

INFLUENCE OF WEATHER CONDITIONS ON GLASS PROPERTIES

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ABSTRACT

The goal of this study is to establish some of the most important natural factors that can lead to the corrosion of the glass. Unlike most materials, glass is very resistant to corrosion and in a sense it can be thought of as corrosion-proof. Nevertheless, under certain conditions, the glass is “chemically attacked”. The main environmental parameters examined are: temperature fluctuations, acidic environments, airborne pollutants (sulfur dioxide and carbon dioxide), UV-radiation and relative humidity. Under certain exposure conditions its optical properties, chemistry and structure are modified by different weathering processes. The extent to which the glass weathers depends strongly on the fate of cations which either occupy the places of hydrogen ions and stop the corrosion or react with airborne pollutants such CO₂ and SO₂ and form new crystalline phases (neocrystallization). The above mentioned phenomenon is moreover enhanced by the relative humidity of the environment the glass is exposed. Furthermore, temperature variations (thermal shocks) can also lead to neocrystallization as well, and affect the way radionuclides are released during corrosion. Finally UV-radiation favors the formation of Si-ions with lower valence and non-bringing oxygen ions which leads to glass cracking. Other variables including the thickness of the glass, any cracks or damages that the glass might have sustained prior to the testing can also affect the rate at which glass decays. Last but not least, the type and the age of the glass are additional parameters that should not be overlooked and their effect on all factors must be examined and taken into consideration. Of particular interest is the relative humidity of the exposure environment. The exposure of glass in a dry environment instead of a humid one could impede glass decay since the time of hydration is inversely proportional to hydration rate squared. Moreover from a chemical perspective the glass appears unweathered if the hydrogen ions sites are saturated with the cations released from the non-bringing oxygen sites. Additionally, glasses can be protected by coatings such as epoxy resins.

Keywords: weathering, glass, degradation, corrosion mechanisms, analytical techniques.

INTRODUCTION

Unlike most materials, glass is very resistant to corrosion and in a sense it can be thought of as corrosion-proof. Nevertheless, under certain conditions, the glass is “chemically attacked”. The chemical composition of a glass is the key factor in the interaction of glass with

the environment. Under certain exposure conditions its optical properties, chemistry and structure are modified by different weathering processes.

The interest in glass corrosion or glass weathering comes from the need of scientists to understand the stability of glass containers used for food or drugs, sheet glass as well other glasses old or new subject to the

environment and other extreme conditions. A detailed understanding of the stability of glasses toward liquid or atmospheric attack is of considerable importance for preserving numerous objects of our cultural heritage. [1, 2].

Glasses produced in the ancient periods (Egyptian, Greek, or Roman glasses), as well as modern glass, can be classified as soda-lime-silica glasses. In contrast, potash was used as a flux in medieval Northern Europe for the production of window panes for churches and cathedrals. The particular chemical composition of these potash-lime-silica glasses (low in silica and rich in alkali and alkaline earth components), in combination with increased levels of acidifying gases (such as SO_2 , CO_2 , NO_x , or O_3) and airborne particulate matter in today's urban or industrial atmospheres, has resulted in severe degradation of important cultural relics, particularly over the last century [5].

Defining the general term *corrosion* is the deterioration of a (glass) material caused by external or internal factors leading to a more or less complete loss of its aesthetics, functionality, structure or shape. The *weathering* of glass comprises the degradation of glass by atmospheric pollutants, such as acidifying gases or airborne particulate matter. This can then be seen as a special type of corrosion and is therefore often referred to as *atmospheric corrosion* [10].

CORROSION MECHANISMS

If we consider glass as a monophasic ceramic material we cannot assume that it behaves as a single chemical compound. However, we can, approximately, treat the dissolution of the individual phases separately. This means we can study the kinetics and the dissolution mechanism of each phase separately.

