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Sequential chemical etching of glass surfaces in the nm range

The characterization of the early stages during the glass corrosion process represents always a demanding task for the existing techniques of chemical analysis. In this case the implementation of instrumental methods like SIMS and SNMS has been to a certain degree effective. The current research contribution introduces an additional optimized direct chemical technique which aims at the reliable quantification of the initially dissolved glass surface layers in particular with a thickness below 20 nm. It is based on the established etching procedure [1] using hydrofluoric acid in combination with other mineral acids. The above method is modified and appropriately extended by enhancing the precision of the selected exposure time with the help of an automatic dipping device. New improvements are the minimization of the dissolution rate by lowering the test temperature to –10°C and also the decrease of the aqueous activity by adding alcohol instead of water into the acid solutions. Furthermore, by applying sequential etching with low concetrations of HF and HNO_3, very small removal depths within the range between 5 and 10 nm per step are obtained. The equivalent components extracted from the examined float glass are detected by subsequent chemical analysis of the etchants via AAS and ICP-OES. Their dissolution character can be well distinguished through a comparison between the gravimetric weight loss q_{gravim} and the normalized mass release q_{sol}, calculated from the chemical composition of the used solutions.

Experimental

The chemical durability of the glasses as well as the achieved removal depths and dissolution rates by the primary steps of the corrosion process significantly depend on the composition and the prehistory, the current state of the surface, the volume and the type of the used aggressive solutions, the temperature and the time. Concerning these multiple und very important parameters the planned etching experiments are executed on rectangular glass chips through an appropriately modified method resembling the MCC-1-Tests. The Materials Characterization Center MCC-1 test procedure [2]

represents a monolithic glass durability test for determining the relative corrosion of glasses under static conditions. It is conducted in teflon vessels, where the SA/V ratio is held always constant. Monolithic shapes are used so that a geometric surface area can be measured. In the present research case the chosen one millimeter thick float glass is cut in small (2·2) cm^2 pieces and is cleaned before the ultimate corrosive exposure, while its surface is treated by a 3-minutes soaking in 10% HF at ambient temperature. Then the cleaning continues by rinsing with distilled H$_2$O and afterwards with acetone, as well as drying in water-jet vacuum for 10 min. As a final step, the dried glass samples are weighed with an analytical balance.

The composition of the float glass, serving as experimental material throughout the implemented etching technique, has been identified with the help of X-ray fluorescence (XRF) analysis (check the following table).

Table 1. Chemical composition of the used float glass in weight-%.

Oxide	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	TiO$_2$	CaO	MgO	Na$_2$O	K$_2$O	P$_2$O$_5$	SO$_3$
%	74.05	1.00	0.08	0.04	5.45	4.31	14.20	0.70	0.02	0.15

The prepared glass chips are clamped vertically in a polyethylene sample holder and then are dipped into a teflon cuvette (150ml) with the respective corrosive solution using an automatic dipping device. Due to the application of a cryostat, the designated temperature of -10°C is easily reached and retained unchanged during the test series. The etching agent used for the experimental surface treatment consists of a 88 ml solution from 0.5% HF and 1.0% HNO$_3$ with distilled water and different proportions (from 20% to 95%) of alcohol. For the determination of the concentration profiles, a sequential etching consisting of up to 10 immersion steps with 5 to 20 nm removal depth is implemented. Thereby the ratio s of glass surface area to solution volume remains always constant and amounts to 0.10 cm^{-1}. The programmable dip-coater allows a precise regulation of the desired treatment duration from 20 to 60 sec per step depending on the temperature and the concentration of the cooled alcohol/water solutions. After each finished step, the chips are first washed with distilled water, and then with acetone. Next they are dried for 10 minutes in water-jet vacuum at room temperature. Their slightly decreased masses are detected with an analytical 6-digit balance to the nearest 1 µg. Meanwhile the utilized corrosive solutions are changed after every dip and analyzed separately via AAS and ICP-OES. The amount of the extracted glass components by these short-time etching experiments is very small. Therefore,

blank solution samples have been measured. The detection of Na_2O and K_2O is done by AAS. The content of CaO and MgO is analysed with ICP-OES.

