite precipitation is accompanied by that of amorphous calcium silicate hydrates in tests T2 and T3.

Corrosion rates measured during the plateau stage ($r_{plateau}$) and the resumption of alteration stage (r_{RA}) are summarized in Table 3. The resumption of alteration rate is extremely sensitive to changes in pH: r_{RA} is multiplied by 2.6 between pH 10.7 (T3) and 11.0 (T2) and by 1.7 between pH 11.0 and 11.3 (T3).

Table 3. Plateau stage duration ($\Delta t_{plateau}$) and rate ($r_{plateau}$); resumption of alteration occurrence time (interval t_{RA}) and rate (r_{RA}).

Test	$\Delta t_{plateau}$ (days)	$r_{plateau}$ (nm·d⁻¹)	$r_{plateau}$ (g·m⁻²·d⁻¹)	t_{RA} (days)	r_{RA} (nm·d⁻¹)	r_{RA} (g·m⁻²·d⁻¹)
T1	not observed	-	-	1.0 – 2.2	$5.7\cdot10^2$	1.43
T2	9 (day 6 to 15)	2.2	$5.6\cdot10^{-3}$	15 – 21	$3.4\cdot10^2$	0.85
T3	23 (day 6 to 29)	1.5	$3.9\cdot10^{-3}$	29 – 40	$1.3\cdot10^2$	0.33

On SON68 glass at 90°C and $S/V = 50$ cm⁻¹ (Gin and Mestre, 2001), a resumption of alteration occurs between 56 and 97 days for pH buffered at 11.5 and between 240 and 372 days for pH 11 and is not seen at pH 10.5 during the 600 first days of experimentation confirming that resumption of alteration occurs even later when pH is low. ISG is the six-oxide simple glass corresponding to the complex SON68 glass; in addition, close experimental conditions allow a comparison between the present study and that by Gin and Mestre (2001). Resumptions of alteration are observed earlier on those ISG experiments. Three hypotheses can be advanced to explain these differences:

- *Effect of glass composition.* On the one hand, phyllosilicates precipitation is not observed during ISG alteration, but is common in the case of SON68 glass. The formation of these minerals consumes aluminum changing solution chemistry and alteration layer/solution equilibriums. These thermodynamic changes may explain why resumption is largely deferred on SON68 glass. On the other hand, "minor" components of glass may play a role. Such an effect has already been observed in cementitious environments at 50°C, however the effect was the opposite: the plateau stage was shorter for the complex borosilicate CSD-B glass than for its seven-oxide simple glass surrogate (Depierre, 2012).
- *Effect of sodium.* pH is buffered by NaOH additions in this study and by KOH additions in the one of Gin and Mestre (2001) and sodium seems to slightly favor resumption of alteration compared to potassium (Ribet and Gin, 2004, Inagaki et al., 2002, Inagaki et al., 2006), possibly because of the important "structure-forming" function of Na⁺ during zeolite precipitation (Liu et al., 2014).
- *Effect of pH stability.* pH regulations were not made with the same regularity in the two studies: they are much more frequent in this study allowing good pH stability throughout the experiments.

3.2. Initial rate measurements

Linear regressions from measurements of silicon concentrations versus time (Fig. 4.a) indicate a low uncertainty associated with solution analysis (standard deviation on the slope < 1% or < 10% if (0,0) point is taken into account in the regression). In addition, repeatability between tests is satisfactory, giving a maximum uncertainty of 15%, consistent with uncertainty values generally encountered in r_0 measurements. Initial rate values for each pH are summarized in Table 4 and linked (Fig. 4.b) with those measured by Inagaki et al. (2013) and Gin et al. (2012). The pH dependence laws obtained from previous studies and from this work are consistent and compared in Table 5.

Table 4. r_0 measurements (g·m⁻²·j⁻¹) for various sodium hydroxide concentrations at 90°C.

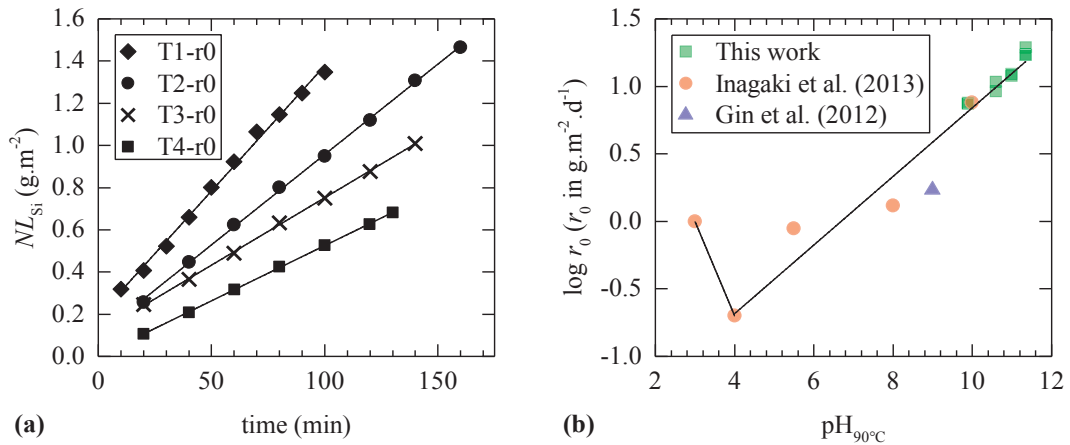| Test	NaOH concentration	pH$_{90°C}$	Replicate 1	Replicate 2	Replicate 3	Average
T1-r0	$2.5\cdot10^{-1}$ M	11.3	19.41	17.11	17.08	17.87
T2-r0	$7.9\cdot10^{-2}$ M	11.0	12.34	11.97	-	12.16
T3-r0	$2.5\cdot10^{-2}$ M	10.7	10.78	9.21	-	10.00
T4-r0	$2.5\cdot10^{-3}$ M	9.9	7.41	7.54	-	7.48