Four are the main mechanisms for studying the corrosion of crystalline as well as glassy materials:

i) Congruent dissolution by simple dissociation. The ratios of the various elements in the solution match those of the dissolving solid. This reaction is not pH dependent and when at equilibrium it reaches a saturation limit. As the crystals dissolve the surface of the crystals, not necessarily uniformly, retreats. The dissolved crystals do not form a protective layer on the crystal surface.

ii) Congruent dissolution by chemical reaction. The dissolution in this case is caused by an acid-base or a hydrolysis reaction. There are no solid reaction prod-

ucts and therefore no protective layer formation. In low pH values the hydrogen ions directly attack the crystal whereas in neutral pH values hydrolysis is the prevailing phenomenon. The surface of the solid retreats uniformly.

iii) Incongruent dissolution with the formation of crystalline reaction products. When the crystals react with the dissolution medium a new solid phase is created. The composition of this solid phase differs significantly from the original's one. This means that the ratio of the dissolved species is different than that of the parent solid. The rate of the reaction is fast and the retreating interface is very sharp.

iv) Incongruent dissolution with the formation of non-crystalline layers. The reaction product has different chemical composition from the parent solid but certain structural entities such as hydrolyzed or polymerized silica remain. This leads to the formation of a non-crystalline product often referred to as the "gel layer". The "gel layers" acts as a protective medium to the chemically attacked surface and in some cases allows it to "heal" itself.

v) Ion exchange (selective dissolution). In this type of reaction the mobile ions are leached but the parent material remains relatively unharmed. The original matrix keeps its dominant ions ratio although its secondary and most mobile ions continue to leach through the matrix. The ion exchange reaction and the "gel layer" formation reaction cannot easily differentiate with each other when they happen. Also, it has been observed some congruent dissolution as a background reaction [1].

ENVIRONMENTAL PARAMETERS

Temperature fluctuations

The main concern when ceramics and glasses are exposed at extreme temperatures, or better thermal shocks or cycles, is their resistance to it. The various temperatures at which the glasses are exposed in the environment can affect its properties and structure. Talking about thermal shock fracture we know that is caused by transient thermal stress generated during sudden temperature change. Many analytical models were proposed to predict the critical temperature change ΔT_C and the residual strength using fracture mechanical approaches.

According to W. White the rate of the dissolution reaction obeys the Arrhenius Rate Law (1):

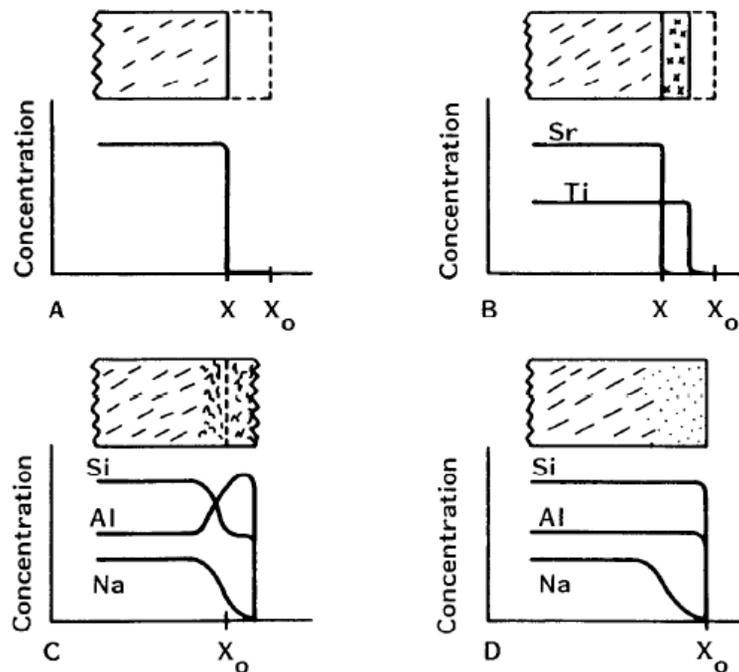


Fig. 1. Dissolution mechanisms for ceramics and glasses A) Congruent dissolution with uniform retreat of dissolving interface, B) Incongruent dissolution with reaction product remaining in place, C) Corrosion of surface by chemical reaction between solvent and solid, D) Leaching of sodium aluminosilicate glass [1].

