

## Chemical durability of sodium disilicate glasses in different corrosion media at neutral to basic pH values

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The chemical corrosion of sodium disilicate glasses in neutral to basic media was investigated. H<sub>2</sub>O, 1 mol/l NaOH, 1 mol/l LiOH, and a dilution series of sodium silicate solutions with a molar SiO<sub>2</sub>:Na<sub>2</sub>O ratio of 2.18 were used as corrosion media in static corrosion tests at temperatures of 30 °C and corrosion times up to 180 d. The corrosion process was characterized gravimetrically and – in some cases – by chemical analysis. Additionally, the temperature dependence of the corrosion in H<sub>2</sub>O at temperatures up to 70 °C was investigated. The nature of the corrosion process depends on the character of the corrosion media: The corrosion in 1 mol/l NaOH and 1 mol/l LiOH follows predominantly a square root time law, whereas corrosion in H<sub>2</sub>O or in sodium silicate solutions can be described by a linear time law. An additional result is that the corrosion rates increase in all cases with pH: in the case described here corrosion in H<sub>2</sub>O and in alkaline silicate solutions proceeds faster than corrosion in sodium or lithium hydroxide solutions with higher pH values. The dilution series of sodium silicate solutions was used to check the dependence of the corrosion process on the concentration of glass dissolution products in the leachate. The results indicate the importance of surface adsorption processes.

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### 1. Introduction

Sodium silicate glasses are – due to their simple chemical composition – subject of many scientific investigations. They contain one network former, silica, and one network modifier, sodium oxide. Sodium silicate glasses are of technological importance for the production of sodium silicate solutions. The latter technology requires fast and total dissolution of glass pieces to highly concentrated solutions in short times, a technology for which low chemical durability is the basis. The same property prohibits conventional glass applications of sodium silicate glasses. Two types of sodium silicate glasses are produced in large quantities for the preparation of sodium silicate solutions. These glasses are characterized by molar SiO<sub>2</sub>:Na<sub>2</sub>O ratios of 3.3 and 2.0. In this study the disilicate composition was investigated which is supposed to have a lower chemical durability.

Many investigations concerning sodium silicate glasses are reported in the literature. Important data of physical and chemical properties were compiled by Mazurin [1].

The compositions of the pure sodium disilicate glasses correspond to the composition of crystalline phases, whereas the immiscibility dome does not extend to the disilicate composition [2]. Therefore, crystallization is regarded as a more severe threat to homogeneity than phase separation. Dietzel and Wickert [3] reported a maximum of the crystallization rate for the sodium disilicate composition. Recent investigations by Deubener [4 and 5] showed that maximal nucleation rates occur in the vicinity of glass transition.

The corrosion of alkali silicate glasses was investigated by several authors. According to the textbooks on chemical durability the reaction of alkali 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). This interpretation goes back to Charles [6], who investigated the static fatigue of glass under the influence of H<sub>2</sub>O.

El-Shamy et al. [7 and 8] investigated the corrosion of powdered alkali silicate glasses as a function of pH which was varied between 1 and 12.6. The different pH values were realized by buffer solutions. They evaluated their data with a combined linear and square root time law (alkali loss  $q = m \cdot t + n \cdot \sqrt{t}$ ,  $t$ : corrosion time). Although they included the lithium disilicate composition into their study, the corresponding sodium disilicate glass was not investigated, probably because of the high reaction rates. They confirmed a square root time law for the extraction of Na<sup>+</sup> from a sodium silicate glass with 15 mol% Na<sub>2</sub>O. Generally, they expected a constant change of the rate law from a pure square root time law at the beginning to a linear time law at the end. This corresponds to the model of Boksay et al. [9], who predicted a steady-state corrosion process as final stage, during which the progress of the alkali depletion zone into the glass by diffusion is as fast as the dissolution of the network on top of the glass. White et al. [10] investigated the short time corrosion (up to 15 min) of lithium and sodium disilicate glasses in water and some organic solvents at room temperature and verified the square root time law.

The technological process of dissolving alkaline silicate glasses found little attention in the literature. Some hints are given by Vail [11], who reported that dissolution of a

$\text{Na}_2\text{O}\cdot 3\cdot 3\text{SiO}_2$  glass is accelerated a bit after the start of the process, then stays constant for a longer period, and slows down by a factor of 10 at the end of the process. It is not clear whether the slowing down of the corrosion rate at the end of the process is due to the high concentration of the solution ( $\approx 25$  wt%  $\text{SiO}_2$ ) or to the decrease of surface area of the glass pieces.

The corrosion of mixed alkali trisilicate glasses ( $\text{R}_2\text{O}\cdot 3\text{SiO}_2$ ; R: Na, K) was investigated by Bunker et al. [12]. They investigated the short time corrosion of the glasses at constant pH via solution analysis. Additionally, proton and alkali depth profiles were analysed. They found the diffusion of  $\text{H}_3\text{O}^+$  ions to be rate determining in the square root time region. Deviations of the square root time law were attributed to structural changes in the ion-exchanged surface zone.

The important influence of the composition of the solution phase on corrosion was investigated in the course of corrosion studies on vitreous high-level waste forms. An overview was given by Lutze [13]. These so called high-level waste studies were focused on the corrosion of highly stable glasses. They allow the conclusion that each component of the leachate influences the corrosion process.

The literature review shows that especially the corrosion of highly soluble sodium disilicate glasses at basic pH values found little attention so far. Additionally, appreciable progress in understanding glass corrosion processes was achieved in the meantime. Therefore, the aim of the presented study was to

- investigate the dissolution behaviour of highly soluble sodium disilicate glasses at high pH values,
- describe the corrosion of simple glasses as a basis for the validation of corrosion models,
- analyse the interaction between leachant and glass by using leachants containing dissolved glass components, e. g. solutions of the system  $\text{Na}_2\text{O} - \text{SiO}_2 - \text{H}_2\text{O}$ , and
- introduce a second alkali component to the solution.