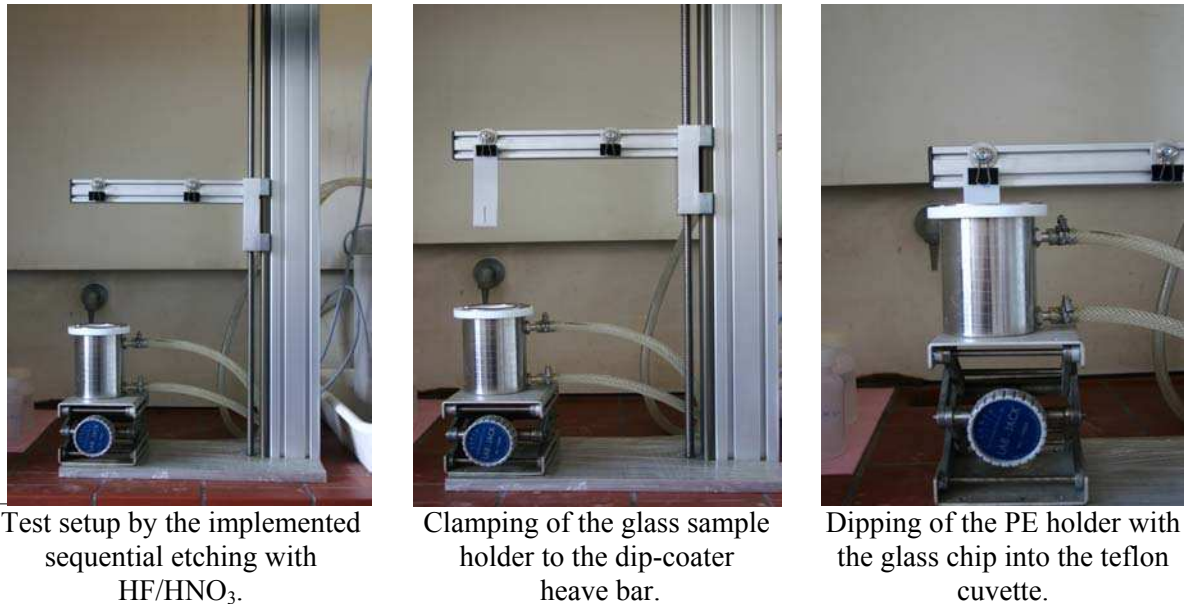| Test setup by the implemented sequential etching with HF/HNO_3. | Clamping of the glass sample holder to the dip-coater heave bar. | Dipping of the PE holder with the glass chip into the teflon cuvette. |

Fig. 1: Experimental equipment for the established etching procedure.

Evaluation of the executed experiments

The realised sequences by the etching experiments and in particular the thickness d of the initially dissolved surface layers can be characterized by q_{gravim}, which represents the overall mass release per surface area of the glass, observed after a certain time t. It can be derived from the mass difference of the glass sample Δm in µg. Therefore, the next formulas are used: $q = \Delta m/A$ and $d = q/\rho$, where A marks the surface area of the glass chip in cm^2, ρ is the glass density in g/cm^3 and q_{gravim} carries the dimension $µg/cm^2$. The concrete values for one representative example of the conducted test series with etching solutions composed of 0.5% HF and 1.0% HNO_3 diluted in an equimolar water:isopropanol mixture are shown in the following table.

Table 2. Example with experimental results from the gravimetric analysis of the chips

dipping step	time, t (s)	$m_{initial}$ (µg)	m_{final} (µg)	Δm (µg)	q (µg/cm²)	d (nm)
1	20	1524242	1524174	68	7,73	31
2	40	1524174	1524136	38	4,32	17
3	60	1524136	1524110	26	2,95	12
4	80	1524110	1524084	26	2,95	12
5	100	1524084	1524063	21	2,39	10
6	120	1524063	1524039	24	2,73	11
7	140	1524039	1524015	24	2,73	11

From the collected data after every etching step q-t- or d-t-diagrams are constructed.