$$Rate = Aoe^{-Ea/RT} \quad (1)$$

The loss of ions from the glass matrix is increasing exponentially with the increase of temperature. The activation energy E_a differs among the various types of reactions. More specifically diffusion processes need very low energy in order to occur, surface reactions typically on the order of 80KJ/mol and neocrystallization several hundred KJ/mol. Figure illustrates the rate of silica loss from crystalline quartz, silica glass and tektite glasses as a function of temperature [1].

Hasselmann *et al.* also predicted thermal fatigue life of soda-lime-silica glass from a slow or subcritical crack growth (SCG) concept. Kamiya and Kamigaito discussed the SCG law together with Weibull probabilistic failure. They concluded that thermal fatigue life is approximately proportional to ΔT^{-n} , where n represents a crack propagation exponent in the SCG law, by assuming that crack length at failure is sufficiently larger than the initial one.

The above assumption does not remain true when the critical crack length has the same order as the initial crack length, or thermal shock fatigue life is relatively short.

The higher temperature results reinforce the assumption that the formation of crystalline phases on the glass surface can influence the dominant process by which the glass corrodes (diffusion vs. ion exchange and hydrolysis) and the type of layers that are formed (water-containing glass vs. reacted layers). The nature of the reacted layers or altered glass can ultimately affect how radionuclides are released during the corrosion process. [1, 8, 10, 12].

pH influence

When the pH rises, with values ranging above 7 ($pH > 7$), that is an alkaline environment the type of the mechanism changes and shifts to congruent dissolution. In this scenario the glass structure is strongly affected since fragments of the network are lost. The creation of craters and pits of different size, depth and interconnection degree are usually observed via Scanning Electron Microscopy and Atomic Force Microscopy.

Although all types of glasses are affected by pH the rate by which each type is deteriorates varies. In more resistant glasses, the attack is slower and products generated are accumulated during more time on the surface; while less resistant ones are quickly attacked

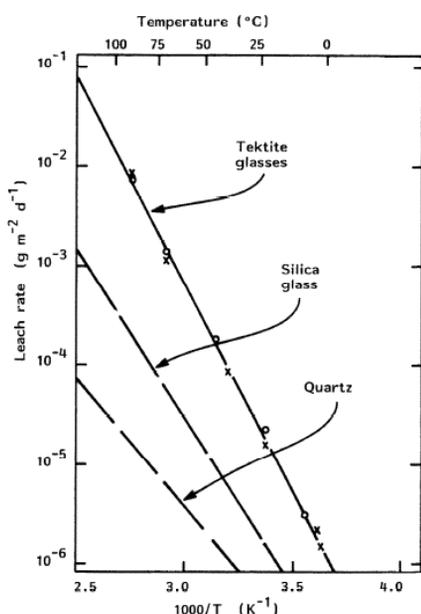


Fig. 2. Rate of silica loss from various types of glasses as function of temperature [1].

and form thick alteration layers which are detached little by little, leaving the glass successively unprotected. Once exposed to the aqueous medium, the glass is quickly attacked again and all the process is repeated. Thus, the glass will be gradually “dissolved”. When the number of cycles is high enough, the attack rate may decrease due to the formation of a thick alteration layer impregnated with salts, which would hold up diffusion of the bath water, thereby producing a stationary situation.

In this figure we can see that the dissolution of silica is increasing exponentially after treating the glass with a solution which pH is above 7. The influence of pH is more indirect in alkaline solutions since the specimens of clear and amber glass were exposed only for 30 minutes.