Therefore, the leachants were varied from pure water via sodium and lithium hydroxide solutions, which introduce the alkalis into the leachant, to sodium silicate solutions, which have nearly the same  $\text{SiO}_2\text{:Na}_2\text{O}$  ratio as the sodium silicate glasses corroded in this study.

In contrast to many previous studies the pH was not kept constant, which surely affects the corrosion in water but is an essential feature of industrial production of sodium silicate solutions.

## 2. Experimental

Sodium disilicate glasses were prepared by two different ways. Glass type I was prepared by melting 130 g batches of silica and soda at  $1450^\circ\text{C}$  for 1 h in a Pt80/Rh20-crucible covered with a lid. The melts were cooled by pouring on a cold brass plate. The solid glass was milled and remelted. To compensate the alkali volatilization, the alkali content of the batch was slightly higher than the stoichiometric composition. After the remelting (30 min at  $1450^\circ\text{C}$ ) the glasses were poured into a brass mold. In order to avoid mechanical stresses the blocks were tempered for 10 min in a muffle furnace at  $470^\circ\text{C}$ , approximately the glass transition temperature measured by thermal analysis, and then

Table 1. Batch composition and  $\text{Na}_2\text{O}$  content (by chemical analysis) of sodium disilicate glasses; glass type I: laboratory samples; glass type II: made by industry (PQ Europe, Dehnitz)

	glass type I	glass type II
	batch in g	
$\text{Na}_2\text{CO}_3$	60.7	as received
$\text{SiO}_2$	66.2	as received
	chemical analysis in wt%	
$\text{Na}_2\text{O}$ content:	34.9	34.0

Table 2. Composition and pH values of the leachants

composition of leachant	pH value
$\text{H}_2\text{O}$	6.9
1 mol/l NaOH	13.4
1 mol/l LiOH	12.7
sodium silicate solutions (molar ratio $\text{SiO}_2\text{:Na}_2\text{O} = 2.18$ ) with $\text{SiO}_2$ in wt%:	
1	11.9
2	12.2
5	12.2
10	12.4
15	12.5
26.3	12.7

slowly cooled to room temperature by switching off the muffle. Glass type II was prepared by remelting a powdered glass produced in an industrial furnace (PQ Europe, Dehnitz) under the same conditions (without remelting for a second time).

The resulting glasses were analysed chemically by dissolving in distilled  $\text{H}_2\text{O}$  and titration with 0.1 mol/l HCl. The batch and the chemical analysis of the glasses are reported in table 1. The cold glass blocks had a size of  $(2 \times 2 \times 5) \text{ cm}^3$ . The glass blocks were cut with a low speed saw with a size of  $(1.5 \times 1.2 \times 0.1) \text{ cm}^3$ . A waterfree sawing liquid (Isocut<sup>®</sup>, Buehler, Lake Bluff, IL (USA)) was applied. The platelets were first cleaned mechanically by wiping off the sawing liquid and secondly by an ethanol bath. With respect to the surface roughness, the applied surface treatment was comparable to grinding with a 600 grid SiC paper.

The following leachants were used:

- $\text{H}_2\text{O}$  (deionized),
- 1 mol/l NaOH (p.a., Merck, Darmstadt (Germany)),
- 1 mol/l LiOH (p.a., Merck, Darmstadt (Germany)), and
- a dilution series of sodium silicate solutions prepared from a commercial stock solution with a molar  $\text{SiO}_2\text{:Na}_2\text{O}$  ratio of 2.18 (technical quality, Woellner) by diluting with deionized water. The  $\text{SiO}_2$  content of the stock solution was 26.3 wt%. The diluted solutions contained 1, 2, 5, 10, and 15 wt%  $\text{SiO}_2$ , respectively.

The pH values of the leachants are listed in table 2.

The surface area of each sample was determined geometrically by measuring the dimensions with a calliper ( $\pm 0.02$  mm). The samples were suspended with a nylon fibre

Table 3. Experimental parameters (surface area and mass of samples, averaged values) and evaluation results of the static corrosion tests of glass type I in different leachants; corrosion temperature 30 °C; coefficients of combined, linear and exponential time laws (if applicable) and the evaluated time range is given

experimental data				
leachant:	H <sub>2</sub> O	NaOH (1 mol/l)	LiOH (1 mol/l)	Na <sub>2</sub> O·2SiO <sub>2</sub> (26.3 wt% SiO <sub>2</sub> )
surface area in cm <sup>2</sup> :	4.37	4.32	4.35	4.31
mass in mg:	611.5	581.3	602.22	565.88
number of samples:	2	3	3	3
<i>q</i> in mg/cm <sup>2</sup> at various corrosion times given in brackets				
	16.4 ± 0.2(1 d)	0.5 ± 0.1(1 d)	0.3 ± 0.0(1 d)	-3.7 ± 2.5(1 d)
	97.7 ± 0.2(7 d)	1.5 ± 0.4(7 d)	0.6 ± 0.0(7 d)	-2.0 ± 1.5(7 d)
	dissolved(14 d)	1.7 ± 0.1(14 d)	0.9 ± 0.0(14 d)	5.2 ± 0.8(14 d)
		2.5 ± 0.2(28 d)	1.3 ± 0.0(28 d)	11.9 ± 0.6(28 d)
		3.9 ± 0.1(56 d)	2.0 ± 0.1(56 d)	26.2 ± 1.9(56 d)
		5.4 ± 0.1(91 d)	3.1 ± 0.1(91 d)	38.9 ± 9.9(91 d)
		9.0 ± 0.1(180 d)	6.6 ± 0.2(180 d)	90.2 ± 2.3(180 d)
combined time law				
<i>m</i> in mg/(cm <sup>2</sup> ·d):	*	0.024 ± 0.003	0.009 ± 0.003	0.52 ± 0.07
<i>n</i> in mg/(cm <sup>2</sup> ·d <sup>0.5</sup> ):	*	0.33 ± 0.05	0.20 ± 0.02	n. s.
<i>a</i> in mg/cm <sup>2</sup> :	*	n. s.	n. s.	-3.6 ± 3.0
time range in d:	*	0 to 180	0 to 56	1 to 180
linear time law				
<i>m</i> in mg/(cm <sup>2</sup> ·d):	*	—	—	0.52 ± 0.02
<i>a</i> in mg/cm <sup>2</sup> :	*	—	—	-3.9 ± 1.2
time range in d:	*	—	—	1 to 180
exponential time law				
exponent <i>w</i>	—	0.65 ± 0.02	0.47 ± 0.04	1.10 ± 0.03
time range in d	=	14 to 180	1 to 56	14 to 180

