

Investigation of glass corrosion in acid solutions with ^{29}Si -MAS-NMR¹⁾

Thure Böhm and Johanna Leissner

Fraunhofer-Institut für Silicatforschung, Würzburg (Germany)

John A. Chudek

University of Dundee, Chemistry Department, Dundee (Great Britain)

Thin foils of potash–lime–silicate glass were corroded in acid solutions for different time periods. The formation of a gel layer was determined by IR spectroscopy and solution analysis. The applicability of ^{29}Si -MAS-NMR spectroscopy as an analytical tool for characterizing gel layers was investigated. The obtained spectra of increasingly corroded foils show the growth of a new peak at the highfield side of the main glass peak. This peak can be attributed to Q4 silicon units. The formation of Q4 silicon is believed to be due to a condensation reaction of previously hydrolyzed Si–OH groups in the gel layer.

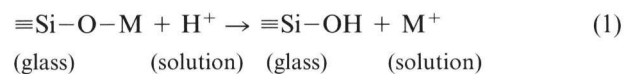
Untersuchung der Glaskorrosion in sauren Lösungen mit ^{29}Si -MAS-NMR

Dünne Kalk-Kalisilicatglasfolien wurden für verschiedene Zeiträume in sauren Lösungen korrodiert. Die Bildung einer Gelschicht wurde IR-spektroskopisch und durch die quantitative Analyse der Korrosionslösungen nachgewiesen. Die Eignung der ^{29}Si -MAS-NMR zur Charakterisierung von Gelschichten wurde untersucht. Im Spektrum der korrodierten Folien zeigte sich ein neues Signal an der zum höheren Feld verschobenen Flanke des Hauptpeaks. Dieses Signal wächst mit zunehmendem Korrosionsgrad an. Es kann Q4-Silicium-Baueinheiten zugeordnet werden. Die Entstehung von Q4-Silicium wird auf eine Kondensationsreaktion der Si–OH-Gruppen in der Gelschicht zurückgeführt.

1. Introduction

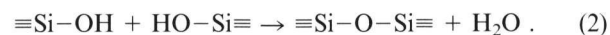
The corrosion of glass is a well-established field of research. Nevertheless, some aspects, in particular the structure of gel layers, are not yet fully understood. The object of this study is to investigate the structure and formation mechanisms of gel layers on potash–lime–silicate glasses. This is done by combining well-established analytical tools (i.e. IR and solution analysis) with a method which is new in the field of glass corrosion: ^{29}Si -MAS-NMR (MAS-NMR = Magic Angle Spinning-Nuclear Magnetic Resonance).

Previous studies of glass corrosion [1 and 2] state that the main reaction in acid solutions is an ion exchange process. The equation



is used to describe the reaction. M represents a network modifier ion (i.e. calcium and potassium in a

potash–lime–silicate glass). Additionally, molecular water diffuses into the glass [3]. A silica- and water-rich layer is thus formed at the glass/solution interface. This layer is often called a “gel layer”. It was suggested that a condensation reaction might follow the ion exchange process:



Experimental evidence for the occurrence of this condensation is not easy to obtain, since most analytical methods such as infrared spectroscopy or solution analysis [4] often cannot distinguish easily between OH groups of Si–OH and molecular water. So one often speaks of “water”, meaning both molecular water and Si–OH.

The technique of ^{29}Si -NMR for solid state samples, however, should give more detailed information about the chemical environment of the silicon in the gel layer. It should then be possible to detect whether condensation takes place or not, since condensation leads to a change in the bonding structure of the silicon by replacing an Si–OH bond by an Si–O–Si bond. This change should be detectable by ^{29}Si -MAS-NMR.

Received April 20, 1995.

¹⁾ Extended version of a paper presented in German at: 68th Annual Meeting of the German Society of Glass Technology (DGG) on May 31, 1994 in Bad Salzdetfurth (Germany).