The pH influence on glass becomes more complex if we assume there are two types of systems; open and closed systems. Dissolution in closed system continues until the solution reaches a saturation point. In this case during the reaction of the surface of the glass the consumption of hydrogen ions leads to a gradual increase in the value of pH, causing the dissolution rate to decrease. Furthermore, the dissolution rate decreases by the creation of leach layers which become thicker as the phenomenon continues. On the other hand, when studying open systems, where the pH is buffered or auto-

matic controlled to maintain a constant value we can observe that the rate of dissolution is more stable [4].

It has been reported that the addition of CaCl_2 to NaOH solution drastically reduces the glass attack by forming an insoluble Ca–Si-layer. An increasing alkalinity of the solution leads to an enhanced deposition of calcium on the surface of glass plates made of pure SiO_2 . The treatment with pure CaCl_2 did not cause a calcium deposition on the glass surface. The inhibiting effect of calcium in alkaline solution was also found. Other metal ions also reveal inhibiting effects on glass corrosion.

Airborne Pollutants

Studies indicate that environmental pollution with 5 ppm SO_2 or 1 ppm NO , does increase the rate at which glass corrodes by a factor of approximately 3 as compared to glass exposed at the same temperature and RH in an ambient of laboratory air. There was no indication that these two pollutants interact to give a synergistic effect. The hydration rate was found to increase with increasing SO_2 concentrations up to a saturation SO_2 level of approximately 3 ppm at which the hydration rate remained constant at about three times that observed in clean air. Hydrogen concentration profiles in samples exposed to polluted environments did not differ noticeably in shape from those measured in samples exposed to clean moist air or liquid water in any respect. This effect is compounded in glass compositions. In glasses not subject to cracking, the leaching of alkali ions from the surface of the glass results in a depleted region which behaves as a diffusion barrier. However, cracking provides access to a fresh (alkali ion rich) surface in which the process can begin again. Therefore, although the ionic inter-diffusion process progresses as the square root of time, the decay process will progress linearly in time for glass in which cracking occurs. For these glass types, an increase in the hydration rate is even more detrimental [5,13].

Fig. 6 presents a simplified scheme for the physical and chemical processes of the atmospheric weathering of glass surfaces. Under typical ambient conditions, a thin water layer is formed on the glass surface as a result of the condensation of air moisture or by rain causing an ion exchange between hydrogen-bearing species from the water film and the network modifier ions of the glass similar to the aqueous corrosion

