On the Dissolution of Na_2O-CaO-SiO_2 Glass in Acid and in Water

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The "chemical durability of glass" is one of the research items of great academic interest, and of leading technical importance as well. Accordingly, there have been many papers published on this subject.

The usual way of representing the results of durability tests is to express them in the equivalent concentration of sodium oxide leached out from the glass surface; sometimes from glass powder to accelerate the attack on glass, or from the glass container itself to make the data more practical. For many purposes this way of presenting data is very useful, because the varying alkalinity of the solution stored in a glass container is often a matter of serious concern.

In multi-component glasses, sodium oxide is not the only substance which passes into solution, even in the initial stage when the silica network remains unchanged. Investigating the change of interference colors produced by the changing thickness of the silica-layer remaining on the surface of some flint glasses immersed in nitric acid solution, the author could confirm the fact that the chemical attack proceeds through the exchange reaction between cations such as Na^+, K^+ and Pb^{2+} in glass on the one hand and H^+, or H_3O^+ in solution on the other[1]. Moreover, the exchange between Na^+, K^+ in glass and H^+ in solution takes place at a rate far greater than that between Pb^{2+} in glass and H^+ in solution, so that the rate of diffusion of Pb^{2+} through glass network determines the rate of reaction.

In studying the mechanism of chemical attack on glass by using soda-lime-silica glass which is simpler in composition and of more practical importance, the optical method fails in its object, because both the rate of reaction and the difference in refractive index between the surface layer and the body are smaller than when we use flint glass.

Hence, in order to draw a clear picture of the complete set of chemical reactions, the components leached out from glass by the conventional powder method were completely analyzed.

Experimental Methods

Preparation of the Solution for Analysis.—1) *Sample.*—The glass plates of composition given in Table I were crushed in a percussion mortar, and the powder was sieved to classify it into three meshes, namely, 16~20 (0.833~0.991 mm.), 20~24 (0.701~0.833 mm.), 24~32 (0.495~0.701 mm.), washed thoroughly with methanol to remove all fine particles adhering to the grains, and finally dried at 120°C.

TABLE I. COMPOSITION OF GLASS (weight %)

SiO_2	Na_2O	CaO	MgO	$Fe_2O_3+Al_2O_3$
73.64	13.12	8.44	2.37	2.37

2) *Acid solution.*—As it is necessary to deal exhaustively with an extremely small amount of ions, the water used for the experiments was completely demineralized by treating it successively with ion-exchange resins. This treatment was used also for preparing hydrochloric acid and sulfuric acid solutions, the concentrations of which were 1 N throughout the experiments.

3) *Apparatus.*—The apparatus used for the leaching out experiments is shown in Fig. 1. It is a three-necked flask with a stirrer, both of which are made of Pyrex glass.

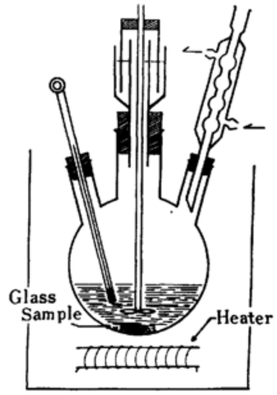

Fig. 1. Apparatus used for the durability test.

4) *Procedure.*—1.00 g. of the glass powder was accurately weighed out and transferred into the flask containing 100 ml. of reagent. Under continuous stirring the temperature was raised as quickly as possible to 100°C, at which it was kept

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[1] S. Tsuchihashi, This Bulletin, **24**, 161 (1951).

constant for one or three hours, and then the flask was cooled to room temperature. The solution was separated carefully from the glass powder and subjected to chemical analysis.

A series of blank tests were made in order to determine the amount leached out from the container wall and from the stirrer. The figures obtained, although negligibly small, were subtracted from the results in order to obtain the actual net values.

Chemical Analysis of the Solution.—I. *Silica.*—In order to determine an extremely small amount of silica which had passed from the glass into the liquid, the spectrophotometric method based on the measurement of yellow or blue molybdo-silicic acid was used. There are, however, some points which should be made extremely clear in order to get reliable results. It is known that the color developed changes with the state of existence of silica in solution, namely, whether it is in ionic state, in molecular state or in colloidal state[2-5]. The following conditions should be taken into account.