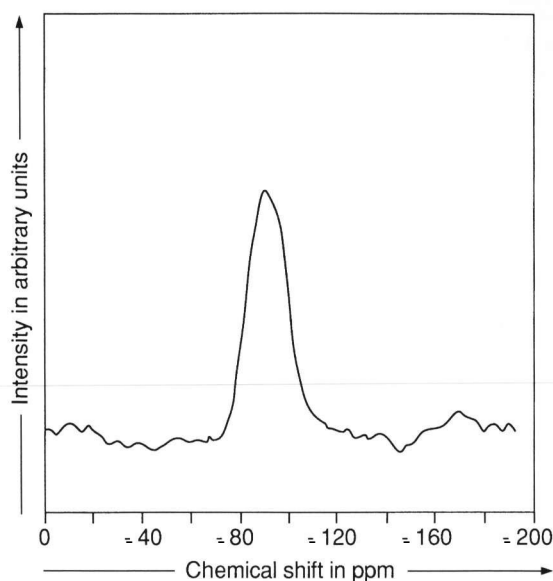


Figure 1. ^{29}Si -MAS-NMR spectrum of a fresh glass-sample. Chemical shift in ppm from TMS (tetramethylsilane), intensity in arbitrary units.

2. Experimental procedure

2.1. Model glasses

The glass used in this study has the molar composition (in %) 59.8 SiO_2 , 20.2 K_2O , 20.0 CaO . The ratio of network former (i.e. SiO_2) to network modifiers (i.e. CaO and K_2O) is 1.49 (expressed in moles). Samples were prepared by melting reagent-grade materials in a platinum crucible at 1450°C for 2 h. Hollow spheres (diameter approximately 20 cm) were blown and broken into smaller pieces. These had a thickness between 20 and $50\ \mu\text{m}$.

2.2. Corrosion experiments

A Tris-HCl buffer (Tris(hydroxymethyl)-aminomethane-hydrochloride, pH 5.5) was used as corrosive medium. 50 ml of solution were poured into teflon containers and kept at 55°C for 2 h. Approximately 1 g of glass foil was then put into the solution. The exposure time ranged from 7 min to 19 h. Samples were removed from solution, rinsed with distilled water and dried at 55°C for 30 min.

Infrared spectra were then taken using a Fourier-Transform Infrared Spectrometer (model 510P Nicolet Inc., Madison, WI (USA)). In order to achieve sufficient homogeneity for spinning in the MAS-NMR probe, samples were pulverized with an agate ball mill (model „Pulverisette” Fritsch GmbH, Idar-Oberstein-Weierbach (Germany)). A possible influence of agate particles (which contain Q4 silicon) can be neglected, because a Q4 signal should then be visible in the spectrum of an uncorroded sample (figure 1).

2.3. Analytical investigations

The analytical methods used to characterize and investigate the corrosion process are described in the sections 2.3.1. to 2.3.3.

2.3.1. Infrared spectroscopy

Infrared spectroscopy (IR) is widely used in glass corrosion research, because the broad OH band at $3350\ \text{cm}^{-1}$ is suitable to determine the total water content (i.e. Si-OH and H_2O) of gel layers [4 and 5]. IR spectroscopy is especially useful for detecting small amounts of water. If the total amount of water is too large, absorption becomes too strong and the spectrum is a flat zero-transmittance line in the OH region. This is the upper limit for the application of IR spectroscopy as a tool for water detection in glasses.

2.3.2. Solution analysis

Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) was used to determine the concentration of glass components in solution. Solution analysis is easily done and gives indirect information about the composition of the gel layer. One can deduce the composition of the gel layer from the ions found in the solution, assuming that all ions in solution have been leached from the glass [6]. If the ratio of network former to network modifiers in solution is smaller than in the bulk glass, an ion exchange process takes place and a gel layer is formed [4]. If the ratios in solution and bulk are approximately the same, the mechanism of corrosion is a total dissolution of the glass.

2.3.3. ^{29}Si -MAS-NMR

^{29}Si -MAS-NMR spectroscopy is fast becoming a major tool in the analysis of glass. The differences between the chemical environments of silicon atoms with zero, one or two etc. attached O-Si groups (Q0, Q1, Q2 etc., respectively) lead to a significant shift in the position of the ^{29}Si resonance signal in the NMR spectrum [7]. The area of each signal is proportional to the number of nuclei causing the resonance, thus, spectra may be evaluated quantitatively [8].