\*: not evaluated (only 2 data points)

n. s.: not significant

in 50 ml of the leachant. The ratio of surface area to solution volume was 0.083 cm<sup>-1</sup>. Usually, three samples were corroded for each set of corrosion conditions. The numbers of individual samples are listed in tables 3 to 6. Leachant and sample were stored in closed polypropylene containers at 30 °C in an oven. The corrosion time was limited to 181 d. After 1, 3, 7, 14, 28, 56, 90, and 181 d the samples – if they had not been dissolved totally – were dipped in an ethanol bath, dried by a cold air stream and then weighed.

The mass loss of each sample was related to the respective surface area to yield a normalized mass loss (e. g. in mg/cm<sup>2</sup>). The mean values obtained for a set of samples were evaluated. In some cases the samples were dissolved or disintegrated after a certain time, which, of course, limited the corrosion times in these cases.

The glass plates were dissolved in H<sub>2</sub>O within 14 d. Therefore, additional corrosion tests with glass type I samples in H<sub>2</sub>O with shorter weighing periods (1 h, 2 h, 3 h, 5 h, 7 h, 1 d, 2 d, 5 d, and 7 d) were performed. As corrosion temperatures 30, 50, and 70 °C were applied.

In a further series of corrosion test, glass platelets were corroded in H<sub>2</sub>O for fixed times without weighing in between. In these cases the pH values (by glass electrode) and the sodium contents (by titration) of the leachates were analysed.

### 3. Results

The glasses were optically clear and showed no sign of crystallization. The gravimetric results of the corrosion tests on glass type I are listed in table 3, the respective results of corrosion tests on glass type II are listed in table 4. The gravimetric results of the short time tests on the corrosion of the sodium disilicate glass are listed in tables 5 and 6 (with chemical analysis data).

The data were evaluated with different time laws. Where appropriate, a combined time law

$$q = m \cdot t + n \cdot \sqrt{t}$$

was applied [7 and 8]. In some cases the evaluation period was restricted to a certain period to improve the interpretation of the results.

The mathematical evaluation was based on the least squares method. The optimal constants were obtained by applying the regression analysis subroutine of Excel<sup>TM</sup> (spread sheet calculation program). In the regression analysis an additional additive constant *a* was obtained. In most cases the standard deviation of this constant was too large to allow an interpretation. Exceptions are discussed later. If no significant contribution of a square-root times law was found, a simple linear time law was applied.

Table 4. Experimental parameters (surface area and mass of samples, averaged values) and evaluation results of the static corrosion tests of glass type II in different leachants; corrosion temperature 30 °C; 3 samples; coefficients of combined, linear and exponential time laws (if applicable) and the evaluated time range is given

