

Chemical durability of sodium disilicate glasses in aqueous salt solutions

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1 Introduction

According to the textbooks on chemical durability the reaction of silicate glasses with aqueous solutions can be described in terms of ion exchange (resulting in a square root time law of materials release) and network dissolution (leading to a linear time law). Newer corrosion models include interactions between leachant and surface. Hench [1] took the formation of barrier layers or surface passivation by solution into account. Conradt [2] correlated the thermodynamics of glass dissolution reactions and surface adsorption processes with dissolution kinetics. Jiricka, Helebrant et al. [3] described the redeposition of leachate components. The importance of salt components of the leachate was “rediscovered” during investigations of long-term corrosion of vitrified high-level radioactive waste (HLW) under repository conditions [e. g. 4].

Usually, these findings were verified for glasses with medium or high chemical durability. Only a few studies on highly soluble sodium silicate glasses were published. Own results [5] stress the influence of the adsorption of solution components at the glass surface on corrosion kinetics. In this study sodium disilicate glasses were corroded in different types of salt solutions in order to clarify the influence of the specific ions on the corrosion process.

2 Experimental

A detailed description of the preparation of the glass samples and of the corrosion tests is reported in [5]. The glasses have been molten at 1450 °C for 1 h in a

Pt80/Rh20 – crucible covered with a lid. The melts were then cooled, milled, remolten (30 min at 1450 °C), poured into blocks and annealed (470 °C).

The resulting glasses were analysed chemically and have a Na₂O mass content of 34.9 wt %. The glass blocks were cut with a low speed saw to platelets with a size of 1.5 x 1.2 x 0.15 cm³. The surface area of each sample was determined geometrically. Three samples for each set of corrosion conditions were investigated. They were suspended with a nylon fibre in closed polypropylene beakers (one sample in each) containing 50 ml of the leachant. The samples were placed in an oven for up to 181 d. After 1, 2, 3, 4, 7, 14, 28, 56, 90, and 181 d the samples were weighed. The experiments ended when the samples had been dissolved totally or when excessive crystallisation was observed.

The leachants applied here and their initial pH values are listed in Table 1. Distilled water and p.a. grade chemicals were used for their preparation. The mass loss of each sample was related to the respective surface area to yield a normalized mass loss (e. g. in g/cm²). The mean values obtained for a set of samples were evaluated. Where appropriate, a combined time law $q = m \cdot t + n \cdot \sqrt{t}$ was applied. In some cases the evaluation period was restricted to a certain period to improve the interpretation of the results. If no significant contribution of a square root time law was found, a simple linear time law was applied or vice versa. The coefficients of the time laws obtained by this evaluation are listed in Table 1, too.

The corroded glasses were investigated by X-ray diffraction (Seifert XRD 3000 PTS), optical microscopy (Jenapol u, Carl Zeiss Jena), and scanning electron microscopy combined with energy dispersive X-ray analysis (Jeol JSM 6300; samples were coated with carbon). Selected leachates were analysed chemically by colorimetric analysis of the formation of the molybdenum blue complex with Si⁴⁺, and pH – measurement.

3 Results

3.1 Corrosion in alkaline chloride salt solutions

The normalised mass losses of the sodium disilicate glasses in alkaline chloride solutions for a time period up to 30 d are shown in Fig. 1. The samples were totally dissolved in 1 M KCl and 1 M NaCl solutions within 7 d, whereas the samples survived the whole test period when corroded in 1 M LiCl. The time dependencies

can be described by linear time laws. The coefficients m of the time laws decrease in the order $K > Na \gg Li$. Fig. 2 shows compares the corrosion behaviour of sodium disilicate glasses in 1 M LiCl and in 1 M LiOH (latter results published in [5]). Although the pH of 1 M LiOH is higher than the pH of 1M LiCl the corrosion proceeds much slower. In both cases a predominant square root time law is observed, but the coefficients of the time law differ by a factor of 35. The LiCl value at 181 d decreases due to crystallisation detected by X-ray diffraction.