They give important indications about the temporal and spatial course of the initiated short-time glass dissolution (steady and congruent, see the graphs below).
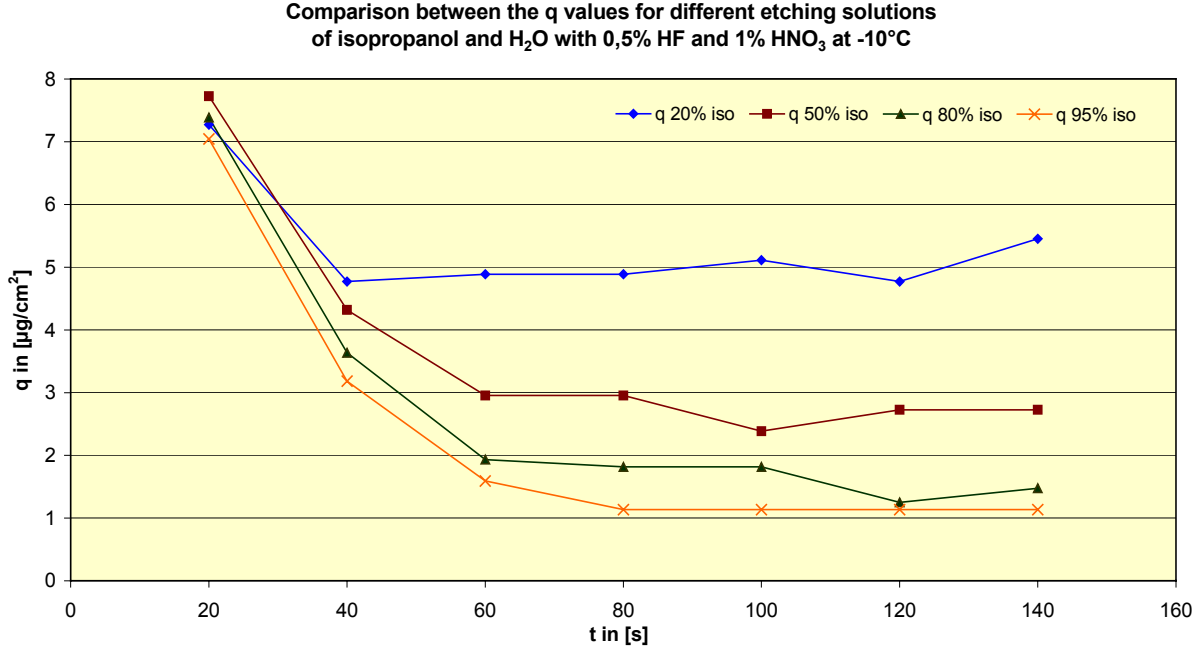
Comparison between the q values for different etching solutions of isopropanol and H$_2$O with 0,5% HF and 1% HNO$_3$ at -10°C

Fig. 2: Sketch of the mass loss per surface area q_{gravim} as a function of the exposure time t.