Fig. 4. (a) Silicon normalized mass loss versus time in r_0 measurements (for each test, only replicate 2 is reproduced as an example); (b) Compilation of initial rates for ISG as a function of pH at 90°C (Inagaki et al., 2013, Gin et al., 2012).

In Inagaki et al. (2013), geometric monoliths were used to calculate S/V ratios and alteration rates whereas in this study, the SSA (measured by the BET method) of powders is used. Icenhower and Steefel (2013) showed evidence that the geometric surface is a better value for the reactive glass surface area for powders than the SSA which could be twice as high. However, the measured r_0 value at pH 9.9 is very close to that measured by Microchannel Flow-Through Test Method by Inagaki et al. (2013) at pH 10. It is unfortunate, however, that the comparison between these two studies is limited to a single common value. Further work to determine this issue could be of great interest.

Table 5. Comparison of the estimated linear dependences between log r_0 and pH for ISG at 90°C.

log $r_0 = f$(pH)	pH range	Reference
$\log r_0 = -1.69 + 0.256 \cdot \text{pH}$	9.9 – 11.4	This work
$\log r_0 = -1.56 + 0.236 \cdot \text{pH}$	4 – 10	Inagaki et al. (2013)
$\log r_0 = -1.73 + 0.259 \cdot \text{pH}$	4 – 11.4	All points (This work, Inagaki et al., 2013, Gin et al., 2012)

3.3. Comparison between alteration rates

Corrosion rates measured during the initial, plateau and resumption of alteration stages are compared in Table 6. For the highest pH studied, r_{RA} is two orders of magnitude above $r_{plateau}$ and deviation from $r_{plateau}$ increases with pH. Data available in the literature – involving very different experimental conditions, but rarely buffered pH – indicate that resumption of alteration increases the corrosion rate by several orders of magnitude compared with residual rate, typically by a factor of 20 (Gin and Mestre, 2001) to 2000 (Ebert et al., 1996).

r_{RA} is an order of magnitude lower than r_0 and the r_0/r_{RA} ratio increases with decreasing pH. The initial rate, however, remains the highest corrosion rate, meaning that a phenomenon slower than congruent hydrolysis, limits r_{RA}. That could be explained by zeolite precipitation, either because their growth kinetics is less than the hydrolysis rate, or because their precipitation is quickly controlled by the low availability of aluminum in solution.

Table 6. Calculated r_0/r_{RA} and $r_{RA}/r_{plateau}$ ratios.

Test	r_0/r_{RA}	$r_{RA}/r_{plateau}$
T1	12	-
T2	14	255
T3	30	85

4. Conclusion

The construction of a model system based on the use of a relatively high temperature (90°C) and high pH in Na-rich environment to facilitate zeolite precipitation allowed accurate measurements of the time and rate of resumption of alteration for ISG. The onset and rate of the resumption of alteration is positively correlated with pH. This pH-dependence is extremely sensitive: a few tenths of a pH unit generates very significant differences. The beginning of the resumption of alteration is associated with a decrease in aluminum concentration in solution, agreeing well with the observed secondary phases of zeolites P and analcime. Initial dissolution rate measurements for high pH at 90°C are consistent with literature data. In a high buffered pH media, r_{RA} is an order of magnitude lower than r_0 and two orders of magnitude higher than the rate of the plateau stage preceding resumption of alteration. The r_0/r_{RA} and $r_{RA}/r_{plateau}$ ratios are not constant, however: with increasing pH, r_{RA} moves away from $r_{plateau}$ and approaches r_0. In any case, the initial rate remains the highest rate observed during aqueous corrosion of waste glass.

Experiments conducted at buffered pH values enable the examination of alteration resumption behavior largely independent of pH-dependent thermodynamic and kinetic mechanisms. This isolated effect will be useful for modeling purposes. Future work should check if pH is the single parameter influencing r_0/r_{RA} and to what extent the available surface for the precipitation of zeolites affects the behavior.

5. Acknowledgements

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