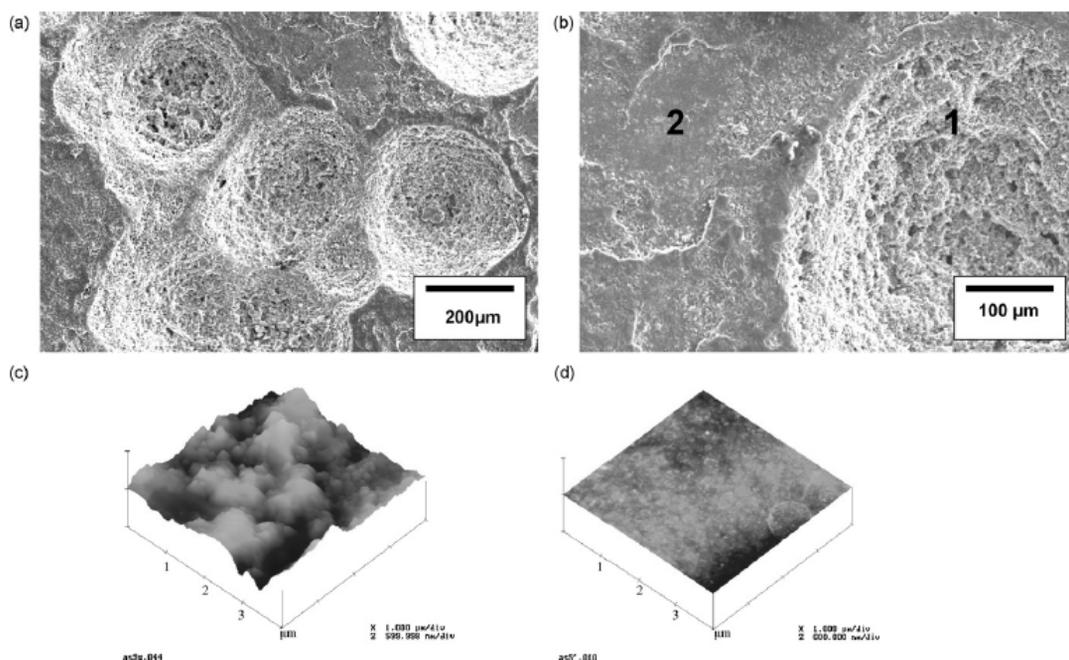


Fig. 3. SEM and AFM images of historical glass [3].

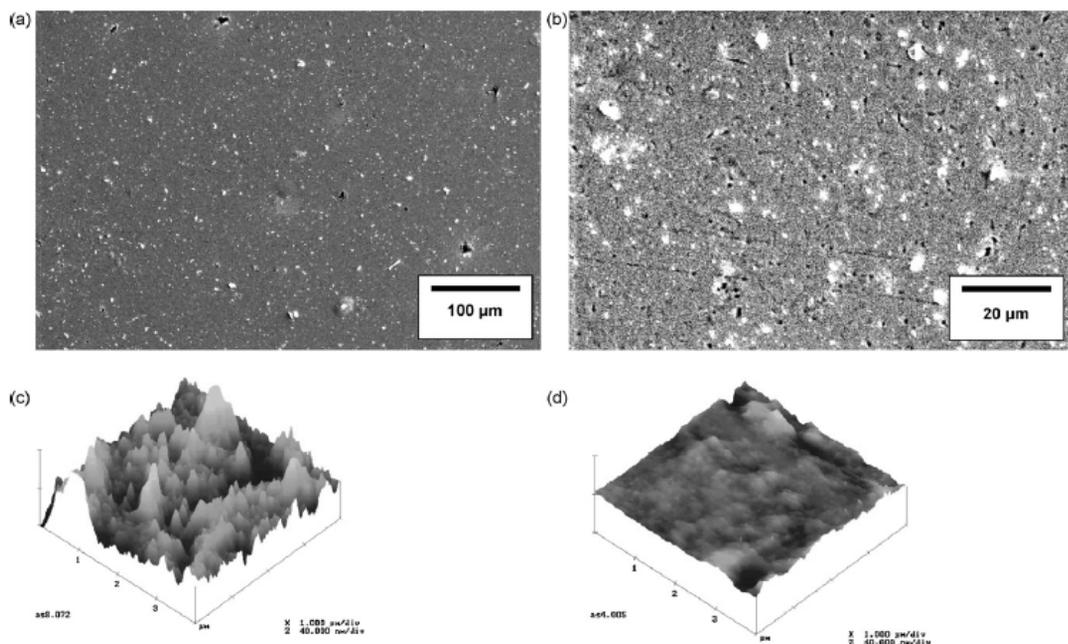


Fig. 4. SEM and AFM images of model glass [3].

of glasses. Atmospheric pollutants such as SO_2 , CO_2 , or O_3 or airborne particulates can dissolve in this water film causing a decrease of its pH and hence an enhancement of the ion diffusion. Increasing temperatures (or a decreasing humidity) may cause evaporation of this film and precipitation of crystalline weathering products on the glass surface. The chemical composition of these weathering products is there-

fore determined by the glass composition and the atmospheric pollutants [5].