1) *pH value.*—Quite recently Narita[6] investigated the relation between the quantity of silica in ionic state and the pH of sodium silicate solutions with the result shown in Fig. 2. Since his experiments covered higher percentages of silica than in the present instance, the authors made experiments on the solutions containing smaller amounts of silica, whose compositions are given in Table II.

The silica content was exactly 5 p. p. m. after 6 hr. and 5 p. p. m. after 6 days in pH 12 solution, but was reduced to 0.5 p. p. m. in a 1 N sulfuric acid solution. By adding Ca^{2+} to the solution the quantity of ionic silica was reduced; for instance, to 0 in a 1 N sulfuric acid solution, and to 2.9 in an alkaline solution of pH 12. From these observations it may be concluded that the quantity of ionic silica does not depend on the pH of that solution alone. As it has already been shown that the optimum pH value to determine the amount of silica is 1～1.6, we also followed these conditions in performing our experiments.

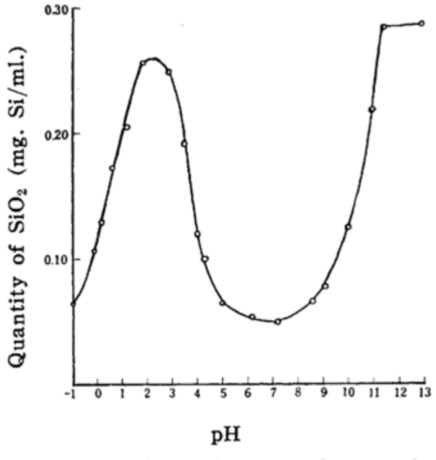

Fig. 2. The relation between the quantity of SiO_2 in ionic state and the pH of solution (after Narita).

TABLE II. DETERMINATION OF SiO_2 INFLUENCED BY OTHER ELEMENTS

Sample solutions	Value of measurements	
	After 6 hr.	After 6 days
5 p.p.m. SiO_2 in 1N H_2SO_4	5 p.p.m.	0.5 p.p.m.
5 p.p.m. SiO_2+5 p.p.m. Ca^{2+}, in 1 N H_2SO_4	5	0
5 p.p.m. SiO_2 in pH 12 solution	5	5
5 p.p.m. SiO_2+5 p.p.m. Ca^{2+}, in pH 12 solution	5	2.9

2) *Quantity of ammonium molybdate.*—The absorption spectra of the solutions, one containing 2 p. p. m. of silica and various amounts of molybdate and the other 20 p. p. m. of silica and various amounts of molybdate, were measured with the result that the addition of 5 ml. of 10% solution of molybdate to 50 ml. solution containing silica gave the greatest sensitivity to the spectra, and that the addition of a larger amount than 5 ml. brought about an undesirable influence[5,7].

3) *Wavelength.*—The published photometric procedures have proved to be of no practical use for measuring the absorption of the yellow molybdo-silicic acid at the optimum wavelength. The recommended wavelengths in millimicrons were: 370[8], 380[7], 390[9], 390 to 400[10], 400[11], 405[12], 416[6,7,13], 420[14], 425[15] and 436[16]. Taking into account these facts, the authors used 410 mμ ("yellow" method) and 810 mμ ("blue" method).

4) *Calibration curve.*—Beer's law was applicable whithin the range from 0 to 60 p. p. m. of silica, and the authors used this calibration curve for the quantitative determination of silica.

We measured the absorbance of the solution as soon as possible after adding the ammonium molybdate to that solution to prevent the influence of Ca^{2+} and other ions. Moreover, in order to examine whether or not any trace of silica might escape as colloid without forming silico-molybdate, alkali was added to the solution to digest the last trace of colloid before it was subjected to analysis.

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[2] F. Aoki, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **72**, 17 (1951).

[3] T. Okura, ibid., **72**, 927 (1951).

[4] Y. Iwasaki et al., ibid., **75**, 857 (1954).

[5] M. A. Desesa and L. B. Roger, *Anal. Chem.*, **26**, 1278 (1954).

[6] K. Narita, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **76**, 460 (1955).

[7] K. Narita, ibid., **77**, 271 (1956).

[8] J. Hure and T. Ortis, *Bull. soc. chim. France*, **16**, 834 (1949).

[9] R. Guenther and R. H. Gale, *Anal. Chem.*, **22**, 1510 (1950).

[10] U. T. Hill, ibid., **21**, 589 (1949).

[11] M. Armand and J. Berthaux, *Anal. Chim. Acta*, **5**, 380 (1951).