Comparison between the d values for different etching solutions of Isopropanol and H$_2$O with 0,5% HF and 1% HNO$_3$ at -10°C
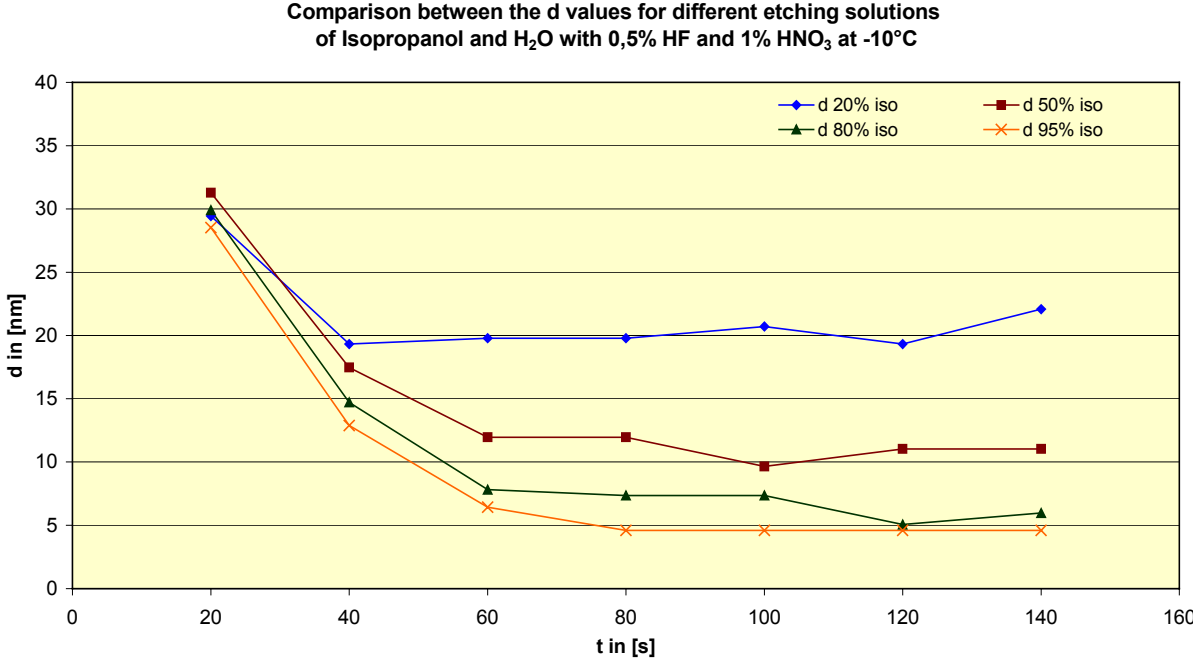

Fig. 3: Sketch of the dissolved layer thickness d as a function of the exposure time t.

Apart from the higher q and d values detected after the first dip the above graphs illustrate a glass dissolution process, which is proceeding in a rather homogeneous way, viz. after the passage of the indicated emerging circa 30 nm thick subsurface zone. Furtermore the etching solutions are examined by AAS and ICP-OES with regards to the