MAS-NMR spectra were acquired on a Fourier transform NMR spectrometer (Bruker Spectrospin AM/3000/WB, Bruker GmbH, Karlsruhe (Germany)) resonating at 300.13 MHz for protons, 71.93 MHz for ^{29}Si . The spectrometer was equipped with a Chemagnetics MAS probe. Samples were spun at approximately 4 kHz.

3. Results and discussion

Figure 1 shows the ^{29}Si -MAS-NMR spectrum of an uncorroded potash-lime-silicate glass. One broad resonance at around $-90\ \text{ppm}$ is visible, this is the region where peaks corresponding to Q2 and Q3 silicon might be expected [9]. The mean number of bridging oxygen neighbours per silicon atom of the glass, calculated from the composition [10], is 2.67. This corresponds with the evidence from figure 1. It can be concluded from this spectrum that the concentration of Q4 silicon atoms in the glass is very low. Otherwise, a shoulder at the high-field side of the peak should be visible [9].

Solution analysis data are presented in table 1. The concentrations of the glass components are shown as molar percentages. The concentration of SiO_2 in solution in all experiments is very low as compared to the concentrations of CaO and K_2O . The ratio of network former to network modifiers is much smaller than in the bulk. Values in solution vary from 0.04 to 0.12, the value for the bulk is 1.49. From these data it can be concluded that the ion exchange process is the dominant mechanism in all experiments and a gel layer is formed on all samples. Total network dissolution plays only a minor role. The relative concentrations of glass components do not change with increasing corrosion time. This indicates that the corrosion mechanism remains the same for all corrosion times in this study. One can therefore expect the same gel layer structure in all experiments. Specifically the total water concentration (as Si-OH and H_2O per volume unit) within the gel layer should be the same for all samples.

Plots of IR spectra of glass foils corroded for different times are shown in figure 2. The increase of OH peak area with corrosion time is clearly visible. Figure 3 shows a plot of the integrated peak area (arbitrary units) versus duration of corrosion. The peak area is proportional to the total water content [4], which is proportional to gel layer thickness (the ICP-AES data (table 1) indicate constant water concentration in the gel layers). Figure 3 therefore shows a direct relationship between corrosion time and gel layer thickness. The upper limit for water detection with IR spectroscopy is visible in the spectrum of the 19 h sample. Here, the water content of the sample is too large and results in zero transmittance around 3350 cm^{-1} .

Infrared spectroscopy and solution analysis thus show that gel layers were formed in all experiments. An increase in gel layer thickness with corrosion time was detected.

^{29}Si -MAS-NMR gives information about the chemical environment of the silicon atoms in the gel layer. Spectra of several samples are shown in figure 4. All spectra are plotted on the same scale, thus, peak heights give quantitative information. A new peak at -110 ppm can be observed in corroded samples. This peak grows with increasing corrosion times. The position of this new peak is at a frequency where Q4 silicon absorptions in glass have been reported [8 and 9]. To prove experimentally that the new peak in the corroded samples is due to Q4 silicon, a spectrum of pure SiO_2 was recorded. Figure 5 shows the spectrum of quartz sand. It has one single peak at -108 ppm . Quartz consists of a complete SiO_2 network, i.e. all silicon atoms are Q4 silicons. This proves that the new peak at -110 ppm in the corroded samples is caused by Q4 silicon. The formation of Q4 silicon during corrosion indicates that a condensation reaction according to equation (2) took place in the gel layer.

A quantitative analysis of peak intensities gives the portion of Q4 silicon as a percentage of all silicon in the

Table 1. ICP-AES data of corrosion solutions, molar fractions of glass components in solution (in %)

duration of corrosion	SiO_2	CaO	K_2O	SiO_2
				$\text{CaO} + \text{K}_2\text{O}$
7 min	6.0	46.9	47.1	0.06
15 min	7.8	45.9	46.3	0.08
30 min	3.8	46.9	49.3	0.04
60 min	10.9	42.8	46.3	0.12
2 h	7.6	46.7	45.7	0.08
19 h	5.9	47.9	46.2	0.06