experimental data								
leachant:	H <sub>2</sub> O	Na <sub>2</sub> O·2SiO <sub>2</sub> (1.0 wt% SiO <sub>2</sub> )	Na <sub>2</sub> O·2SiO <sub>2</sub> (2.0 wt% SiO <sub>2</sub> )	Na <sub>2</sub> O·2SiO <sub>2</sub> (5.0 wt% SiO <sub>2</sub> )	Na <sub>2</sub> O·2SiO <sub>2</sub> (10 wt% SiO <sub>2</sub> )	Na <sub>2</sub> O·2SiO <sub>2</sub> (15 wt% SiO <sub>2</sub> )	Na <sub>2</sub> O·2SiO <sub>2</sub> (26.3 wt% SiO <sub>2</sub> )	NaOH (1 mol/l)
surface area in cm <sup>2</sup> :	4.28	4.46	4.37	4.50	4.38	4.42	4.41	4.33
mass in mg:	547.4	579.1	572.9	570.6	570.7	563.6	575.0	557.3
<i>q</i> in mg/cm <sup>2</sup> at various corrosion times given in brackets								
	10.4 ± 0.1 (1 d)	7.5 ± 0.6 (1 d)	5.6 ± 0.7 (1 d)	2.4 ± 0.2 (1 d)	0.6 ± 0.1 (1 d)	-0.5 ± 1.1 (1 d)	-8.0 ± 2.5 (1 d)	0.1 ± 0.0 (1 d)
	77.0 ± 2.9 (7 d)	78.9(7 d) (1 sample)	54.9 ± 2.0 (7 d)	22.5 ± 2.2 (7 d)	6.6 ± 0.2 (7 d)	4.8 ± 0.5 (7 d)	-0.1 ± 0.2 (7 d)	0.7 ± 0.0 (7 d)
	118.0 (14 d)	dissolved (14 d)	dissolved (14 d)	56.0 ± 0.2 (14 d)	13.3 ± 0.9 (14 d)	9.1 ± 1.0 (14 d)	3.1 ± 0.7 (14 d)	1.0 ± 0.2 (14 d)
	(1 sample)			(2 samples)				
	-	-	-	-	31.0 ± 3.6 (28 d)	17.1 ± 1.4 (28 d)	9.4 ± 0.5 (28 d)	2.3 ± 0.3 (28 d)
	-	-	-	-	101.6** (56 d)	39.1 ± 3.5 (56 d)	18.5 ± 2.5 (56 d)	3.5 ± 0.2 (56 d)
	-	-	-	-	dissolved (91 d)	67.1 ± 4.6 (91 d)	38.8 ± 0.4 (91 d)	5.1 ± 0.3 (91 d)
	-	-	-	-	-	dissolved (180 d)	85.4 ± 2.3 (180 d)	8.4 ± 0.4 (180 d)
combined time law								
<i>m</i> in mg/(cm <sup>2</sup> ·d):	-	-	-	-	-	0.84 ± 0.07	0.52 ± 0.07	0.026 ± 0.004
<i>n</i> in mg/(cm <sup>2</sup> ·d <sup>0.5</sup> ):	-	-	-	-	-	-1.1 ± 0.8	n. s.	0.29 ± 0.05
<i>a</i> in mg/cm <sup>2</sup> :	-	-	-	-	-	n. s.	-5.6 ± 3.2	n. s.
time range in d:	-	-	-	-	-	1 to 91	1 to 180	1 to 180
linear time law								
<i>m</i> in mg/(cm <sup>2</sup> ·d):	11.0 ± 0.1	11.5 ± 0.5	8.0 ± 0.3	4.0 ± 0.3	0.96 ± 0.02	0.74 ± 0.02	0.50 ± 0.02	-
time range in d:	0 to 7	0 to 7	0 to 7	0 to 14	1 to 14	1 to 91	1 to 180	-

n. s.: not significant

\*\*: only one sample left

Table 5. Experimental parameters (surface area and mass of samples, averaged values) and evaluation results of the static corrosion tests of glass type I in H<sub>2</sub>O at different temperatures; corrosion temperature 30 °C; 3 samples; coefficient *m* of linear time law and the evaluated time range is given

experimental data			
temperature in °C:	30	50	70
surface area in cm <sup>2</sup> :	4.64	4.61	4.57
mass in mg:	721.2	740.7	687.5
<i>q</i> in mg/cm <sup>2</sup> at various corrosion times given in brackets			
	0.4 ± 0.1(1 h)	3.2 ± 1.5(1 h)	42.9 ± 2.3(1 h)
	0.9 ± 0.0(2 h)	8.8 ± 0.7(2 h)	82.0 ± 4.9(2 h)
	1.8 ± 0.5(3 h)	9.1 ± 1.0(3 h)	119.8 ± 4.7(3 h)
	3.1 ± 0.1(5 h)	34.7 ± 1.1(5 h)	dissolved (5 h)
	5.5 ± 0.1(7 h)	51.5 ± 1.4(7 h)	
	28.6 ± 0.5(1 d)	dissolved (1 d)	
	64.3 ± 1.1(2 d)		
	96.3 ± 18.0(5 d)		
	123.7 ± 14.6(7 d)		
linear time law			
<i>m</i> in mg/(cm <sup>2</sup> ·d):	19 ± 2	106 ± 17	960 ± 20
time range in d:	0 to 0.3	0 to 0.13	0 to 0.13
<i>m</i> in mg/(cm <sup>2</sup> ·d):	35 ± 2	205 ± 2	
time range in d:	0.3 to 2	0.13 to 0.3	

Additionally, the data were evaluated according to an exponential time law

$$q = v \cdot t^w$$

The logarithmic form of this equation

$$\lg q = w \cdot \lg t + \lg v$$

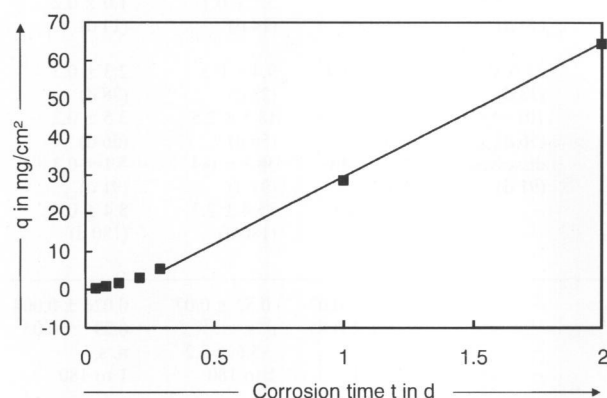
was fitted with a least squares method to yield optimal values of the exponent *w*. The results of the evaluations and the time periods they were obtained for are listed in tables 3 to 5.

### 3.1 Corrosion in H<sub>2</sub>O

At the corrosion conditions applied in this study, H<sub>2</sub>O is the most severe corrosion medium. The glasses were dissolved within 14 d. The results of short time tests are listed in table 5 (additional data for 1 and 2 d corrosion times, see table 3). The data obtained at 30 °C are represented in figure 1. Within the first hours an acceleration of the corrosion process was observed, which is either due to the initial pH increase or to starting effects. Depending on the time period, which was evaluated, coefficients of the linear time law of (19 ± 2) mg/(cm<sup>2</sup>·d) for 0 to 0.3 d or (35 ± 2) mg/(cm<sup>2</sup>·d) for 0.3 to 2 d were obtained. A curve calculated with the respective time law (0.3 to 2 d) is included in figure 1.