content of the accumulated glass components. A more specific picture of the corrosion progress can be obtained by tracing the concentrations c_i of the individual elements i dissolved in the solutions, where c_i is given in mg/l. The quantity $c_i/s = q_i$ describes the fractional elemental release. Its division by the weight fraction y_i in the etched specimen, yields the so-called normalized elemental mass loss $q_{sol} = q_i/y_i = c_i/(s \cdot y_i)$, released from the glass and measured in µg/cm^2. A comparison between the gravimetric mass loss per geometrical surface area q_{gravim} and the calculated elemental release q_{sol} reveals the different phenomena of congruent dissolution ($q_{gravim} = q_{sol}$), preferred element leaching ($q_{gravim} < q_{sol}$), or enrichment ($q_{gravim} > q_{sol}$). As a matter of fact first trend-setting conclusions on the status of the residual glass surface can be drawn even without applying surface analysis.
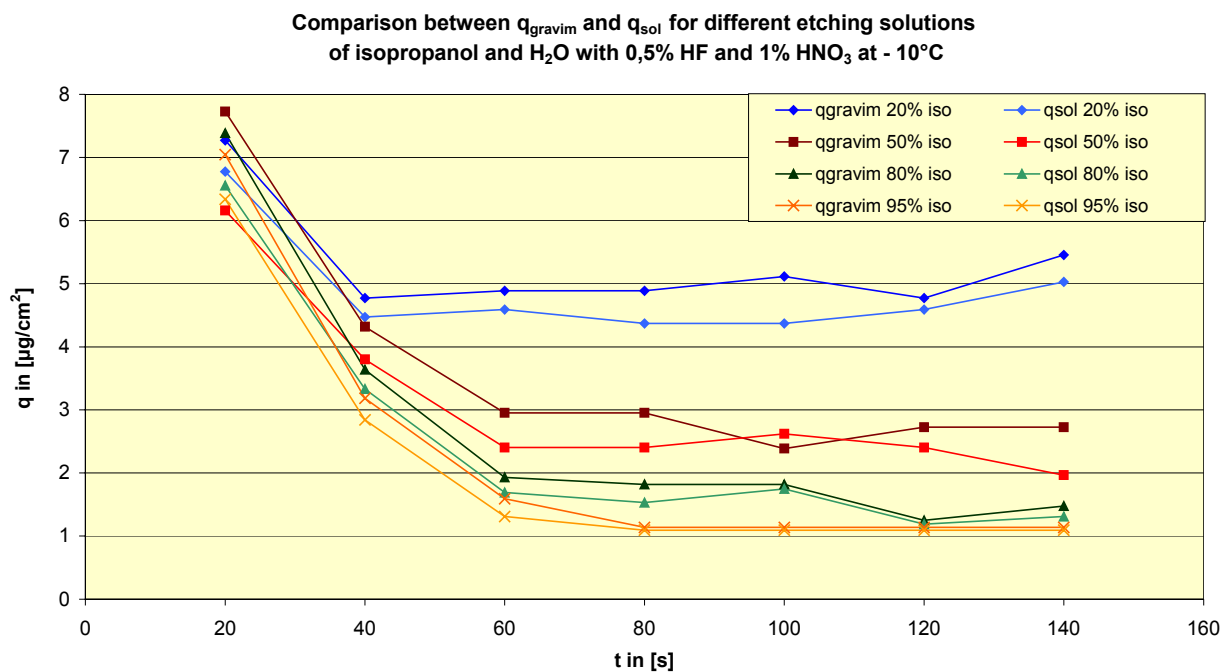

Fig. 4: Comparison between q_{gravim} and q_{sol}, based on the Mg content in the used solutions.

The above evaluation diagram shows an almost perfect equality between the compared q_{gravim} and q_{sol} values after the executed various etching sequences, which represents an additional unambiguous evidence of the observed congruent dissolution behaviour. The depicted constancy by the detected elemental concentrations in the analysed etchants corresponds directly to the measured stability by the gravimetric weight losses of the corroded glass chips. This exceedingly important circumstance makes the conducted etching process in the nm range assessable and repeatable. Based on that, the method should be able to deliver reliable quantitative data which are meant as reference points for the interpretation of the high-resolution SNMS depth profiles.