[12] J. R. Boyd, *Anal. Chem.*, **24**, 805 (1952).

[13] O. P. Case, *Ind. Eng. Chem., Anal. Ed.*, **16**, 309 (1944).

[14] D. Rozental and H. C. Campbell. idid., **17**, 222 (1945).

[15] G. N. Cade, ibid., **17**, 372 (1954).

[16] H. Pinsl, *Z. Metallkunde*, **27**, 107 (1935).

The results obtained with such treatment and those without it were quite the same, which proves that the present method is satisfactory.

II. *Sodium Oxide*.—Sodium oxide was determined by flame photometry using the spectral line at 589 mμ. As long as the concentration of alkali ions was in the order usually found in the durability tests, all substances except acids[17] were found to be harmless. The disturbance of acids was taken into full account, and the calibration curves were used to prevent the data from being influenced by coexisting anions.

III. *Calcium Oxide*.—Calcium oxide was determined by flame photometry using a calcium oxide band spectrum at 554 mμ. As it was found necessary to make clear the influence of coexisting ions on the result, a series of preliminary experiments were carried out.

1) ***Influence of sodium ion***.—A 5 p. p. m. calcium standard solution containing 0 to 100 p. p. m. Na^+ and a 1 p. p. m. solution containing 0 to 20 p. p. m. Na^+ were aspirated to observe the change of the flame intensity, and it was possible to confirm the fact that there was no detectable influence of coexisting Na^+ so far as its concentration did not exceed 15 times the amount of Ca^{2+}.

2) ***Influence of iron(III) ion***.—Carrying out the same experiments as the above using a 20 p.p.m. calcium standard solution containing 0 to 50 p.p.m. Fe^{3+}, it was recognized that the limiting concentration of Fe^{3+} was 0.5 times the amount of Ca^{2+}. As the amount of Fe^{3+} in the durability tests never exceeded this limiting value, the influence of coexisting Fe^{3+} may be ignored.

3) ***Influence of silica***.—The change of the flame intensity of a 2 p. p. m. calcium standard solution containing silica (up to 5, 10 and 20 p.p.m., respectively) is shown in Figs. 3, 4 and 5. The curves show a general trend indicating that the flame intensity was reduced at first by the addition of silica and brought, by further addition, to a constant value approximately at the point corresponding to the composition Ca : SiO_2=2 : 3. Thus, for the solution containing silica more than 3/2 of calcium, the calibration curve was drawn by analyzing the solution containing a known quantity of Ca^{2+}.

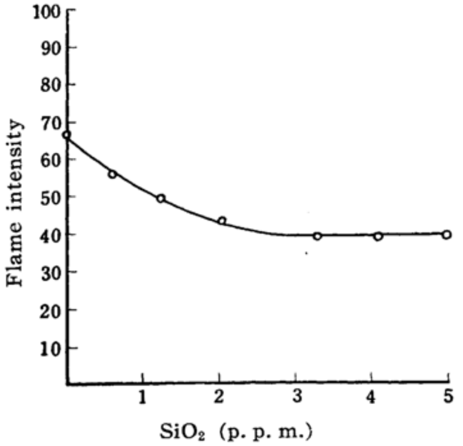

Fig. 3. Flame intensity of Ca^{2+} containing SiO_2
(Ca, 2 p. p. m.; SiO_2, 0∼5 p. p. m.)

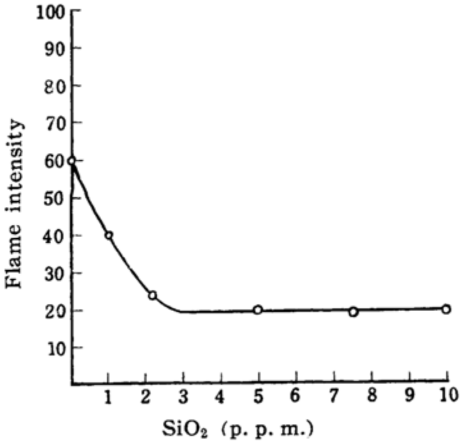

Fig. 4. Flame intensity of Ca^{2+} containing SiO_2
(Ca, 2 p. p. m.; SiO_2, 0∼10 p. p. m.)