Table 1. Composition and pH (initial) of the aqueous leachants; coefficients m (linear term) and n (square root term) of time laws; pH after corrosion test (final); Δt : evaluated corrosion time interval; **: test runs not yet finished

Composition	pH (initial)	pH (final)	m in $g/(cm^2 \cdot d)$	n in $g/(cm^2 \cdot d^{0.5})$	Δt in d
1 M NaOH	12.4		$3.0 \cdot 10^{-5} \pm 5 \cdot 10^{-6}$	$3.3 \cdot 10^{-4} \pm 5 \cdot 10^{-5}$	0 – 181
1 M NaCl	6.4	11.4	$2.2 \cdot 10^{-2} \pm 1 \cdot 10^{-3}$	-	0 - 4
1 M NaNO ₃	7.2	11.5	$2.4 \cdot 10^{-2} \pm 1 \cdot 10^{-3}$	-	0 - 4
0.5 M Na ₂ SO ₄	6.1	11.7	$2.5 \cdot 10^{-2} \pm 1 \cdot 10^{-3}$	-	0 - 4
0.5 M Na ₂ CO ₃	11.5	11.8	$2.5 \cdot 10^{-2} \pm 5 \cdot 10^{-3}$	-	0 - 3
1 M LiCl	6.9	10.8	$4.0 \cdot 10^{-4} \pm 1 \cdot 10^{-4}$	$7.0 \cdot 10^{-3} \pm 1 \cdot 10^{-3}$	0 – 90
1 M LiOH	12.7		$8.5 \cdot 10^{-6} \pm 3 \cdot 10^{-7}$	$2.0 \cdot 10^{-4} \pm 2 \cdot 10^{-5}$	0- 181
1 M KCl	6.3	11.9	$2.8 \cdot 10^{-2} \pm 2 \cdot 10^{-3}$	-	0 - 3
1 M MgCl ₂	8.0	8.8	$-3.9 \cdot 10^{-3} \pm 4 \cdot 10^{-4}$	-	0 - 4
1 M CaCl ₂	9.5	11.4	$-3.7 \cdot 10^{-3} \pm 1 \cdot 10^{-4}$	-	0 - 4
1 M SrCl ₂	6.9	12.0	$-6.2 \cdot 10^{-3} \pm 1 \cdot 10^{-4}$	-	0 - 4
1 M ZnCl ₂	3.6	**	$-8.5 \cdot 10^{-3} \pm 5 \cdot 10^{-4}$	-	0 - 4
1 M FeCl ₂	0.9	**	$-2.6 \cdot 10^{-3} \pm 2 \cdot 10^{-4}$	-	2 - 14
1 M FeCl ₃	0.1	**	$-4.7 \cdot 10^{-3} \pm 2 \cdot 10^{-6}$	-	0 - 14

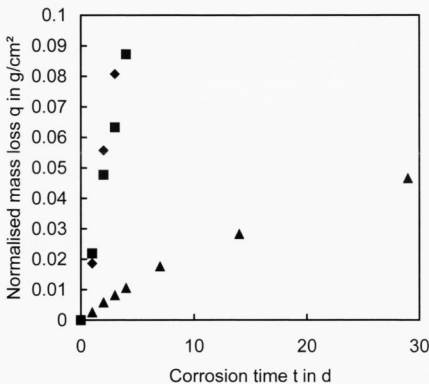


Fig. 1. Normalised mass loss (q) of sodium disilicate glasses in 1 M KCl (\blacklozenge), 1 M NaCl (\blacksquare), and 1 M LiCl (\blacktriangle) solutions as a function of corrosion time t ; corrosion temperature 30 °C

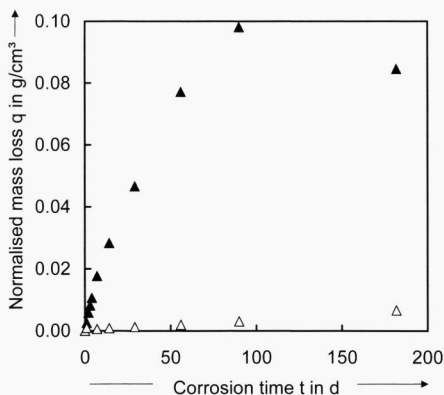


Fig. 2. Normalised mass loss (q) of sodium disilicate glasses in 1 M LiCl (\blacktriangle) and 1 M LiOH (\triangle) solutions as a function of corrosion time t ; corrosion temperature 30 °C

3.2 Corrosion in sodium salt solutions with various anions

The results of corrosion in sodium salts with various anions are shown in Fig. 3. The initial sodium concentrations of the leachates are identical. In all cases, the glass samples were totally dissolved within 7 d. The coefficients m of the linear time law (Table 1) of the corrosion in 1 M NaCl, 1 M NaNO₃, 0.5 M Na₂SO₄, and 0.5 M Na₂CO₃ are also nearly identical. The choice of the anion has little influence on corrosion kinetics, although the initial pH varies between 6.1 and 11.5.

