CORROSION OF SILICATE GLASSES BY ALKALINE SOLUTIONS

COMMUNICATION 1. BREAKDOWN OF QUARTZ, QUARTZ GLASS, AND SOME LABORATORY GLASSES
BY SODIUM HYDROXIDE AND SODIUM CARBONATE SOLUTIONS

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Alkaline solutions have an appreciable destructive effect on natural silicates and on manufactured silicate materials, in particular, glasses, their destructive action being exceeded only by that of hydrofluoric acid. In all kinds of preparative work, in precise analytical determinations, and in the operations of cleaning and degreasing the surface of glass apparatus, it is important to know the susceptibility of the particular glass to the action of alkaline solutions. The problem of stability to alkali forms a little-studied aspect of the corrosion of silicate glasses. Not only do various chemical phenomena occurring during the alkaline breakdown of glasses remain unexplained—e.g. "soda paradoxes" or the phenomenon of corrosion inhibition [1]—but erroneous views are widespread concerning the alkali-stability of the glasses with which physicists and chemists are constantly dealing in the laboratory. In particular, many incorrectly regard the thermally stable glass Pyrex as also highly stable chemically. A fairly prevalent view is that the best available glass for work with neutral and acid solutions is quartz glass, although it is inferior to many other glasses in its resistance to alkalis, and that complex silicate glasses are attacked by these substances to an extent that is directly proportional to the silica content. Data in recent literature, and also the data presented below, do not support these views. It is only quite recently that a group of glasses (zirconium-containing) has been discovered with alkali-stabilities equal to, or even greater than, that of quartz glass [2]. In most cases, however, quartz glass remains a material of very high chemical stability among silicate glasses.

At the basis of the destructive action of alkaline solutions on silicates lies the passage of silica into the soluble condition, which, in the case of quartz glass, can be conventionally represented as:

$$\text{SiO}_2 + 2\text{NaOH} \rightarrow \text{SiO}_4^{2-} + 2\text{Na}^+ + \text{H}_2\text{O}.$$  

Alkalis have the same action also on the polymeric silicon-oxygen anions entering into the composition of crystalline silicates and glasses, i.e. bring about their depolymerization and passage into solution in the form of relatively simple ions. In this process the cations of the glass form either hydroxides or silicates that are simpler in composition and are more highly hydrated than the silicates present in the original glass.

Views on the kinetics of the breakdown of glasses by alkaline solutions were developed by Berger and Geffcken [3], who considered that the action of alkali on silica begins with the adsorption of NaOH on its surface, an unstable compound being formed. The formation of this adsorption compound is rapid, requiring not more than one-thousandth of a second. This compound then breaks down with rupture of $$\text{Si} - \text{O} - \text{Si}$$ links and the formation of two bonds of the type $$\text{Si} - \text{O} - \text{Na}$$ and $$\text{Si} - \text{O} - \text{H}$$ in place of each original link. Breakdown of sufficient $$\text{Si} - \text{O} - \text{Si}$$ links results in complete breakdown of the crystalline lattice of the silicate—or of its equivalent in the case of glasses—and consequent passage of the broken-down material into solution. The breakdown of the adsorption com-
pound is a slow process, requiring but one second, according to Berger and Geffcken's estimate. The rate of this stage determines the rate of the breakdown process as a whole, and the specific effects of temperature, concentration, and stirring of the solution on the corrosion of glasses are also dependent on this stage.

Owing to the appreciable solubility of the corrosion products—hydroxides and silicates—when considered in relation to the small absolute amount of glass attacked, the final result of the action of the alkaline solution is the complete removal of substance from the surface down to a definite depth without formation of a residual protective layer of breakdown products, such as is formed in the action of acids or water [1]. Only in the corrosion of highly unstable glasses, when attacked to a depth of several microns, is the formation of an incrustation of hydrated silicates, carbonates, and other salts observed, though this does not retard further attack owing to its open structure. The alkali-stability of a glass, therefore, can be characterized accurately by the amount of glass dissolved. For the determination of this amount, use has been made in the past of gravimetric methods, either based on measurements of the loss in weight of the glass in the form of a piece of tubing, a flask, a plate, or powder, or based on determination of the weight of dry residue obtained on evaporation of the reagent used for the treatment of the glass. The low accuracy with which the very small loss in weight of samples of low specific surface can be measured, the phenomenon of "poisoning" of the reagent by breakdown products in the case of glass powders*, and the enormous correction for the value of the dry residue of the reagent itself all make it preferable to adopt the methods, based on interferometry, used for the measurement of the alkali-stability of glasses in 1935 by workers at the National Bureau of Standards (US) [5] and later by other workers. The only difficulty in the application of this method—the lack of availability of interferometers—has now been removed. Thanks to the efforts of the school of Academician V. P. Linnik, Soviet science has been enriched by several interferometers [6] of Soviet manufacture which are available for the ordinary laboratory. These include the microinterferometer IZK-46 and the interference microscopes MII-1 (high-precision) and MII-5 (simplified version). Although these instruments are intended mainly for the study of the highly reflecting surfaces of metals, they may be used without modification for the study of glass surfaces. If to these instruments we add Linnik's double microscope MIS-11, then we have the means of measuring the depths of breakdown of glass over a very wide range—0.03-60 μ— which more than covers the range of values with which we are concerned in the investigation of the alkali-stability of glasses.

These considerations prompted us to use the interference microscope MII-1 and the double microscope MIS-11 (for very highly corroded glasses) and determine with their aid the degree of breakdown brought about by alkaline treatments in quartz, quartz glass, and some laboratory glasses.

EXPERIMENTAL

The determination of the alkali-stability of glasses by the interferometric method amounts to the measurement of the thickness of the layer of glass dissolved by the alkaline solution by estimating the degree of distortion of the interference bands observed when the glass surface is examined in the interferometer. The bands are distorted at the boundary between the corroded and uncorroded sections of the glass surface. We obtained such a boundary by clamping polished (accurately within 2 — 1/2 bands) glass plates (20 x 20 x 10 mm) between two silver plates which could be drawn together by means of two silver screws (Fig. 1). Interlayers of soft rubber were placed between the glass and the silver plates. The samples were clamped so that a narrow strip of the surface, parallel to the edge of the clamp and about 0.5 cm² in area, was exposed below the interlayer. This exposed strip was subjected to the action of the alkaline solution. The assembly was placed in a silver beaker contained in an ultrathermostat that maintained the temperature constant within 0.1°. The appropriate alkaline solution (950 ml) was previously heated in the beaker. A rod fixed to one of the silver plates of the clamp was coupled with the shaft of a motor, so that the clamp itself could act as a stirrer. The motor was run at 200 r.p.m. In order to prevent evaporation of the water, the beaker was covered with a transparent plastic disc having a central hole to take the rod carrying the clamp. After the necessary time, the clamp was removed from the solution.

* This phenomenon, specific for the breakdown of glasses by alkaline solutions, was described by Geffcken [4].