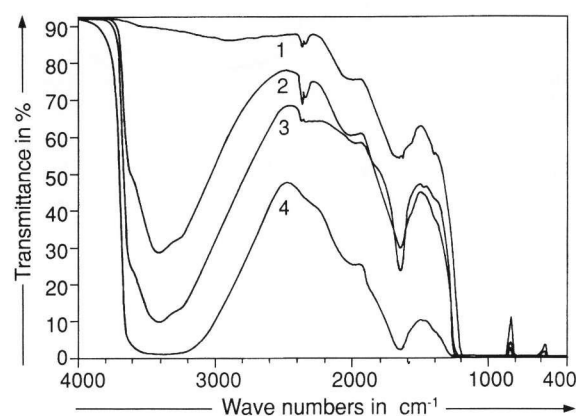


Figure 2. Infrared spectra of different glass samples; uncorroded (curve 1); corroded for 15 min (curve 2), 2 h (curve 3), 19 h (curve 4).

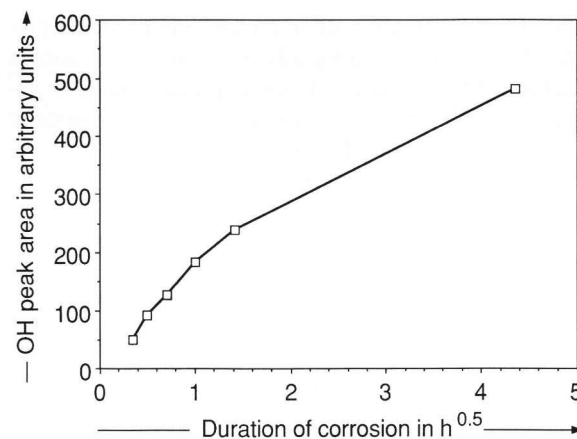


Figure 3. OH peak area in arbitrary units versus corrosion time.

sample. A further analysis of the ICP data provides the portion of silicon which formed Si-OH at first, due to the ion exchange process. The ratio of both is the degree of condensation. Table 2 shows the results.

A high degree of condensation is visible for all samples. Even after 15 min of corrosion more than 80 % of the Si-OH groups which were formed by the ion exchange process condensate to Si-O-Si . There is no significant change in the degree of condensation for longer corrosion times. This fact supports the assumption that the structure of the gel layer does not change for longer corrosion times. Only the thickness of the layer increases with time.

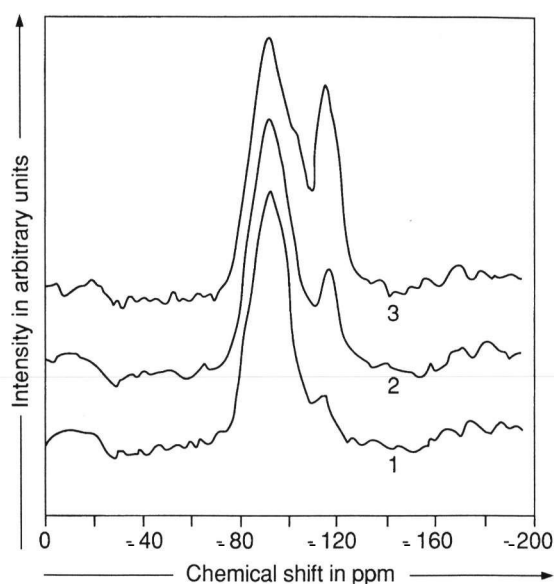


Figure 4. ^{29}Si -MAS-NMR spectra of corroded samples; corroded for 15 min (curve 1), 2 h (curve 2), 19 h (curve 3). Chemical shift in ppm from TMS, intensity in arbitrary units.