3.3 Corrosion in chloride salt solutions of di- or trivalent cations

The samples corroded in chloride salt solutions of di- or trivalent gain weight during corrosion, which can be attributed to crystallisation. Corrosion in 1 M MgCl₂ and MgCl₂ was stopped after 21 d, corrosion in CaCl₂ after 56 d, corrosion in the other solutions after 90 d. The weight gain continued in all cases up to the end of the observation time with the exception of corrosion in 1 M FeCl₃. In this case a short period of weight loss (up to 2 d) is followed by a period of weight gain (2 to 14 d), which is then followed again by a continuous weight loss.

Optical microscopy showed that crystallisation occurred predominantly at the outside of the sample. In one case (corrosion in SrCl₂) a thoroughgoing crystallisation was observed. Scanning electron microscopy of samples corroded in MgCl₂ (Fig. 4), CaCl₂, and SrCl₂ showed that the core of the sample is altered glass with a gel structure. EDX analysis demonstrated the partial sodium depletion of the

core. According to chemical analysis the leachates contained only small (64 ppm; MgCl_2) or not detectable (CaCl_2 , SrCl_2) SiO_2 concentrations.

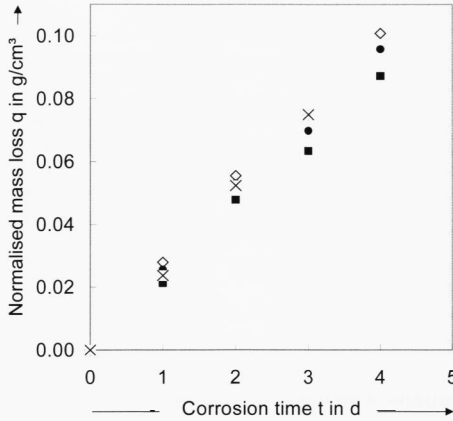


Fig. 3. Normalised mass loss (q) of sodium disilicate glasses in 1 M NaCl (■), 0.5 M Na_2SO_4 (◇), 1 M NaNO_3 (●), and 0.5 M Na_2CO_3 (x) as a function of corrosion time t ; corrosion temperature 30 °C

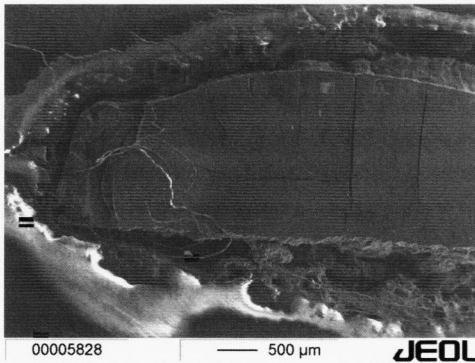


Fig. 4. Cross section of a sample corroded in 1 M MgCl_2 in the scanning electron microscope; corrosion time 21 d; corrosion temperature 30 °C; scale bar is given in the picture

4 Discussion

The corrosion of sodium disilicate glasses in salt solutions is strongly influenced by the cations. Samples corroded in chloride solutions with di- or trivalent cations or with Li^+ survive a longer time without disintegrating. The analysis of the corroded samples demonstrates the transformation of the original glass into a gel and crystallisation on or in the gel. Cations obviously have a stabilising effect on the gel. The strength of the stabilising effect – which can be quantified at the moment only

for monovalent cations - corresponds probably to the specific adsorption of metal cations on the silica surface discussed by Iler [6]. The crystallisation observed in the same cases (chloride solutions with di- or trivalent cations or with Li) is discussed by Jiricka et al. [3] as redeposition. Corrosion in salt solutions seems to proceed via ion exchange, formation of a gel, partial stabilisation of the gel via cation adsorption, crystallisation of low solubility compounds and disintegration of the gel. The choice of the anion has no great influence on corrosion kinetics, as long as hydroxides are not involved. The slow corrosion kinetics of sodium disilicate glasses in 1 M LiOH and 1 M NaOH (tests with 1 M NaOH reported in [5] were repeated for this study) has to be discussed, too. An explanation may be the assumption that hydroxide solutions immediately dissolve gel layers formed by ion exchange. The alkalis are then directly adsorbed at the original glass surface and may decelerate the ion exchange process.

5 Summary

Cations and gel layers have a major influence on the corrosion of sodium disilicate glasses. An explanation is tried on the basis of surface adsorption of cations at the gel layer or at the original glass surface.

6 Acknowledgements

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7 Literature

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