Table 6. Gravimetric and chemical results of static corrosion tests of sodium disilicate glasses in H<sub>2</sub>O; glass type I; corrosion temperature 30 °C

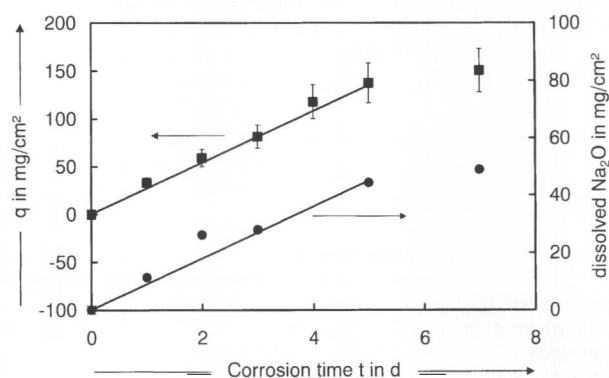
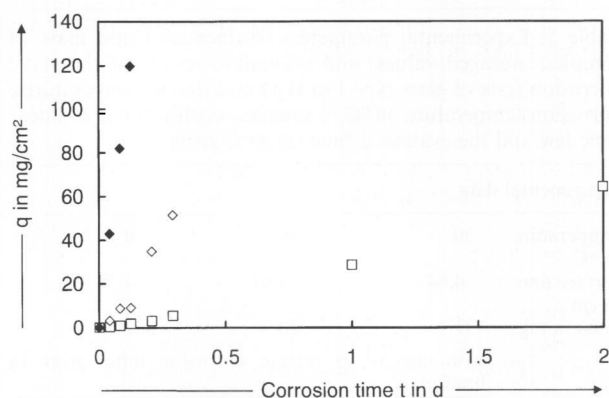
corrosion time in d:	1	2	3	4	5	7
number of samples:	4	1	4	1	1	3
sample mass in mg:	903.3	878.2	802.8	721.5	759.2	841.5
surface area in cm <sup>2</sup> :	5.00	4.97	4.78	4.73	4.87	4.73
mass loss in mg:	166.1	294.1	389.6	558.3	669.7	712.0
pH after corrosion:	10.6	—	11.5	—	—	11.8
Na <sub>2</sub> O content of leachate in mg:	57.2	130	134	209	216	232
SiO <sub>2</sub> :Na <sub>2</sub> O ratio of leachate:	1.9	1.3	1.9	1.7	2.2	2.1
weight fraction of dissolved glass in%:	19	33	49	77	88	88
weight fraction of dissolved Na <sub>2</sub> O in%:	18	44	47	85	84	83

Figure 1. Normalized mass loss  $q$  of sodium disilicate glasses in H<sub>2</sub>O as a function of corrosion time  $t$ ; Corrosion time  $t$  up to 2 d; corrosion temperature 30 °C; glass type I.

A second test series was performed for longer corrosion times without interruptions for balancing. The Na<sub>2</sub>O content of the leachates obtained in these tests were analysed chemically. The mass loss data as well as the Na<sub>2</sub>O analysis data are shown in figure 2 as a function of the corrosion time. The evaluation of the mass loss data yielded values of  $m = (27 \pm 5) \text{ mg}/(\text{cm}^2 \cdot \text{d})$  for the time period between 0 and 4 d. An evaluation of the Na<sub>2</sub>O analysis data yielded  $m = (9 \pm 5) \text{ mg Na}_2\text{O}/(\text{cm}^2 \cdot \text{d})$  for the same period, a value which fits to the chemical composition. Curves presenting these linear time laws are included in figure 2. They present the data rather well if the value of the Na<sub>2</sub>O analysis after 2 d is treated as an outlier. A significant contribution of a square root time law was not found. The discrepancy between  $m$  values calculated for the short time results (0.3 to 2 d at 30 °C, table 5:  $m = 35 \text{ mg}/(\text{cm}^2 \cdot \text{d})$ ) and the longer test (0 to 4 d at 30 °C, table 6:  $m = (27 \pm 5) \text{ mg}/(\text{cm}^2 \cdot \text{d})$ ) can be explained by the different time periods which have been evaluated.

The relative error of a single test results is estimated to be  $\pm 15\%$ , which is probably due to the temperature control which has an accuracy of approximately  $\pm 2 \text{ K}$ . By variation of the coefficients of the terms of the combined time law by  $\pm 15\%$  upper and lower boundaries for the experimental data were obtained.

The temperature dependence is demonstrated in figure 3, which shows the normalized mass losses of the sodium disilicate glass at 30, 50, and 70 °C, respectively. The tests ended with the total dissolution of the samples. Tests at 90 °C failed, since the glass samples were dissolved within 1 h. At 30 and 50 °C, respectively, two time periods with

Figure 2. Normalized mass loss  $q$  (■) and normalized Na<sub>2</sub>O release (●) of sodium disilicate glasses in H<sub>2</sub>O as a function of corrosion time  $t$ ; Corrosion time  $t$  up to 7 d; corrosion temperature 30 °C; glass type I.Figure 3. Normalized mass loss  $q$  of sodium disilicate glasses in H<sub>2</sub>O as a function of corrosion time  $t$ ; corrosion temperatures: 30 °C (□); 50 °C (◇); 70 °C (◆); glass type I.

different linear corrosion rates can be distinguished. Both rates are listed in table 5. The coefficients of the linear time law are presented in figure 4 as a function of the reciprocal temperature. The evaluation of the coefficients for the longer times yields an activation energy of 166 kJ/mol, which is twice as high as values reported by Scholze [14] or Doremus [15] for the corrosion of glasses with high chemical durability. The temperature dependence of the “short” time values at 30 and 50 °C is nearly identical with the “long” time dependence.