SNMS depth profile of the cleaned glass chip surface determined by the sputter rate of 0,16 nm/s
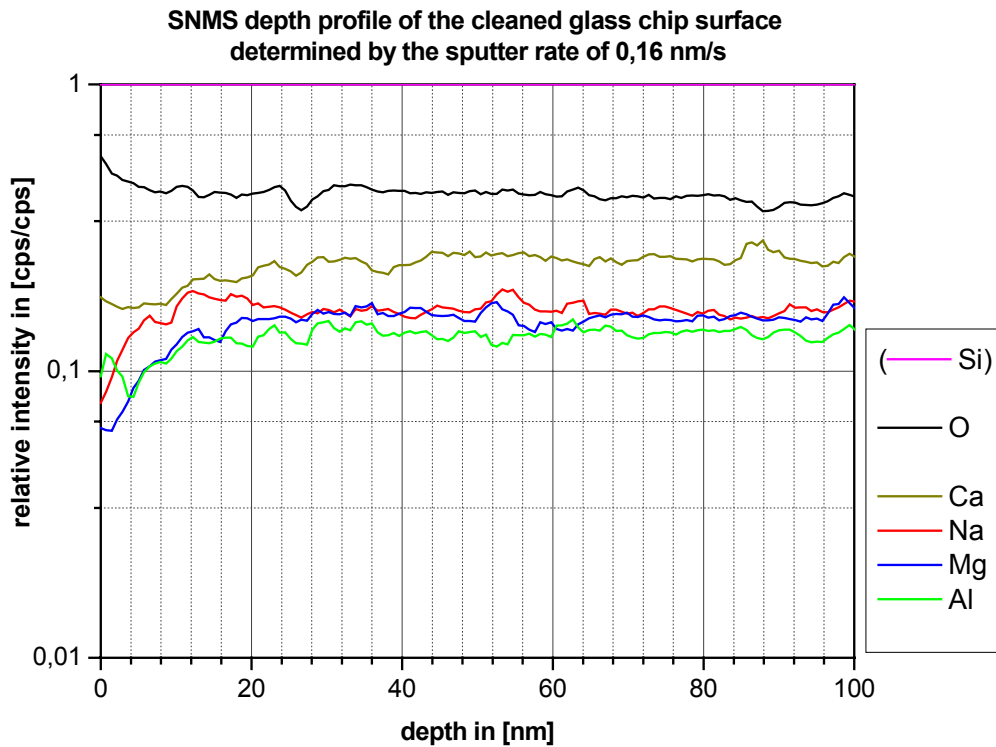
Fig. 5: SNMS depth profile of the cleaned glass surface before the ultimate etching treatment.

The above illustrated parallel measured SNMS depth profiles of the elemental distribution within the investigated glass chip surface confirm the results by the implemented chemical eching technique. Both methods allow the clear distinguishment of a precorroded alkali depleted subsurface zone with an altered chemical composition and transformed structure compared to the glass matrix. The average thickness of this partial hydrated faster dissolving gel-like layer is about 30 to 40 nm. The mentioned findings can be explained by the raised surface energy of all glass oxides after the performed equalizing cleaning process. Consequently these freshly revealed and unsaturated compounds tend to react rapidly with H_2O or other chemical species present in the surrounding atmosphere.

Summary of the obtained results

In the presence of a settled corrosive agent surplus (marked by a small ratio of exposed glass surface area to solution volume $s = 0.10$ cm^{-1}) and by an unchanged test temperature $T = -10°C$, the dissolution of the glass matrix progresses typically with a low constant reaction velocity $v < 1$ nm/s depending on the concentration of the echants.

By the variation of the ratio between isopropanol and H_2O in the etching solutions with the main objective to lower the activity of the solvent, different very thin removal depths within the range of 5 to 10 nm per step can be reached: indeed the increase of isopropanol leads to a decrease in the observed mass release per surface area q and also to a smaller thickness d of the dissolved surface layer. The higher values obtained after the first dip can be refered to structural transformations in the boundary zone, such as element depletion, water penetration, hydration of Si-O-Si bonds and finally formation of one very thin less resistant gel like surface layer (approx. 30 to 40 nm thick). The existence of such partial hydrated and faster dissolving subsurface zone has been confirmed by the parallel measured high-resolution SNMS depth profiles of the traced glass elements. After the passage of the above described film the initiated glass etching takes place in a steady and homogeneous way, which is clearly authenticated by the remaining constant values for q_{gravim} and q_{sol} during the following steps of the conducted test procedure. The comparison between the gravimetric mass loss per surface area q_{gravim} and the normalized elemental mass release q_{sol}, based on the Mg concentration in the analyzed solutions, exemplifies expectedly a well-defined congruence in the dissolution behaviour of the treated glass, whereby the pristine componental relations remain preserved und the experimental material is smoothly corroding layer by layer.

References:

[1] H. Scholze, in: *Glass - Nature, Structure, and Properties,* (Springer Verlag, 1988, Berlin).

[2] D.E. Clark, B. K. Zoitos (eds.), in: *Corrosion of Glass, Ceramics and Supercoductors*, (Noyes, 1992, New Jersey).

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