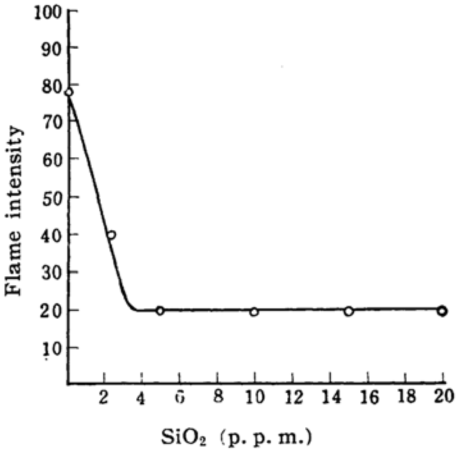

Fig. 5. Flame intensity of Ca^{2+} containing SiO_2
(Ca, 2 p. p. m.; SiO_2, 0∼20 p. p. m.)

4) ***Influence of acids***.—The disturbance of acids[18] was taken into full account and the calibration curves were made to make the results free from the influence of acids.

Results and Discussion

The data obtained by the durability tests are listed in Table III. The figures indicate that much larger amounts of silica were clearly leached out by water than by acids, and that silica probably placed a check on the rate of dissolution. In

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[17] P. Portor and C. Wyld, *Anal. Chem.*, **27**, 733 (1955).

[18] S. Ikeda, *J. Chem. Soc. Japan, Chem. Sec.* (*Nippon Kagaku Zasshi*), **78**, 1434 (1957).

TABLE III. DURABILITY OF Na_2O-CaO-SiO_2 GLASS

Solution	Time (hr.)	Particle size (mesh)	Amount leached out in mg./100 ml.			Na_2O/SiO_2
			SiO_2	Na_2O	CaO	
H_2O	1	16~20	0.20	0.06	0.01	0.29
		20~24	0.47	0.10	0.04	0.21
		24~32	0.68	0.18	0.04	0.25
	3	16~20	0.40	0.08	0.02	0.20
		20~24	1.05	0.21	0.05	0.20
		24~32	2.10	0.37	0.09	0.18
1N HCl	1	16~20	0.05	0.04	0.01	0.80
		20~24	0.09	0.08	0.04	0.89
		24~32	0.13	0.11	0.08	0.83
	3	16~20	0.06	0.05	0.02	0.80
		20~24	0.12	0.09	0.05	0.80
		24~32	0.20	0.16		0.80
1N H_2SO_4	1	16~20	0.10	0.06	0.07	0.58
		20~24	0.15	0.13	0.05	0.87
		24~32	0.20	0.17	0.07	0.83
	3	16~20	0.12	0.10		0.86
		20~24	0.20	0.15		0.73
		24~32	0.35	0.19		0.55
The ratio in base glass (weight per cent)						0.18

every case, however, larger quantities of silica than those of sodium oxide, and much smaller quantities of calcium oxide than of the other two were found in the solution. As usual, the total amount of dissolved matters inceased in proportion to the length of time, and in inverse proportion to the grain size of the glass powder.

As for the ratio Na_2O/SiO_2, the figures in the sixth and last rows show that the solution had practically the same proportion of sodium oxide to silica as the base glass, and also that the attack of water on glass presumably caused the collapse of the whole structure. The acids did not seem to be so destructive to the network structure, since the ratios were always higher. This indicates that the exchange reaction between H^+ in solution and Na^+, Ca^{2+} in glass is governed by the rate of migration of the ions through the glass network to the surface.

The idea of the collapse of the whole glass structure is strongly supported by the experimental results obtained by Tieze[18] and others[20,21] who confirmed the successive exfoliation of the silica layer during the durability test. This was also proved by the gradual increase of the quantity of dissolved substances.

Action of Water on Glass. — Let us first focus our attention on the network former, silica, which has non-bridging oxygen bonded with Na^+, and try to explain why the ratio of components in the solution was practically the same as that in the base glass when it was attacked by pure water. For this purpose it will be convenient to consider the whole process in two separate stages, i. e., (1) the initial stage and (2) the depth action, although there is no sharp boundary-line between them.