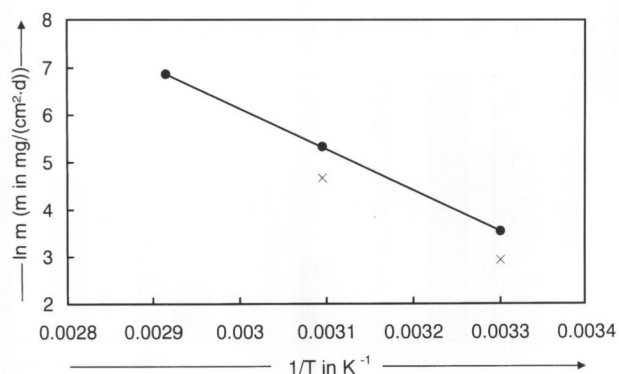


Figure 4. Logarithm of the coefficient  $m$  of the linear time law of the corrosion of sodium disilicate glasses in  $\text{H}_2\text{O}$  as a function of the reciprocal temperature (Arrhenius diagram); glass type I; (●): "long" time value; (x): "short" time value.

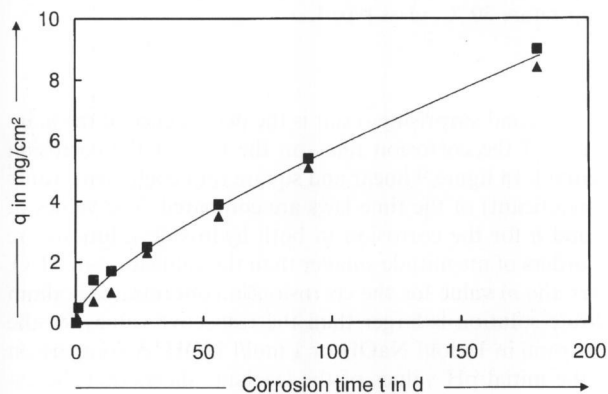


Figure 5. Normalized mass loss  $q$  of sodium disilicate glasses in 1 mol/l NaOH as a function of corrosion time  $t$ ; corrosion temperature 30 °C; comparison of glass types I (■) and II (▲); calculated line for glass type I.

### 3.2 Corrosion in 1 mol/l NaOH

The normalized mass loss of the sodium disilicate glasses corroded in 1 mol/l NaOH is shown in figure 5 as a function of the corrosion time. The corrosion in 1 mol/l NaOH proceeds much slower than the respective corrosion process in water. The coefficients of the square root time law  $n$  are by a factor of 10 larger than the coefficients  $m$  of the linear time law, suggesting that a square root time law predominates in the whole time range. On the other hand, the exponent  $n = 0.65$  of the exponential time law indicates that both time laws, the square root and the linear time law, contribute significantly to the mass loss of the glasses. No change of time law is observed during the applied time range, indicating that a steady state as proposed by Boksay [9] is reached. But it should be noted that at longer corrosion times the deviations between a pure linear time law and combined time law are rather small. The differences between the results for glass types I and II are in the range of experimental error, except within the first 14 d. Again glass type II shows the higher corrosion resistance.

### 3.3 Corrosion in 1 mol/l LiOH

The normalized mass loss of the sodium disilicate glasses corroded in 1 mol/l LiOH is shown in figure 6 as a function

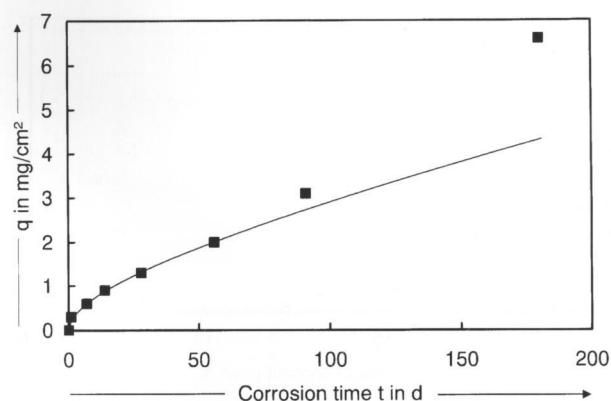


Figure 6. Normalized mass loss  $q$  of sodium disilicate glasses in 1 mol/l LiOH as a function of corrosion time  $t$ ; corrosion temperature 30 °C; glass type I (■); calculated line for glass type I.

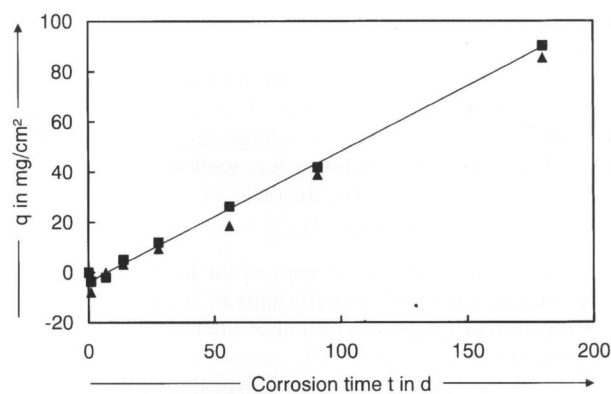


Figure 7. Normalized mass loss  $q$  of sodium disilicate glasses in a concentrated sodium silicate solution ( $\text{SiO}_2$  content 26.3 wt%) as a function of corrosion time  $t$ ; corrosion temperature 30 °C; comparison of glass types I (■) and II (▲); calculated line for glass type I.

of the corrosion time. In the first time period (up to 28 d) the corrosion in 1 mol/l LiOH proceeds even slower than the respective corrosion process in 1 mol/l NaOH. In that time range the coefficient of the square root time law  $n$  is by a factor of 20 larger than the coefficient  $m$  of the linear time law, suggesting that a square root time law predominates in that time range. This finding is backed by an exponent  $n = 0.47$  of the exponential time law. At longer corrosion times a change of the time law is observed, leading to an accelerated corrosion process. This acceleration might be due to the release of  $\text{Na}^+$  from the glass into the leachate.