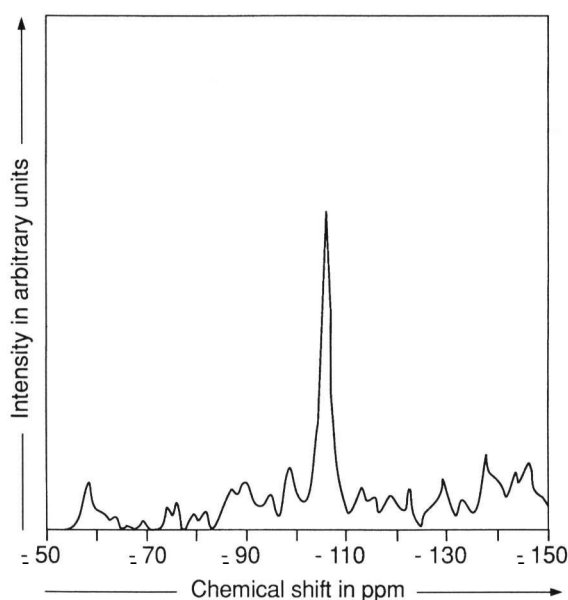


Figure 5. ^{29}Si -MAS-NMR spectrum of quartz sand. Chemical shift in ppm from TMS, intensity in arbitrary units.

Table 2. Relative portions of Q4 silicon and Si-OH groups compared to the total amount of silicon (in mol%)

duration of corrosion	Q4 (MAS-NMR)	Si-OH (ICP-AES)	Q4/Si-OH
15 min	9.8	11.6	0.85
2 h	14.2	18.4	0.77
19 h	25.0	27.8	0.90

4. Conclusion

The aqueous corrosion of a potash-lime-silicate glass was investigated with different analytical tools. The formation of a silica- and water-rich gel layer was detected by infrared spectroscopy and solution analysis. Within this gel layer condensation reactions of silanol groups ($\equiv\text{Si}-\text{OH}$) to a silica network ($\equiv\text{Si}-\text{O}-\text{Si}\equiv$) can be observed in the ^{29}Si -MAS-NMR spectrum by the occurrence of a Q4 peak. These condensation reactions start quickly after the glass is placed in a corrosive solution. Approximately 80% of the silanol groups condensate to Si-O-Si. This value does not change significantly with increasing corrosion times.

The results show furthermore that ^{29}Si -MAS-NMR spectroscopy is a very useful analytical tool for investigating glass corrosion. The information on the chemical environments of the silicon atoms gives a more detailed picture of the gel layer in corroded glasses. A more quantitative analysis of the NMR spectra should follow in the near future. For example, the time dependence of equation (2) has to be investigated in detail to give a better quantitative understanding of gel layer formation.

*

The authors wish to acknowledge NATO CCMS for financial support.

5. References

- [1] El-Shamy, T. M.; Lewins, J.; Douglas, R. W.: The dependence on the pH of the decomposition of glasses by aqueous solutions. *Glass Technol.* **13** (1972) no. 3, p. 81-87.
- [2] Clark, D. E.; Pantano, C. G.; Hench, L. L.: *Corrosion of glass*. New York: Books for Industry and the Glass Industry 1979.
- [3] Conradt, R.; Scholze, H.: Glass corrosion in aqueous media - a still unsolved problem? *Riv. Stn. Sper. Vetro* **14** (1984) no. 5, p. 73-77.
- [4] Scholze, H.; Helmreich, D.; Bakardjiev, I.: Untersuchungen über das Verhalten von Kalk-Natrongläsern in verdünnten Säuren. *Glastech. Ber.* **48** (1975) no. 12, p. 237-247.
- [5] Fuchs, D. R.; Römich, H.; Schmidt, H.: Glass sensors. Assessment of complex corrosive stresses in conservation research. *Mater. Res. Soc. Symp. Proc.* **185** (1991) p. 239-251.
- [6] Sanders, D. M.; Hench, L. L.: Mechanisms of glass corrosion. *J. Am. Ceram. Soc.* **56** (1973) no. 7, p. 373-377.
- [7] Cheetham, A. K.; Day, P.: *Solid state chemistry techniques*. Oxford: Clarendon Press 1987.
- [8] Fyfe, C. A.: *Solid state NMR for chemists*. Guelph (Canada): CFC Press 1983.
- [9] Murdoch, J. B.; Stebbins, J. B.; Carmichael, I. S. E.: High-resolution ^{29}Si NMR study of silicate and aluminosilicate glasses: the effect of network-modifying cations. *Am. Mineralogist* **70** (1985) p. 332-343.
- [10] Scholze, H.: *Glas*. 3rd. ed. Berlin (et al.): Springer 1988.

1295P004