The reactions in the initial stage are illustrated schematically in Fig. 6. At first there will be the migration of Na^+ from the glass into the liquid, which gives rise to the place exchange between H^+ and Na^+. In the meantime Na^+ in the glass

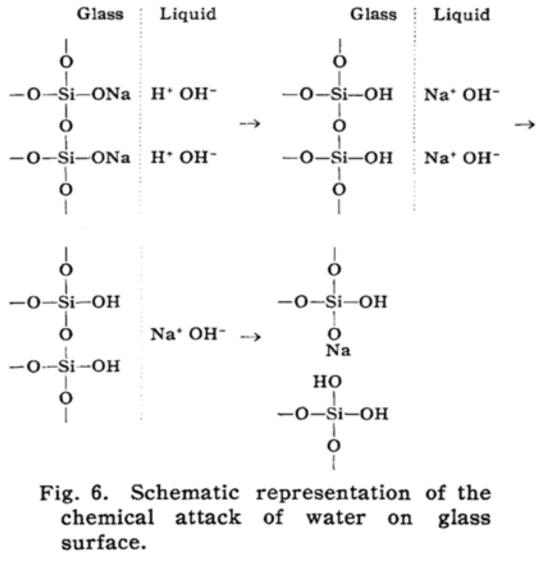

Fig. 6. Schematic representation of the chemical attack of water on glass surface.

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19) P. Tieze, *Sprechsaal*, **61**, 809 (1928).

20) Tielsh and Zimmer, ibid., **66**, 285, 303, 319 (1933).

21) I. Sawai, M. Tashiro et al., *J. Ceram. Assoc. Japan* (*Yogyo Kyokai Shi*), **52**, 258 (1944).

will diffuse to the surface through the network without producing any appreciable influence upon its structure. The continuous supply of Na^+ from inside, however, will accumulate sodium hydroxide at the surface, which then will begin to attack the bonding oxygen to open the network, so that silica also passes into the solution with gradual increase in its concentration. Hence in the initial stage, more sodium oxide goes into the solution than silica; that is, Na_2O/SiO_2 is higher than that of the base glass. The high value of the ratio Na_2O/SiO_2 in the initial stage is shown in Table III.

In the second stage, the depth action extending inward from the surface should be taken into account. As the reaction proceeds through the mutual diffusion of Na^+ and H^+ (this H^+ can easily migrate through the network and can penetrate deep into the electron cloud of non-bridging oxygen), the structure of sodium silicate changes into that of silicic acid in the layer near the glass surface. Using sodium silicate or dense flint glass, existence of a sharp boundary-line at the surface may easily be observed under a microscope.

Protons penetrate into the electron cloud of oxygen. As a result, the change from ONa to OH brings about the change of electronic configuration around the non-bridging oxygen, which in turn induces the stress in the network. The strain thus developed in the surface layer induces the exfoliation of the skeleton en masse so that all glass components go completely into the solution, with the ratio of components remaining unchanged, whether they are in glass or are dissolved in the solution.

Attack of Acids on Glass.—It requires only a glance at Table III to observe the fact that there is a marked difference between the action of water and of acids. Two remarkable features may be pointed out:

(1) Acids accelerated the leaching of the metallic ions, while they reduced notably the rate of dissolution of silica.

(2) Each component showed different behavior when attacked by different acids.

The question why acids check the dissolution of silica may be answered quite easily, when we take into account the fact that silica network can not be opened until a sodium hydroxide attacks the bridging oxygen, since H^+ in acid solution has no power to open the silica network. In fact, vitreous silica is resistant to the attack of acids, though it is not resistant to that of alkalis.

In the glass containing modifier cations in its network there will be only the place exchange between H^+ and the metallic cation.

It should be noticed that, with a few exceptions, sulfuric acid was stronger than hydrochloric acid in the power of leaching out the cations, while the hydrogen ion concentrations of the solutions are in reverse order, namely,

$$HCl : 0.8 > H_2SO_4 : 0.55$$

This discrepancy may be explained by taking into account the nature of the negative charge distribution in the liquid at the boundary layer surrounding the glass particles. The negative charge of anions reduces the repulsion between the cations which are just going to leave the lattice points and those already existing in the solution. In short, the anion plays an important role in drawing out the cations from the glass network.

Summary

(1) The first step in the attack of water on glass is the exchange reaction between the proton and Na^+ on the glass surface. Sodium hydroxide thus produced in the boundary layer opens the Si-O-Si bond, and consequently silica passes into solution.

(2) When the exchange reaction between Na^+ in glass and H^+ in acid solution takes place, more metallic ions will be drawn out of the network owing to the influence of anions existing in the solution. Consequently more cations pass into the solution, while the silica network will be stabilized by acid so that the silica in the solution will be reduced remarkably.

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