### 3.4 Corrosion in sodium silicate solution

The normalized mass loss of the sodium disilicate glasses corroded in a concentrated sodium silicate solution is shown in figure 7. A fit to the combined time law yields insignificant values of  $n$ . The coefficient of the linear time law  $m = n$ . The coefficient of the linear time law  $m = n = 0.52$  has the same value for both glass types. A linear time is a good approximation of the measured values, as the graphical representation in figure 7 shows.

In order to evaluate the influence of leachant concentration a dilution series made from the original concentrated

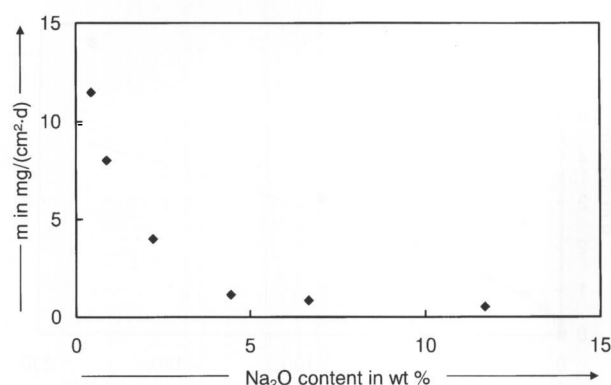


Figure 8. Coefficient  $m$  of the linear term of the combined time law (or of the simple linear time law) of the corrosion of sodium disilicate glasses in sodium silicate solutions as a function of the  $\text{Na}_2\text{O}$  content of the solution; corrosion temperature  $30^\circ\text{C}$ ; glass type I.

stock solution was used as corrosion media. In the case of the less concentrated solutions ( $\text{SiO}_2$  content  $< 5$  wt%) the numbers of data points were not large enough (the samples were totally dissolved within a few weeks) to fit the data with the combined time law. In these cases a simple linear time law was used (see table 4).

Figure 8 shows the coefficients of the linear terms of the combined time law or the coefficients of the linear time law as a function of the  $\text{Na}_2\text{O}$  content of the leachants. The value for pure water is omitted. The reason is that the sodium content of the leachate changes drastically within the first days. In the other cases the starting solutions contained already a certain amount of  $\text{Na}_2\text{O}$  and  $\text{SiO}_2$ . Therefore, the relative change of chemistry was not so severe. Nevertheless, a strong decrease of the corrosion rate with the  $\text{Na}_2\text{O}$  concentration is observed.

In those cases with slower corrosion rates, a mass gain of the samples was observed within the first 7 d of the corrosion test. This mass gain is also reflected in the negative values of the additive constants of the combined time law, which are significantly smaller than zero. This is probably due to the incorporation of water in the surface layer of the corroded glasses or to an adsorption of components of the leachants. A quick decision which process takes place by IR spectroscopy was not possible since IR transmission spectroscopy failed, whereas IR reflection spectroscopy yielded no differences.

#### 4. Discussion

One of the first results to be looked at is the influence of the corrosion medium on the corrosion mechanism: the corrosion kinetics of the sodium disilicate glass in  $\text{H}_2\text{O}$  and sodium silicate solutions can roughly be approximated by a linear time law, whereas the respective corrosion processes in 1 mol/l NaOH and 1 mol/l LiOH are closer to a square root time law, despite the higher pH values. It should be mentioned that the corrosion of the sodium disilicate glass in  $\text{H}_2\text{O}$  is – due to the rapid dissolution and to changing reaction kinetics – a very complex process.

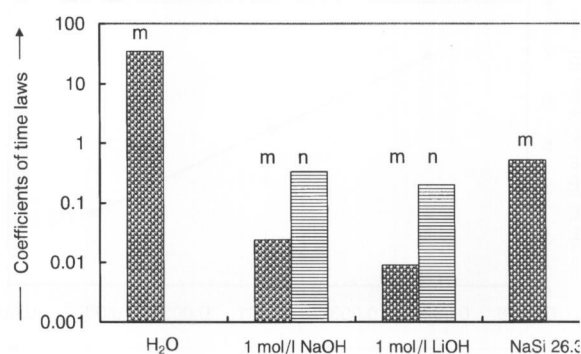


Figure 9. Coefficient  $m$  (pointed bar) of the linear term and  $n$  (lined bar) of the square root term of the combined time law of the corrosion of sodium disilicate glasses in different corrosion media; in the cases of corrosion in  $\text{H}_2\text{O}$  or NaSi 26.3 the coefficient  $m$  of the simple linear time law is presented; corrosion temperature  $30^\circ\text{C}$ ; glass type I.

A second surprising result is the dependence of the magnitude of the corrosion rates on the type of the corrosion medium. In figure 9 linear and square root coefficients (only if significant) of the time laws are compared. The values of  $m$  and  $n$  for the corrosion in both hydroxide solutions are by orders of magnitude smaller than the value for pure  $\text{H}_2\text{O}$ . Even the  $m$  value for the corrosion in concentrated sodium silicate solution is larger than the respective values for the corrosion in 1 mol/l NaOH or 1 mol/l LiOH. A comparison of the initial pH values of the leachant shows that the expected pH influence is not observed. It looks as if basic media slow down the corrosion process, whereas silicatic solutions accelerate corrosion.

A third argument for a separate discussion of the corrosion of sodium disilicate glasses is the high thermal activation energy. The rate controlling process has a higher temperature dependence as those processes reported for soda-lime-silica or borosilicate glasses.

As explained above the long term corrosion processes ( $>28$  d) can be fitted by a linear time law, too, if the time law coefficients  $m$  and  $n$  are of the same order of magnitude. Nevertheless, a steady state process as proposed by Boksay [9] cannot be confirmed for the corrosion in 1 mol/l NaOH or 1 mol/l LiOH on the basis of the presented data. Concerning the corrosion in water or sodium silicate solutions linear time laws were found, which are compatible with a steady state process.

The results of the dilution series, especially the dependence of the corrosion rate on the concentration of the leachants, can be used to check the validity of rate laws.

According to the Noyes-Nernst equation [16] saturation should lead to a proportionality between the corrosion rate  $r$  and  $\Delta c$ :

$$r \equiv \partial q / \partial t \sim \Delta c \equiv (c_{\text{sat}} - c_{\text{act}}),$$

with  $c_{\text{sat}}$  being a saturation concentration and  $c_{\text{act}}$  being the actual concentration of the dissolved species.

A correlation between the coefficients  $m$  and  $\Delta c$  was tried, but the result was not convincing.

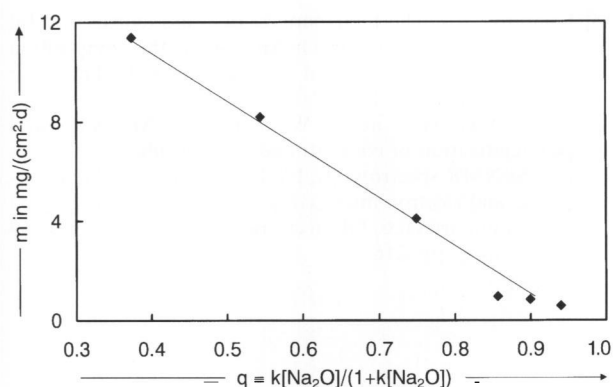


Figure 10. Coefficient  $m$  of the linear term of the combined time law (or of the simple linear time law) of the corrosion of sodium disilicate glasses in sodium silicate solutions as a function of  $\theta = k [c_{\text{Na}_2\text{O}}]/(1 + k[c_{\text{Na}_2\text{O}}])$  ( $[c_{\text{Na}_2\text{O}}]$ :  $\text{Na}_2\text{O}$  content of the leachate); corrosion temperature  $30^\circ\text{C}$ ; glass type I; an eye-line demonstrates the linear dependence.

Re-adsorption should lead to a dependence of  $r$  on  $\theta$ , the fraction of surface sites occupied by the adsorbed species, which is expressed according to Langmuir by the following relation:

$$r \sim \theta$$

with  $\theta = k \cdot c/(1 + k \cdot c)$  and  $c$  being the concentration of the adsorbed species in the leachate. This treatment is based on original work of Kuhn and Peters [17] and on the re-adsorption term of Conradt [18].

Figure 10 shows a plot of the coefficients  $m$  of the linear terms of the combined time law or the coefficients  $m$  of the linear time law as a function of  $\theta = k \cdot [\text{Na}_2\text{O}]/(1 + k \cdot [\text{Na}_2\text{O}])$ , with  $[\text{Na}_2\text{O}]$  being the  $\text{Na}_2\text{O}$  content of the leachate. A linear correlation between  $m$  and the re-adsorption term was found for a wide concentration range (from 0.5 to 8 wt%  $\text{Na}_2\text{O}$ ). In this comparison the value  $m = 14 \text{ mg}/(\text{cm}^2 \cdot \text{d})$  obtained for the corrosion in initially pure  $\text{H}_2\text{O}$  for the time period between 0 and 7 d was regarded.

It should be noted that concentrated sodium silicate solutions contain silicatic colloids, which are stabilized by multiple electrically charged layers containing  $\text{Na}^+$ , as was shown in [19]. Therefore, the  $\text{Na}^+$  ions are distributed between the silicatic colloid surfaces and the – probably – silicatic corroded glass surface. Possibly,  $\text{Na}^+$  stabilizes the glass surface, whereas silicatic colloids might have a destabilizing effect.

Additionally, the slow kinetics of the corrosion in 1 mol/l  $\text{NaOH}$  can be explained by adsorption of  $\text{Na}^+$  from the leachant.

The increase of the corrosion rates with time observed in the individual corrosion runs of the glass platelets in alkaline solution cannot be attributed primarily to the increase of the concentration products in the leachate nor to the increase of pH which accompanies the increase of the concentration of the reaction products, since the overall tendency shown by the dilution series hints to the opposite direction. Selective leaching of alkalis or structural changes of the surface zone might be other reasons.

## 5. Summary and conclusion

The major findings concerning the corrosion of sodium disilicate glasses are:

- The corrosion process in basic media does not exhibit the classic pH dependence.
- The corrosion kinetics in  $\text{H}_2\text{O}$  and sodium silicate solutions follow a linear time law and are appreciably faster than the corrosion kinetics in 1 mol/l  $\text{NaOH}$  or 1 mol/l  $\text{LiOH}$  solutions, which follow a square root time law ( $\text{LiOH}$ ) or a combined time law ( $\text{NaOH}$ ).
- A re-adsorption term describes the dependence of the corrosion kinetics on the concentration of sodium silicate in the leachant.

Some of the conclusions presented above are in contradiction to common understanding of glass corrosion and will need further investigations. Probably, the role of silicatic colloids – which are important species in sodium silicate solutions – as well as surface effects due to alkalis have to be checked.

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