Relative Humidity - Vapor

In general glasses can be hydrated and then re-crystallize when in direct contact with water. Easily leachable and mobile elements from the glass matrix, usually alkalis and alkaline earth elements, built-up on the hydrated surface and form a layer. The glass surface

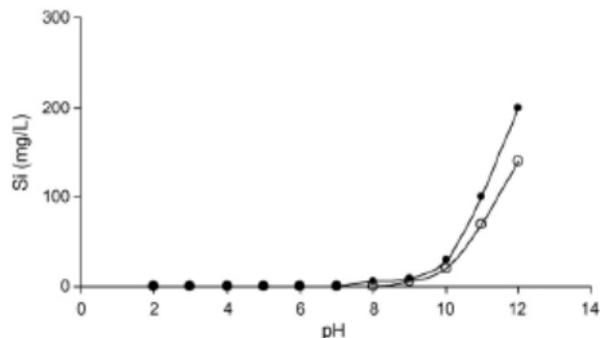


Fig. 5. pH – Si dissolution correlation diagram [4].

will be attacked in the local areas where crystals have formed leading to a pitted surface. RH levels in the environment were found to have a more dramatic effect on the hydration rate than did the levels of SO_2 or NO . Over the range of RHs investigated, (15-100(X)), the hydration rate increased by a factor of 10. The thickness (s) of the altered layer on the surface of the glass is proportional to the square root of exposure time (\sqrt{t}) and the hydration rate (k), i.e. $s = k\sqrt{t}$. Therefore, the time it takes for hydration to progress into the glass to a given depth is inversely proportional to the hydration rate squared. Hence, increases in the RH can have a dramatic effect on the time it takes to hydrate a glass to a given depth. If the hydration rate increases by a factor of 10 the time it takes for a stained glass window to decay to a certain depth decreases by a factor of 100.

The combination of water and temperature leads to vapor which enhances the recrystallization of the glass surface by the formation of many small crystals.

The importance of SiO_2 -coatings has recently grown for a wide range of optical, photovoltaic, and pharmaceutical products. During a product's lifetime these coatings interact with water intermittently (weathering, cleaning cycles) or continuously (chemical reactors, containers). Therefore, the hydrolytic resistance is an important issue and respective investigations are necessary, as the hydrolytic resistance of coatings is supposed to be significantly different from the corresponding solid or grain material (e.g. the surface to volume ratio and morphology) [1,13,14].

UV-radiation

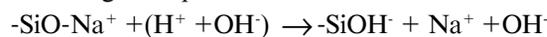
UV-radiation favors the formation of Si-ions with lower valence and non-bridging oxygen ions which leads to glass cracking. However rainfall or rinse water "wets out" and spreads across the glass surface, carrying away

organic contaminants - such as traffic pollution and bird droppings – that have been oxidized or broken down by a 'photocatalytic' reaction triggered by ultraviolet (UV) rays from sunlight. This chemical reaction process clearly requires sunlight but it also needs water, which can be either rainfall or hosing down the glass, to both oxidise and wash away organic contaminants. The oxidation process does not break down inorganic contaminants such as limescale or metal oxides [1, 5, 10].

Influence of the combination of weathering factors

Degradation carried out by the combination of gaseous acid pollutants (like SO_2 and NO_x) and humidity is a kind of chemical attack performed under acid pH, which can become one attack under basic pH, due to the progressive enrichment in alkaline ions and hydroxyl groups leached from the glass network during the acid attack. The extent to which the glass weathers depends on the fate of alkali ions once released from the glass structure. If the alkali ions are released from the nonbridging oxygen sites in the glass and occupy sites previously filled by hydrogen ions (either on the surface or in the glass), then once the available sites are saturated, the reaction must stop and the glasses will appear unweathered. If the alkali reacts with gases such as CO_2 , Cl_2 , or SO_2 to form crystalline phases, then the reaction can continue and the glass will appear weathered. The precipitates act as an alkali sink, and continued weathering can lead to hydrolysis of the glass and subsequent cracking and spalling.

The interaction of an aqueous medium with the glass surface is characterised by different stages. The first stage involves an ion exchange of alkaline ions from the glass surface (Na^+ , K^+) by H^+ ions from the water following the equation.



Simultaneously, water molecules soak the silica gel layer formed producing a light swelling due to the increase of the structural volume. The second stage is the attack of hydroxyl ions (OH^-), which have been released in the aqueous medium, to siloxane bonds of the glass network following the equation.



The Si-O-Si bonds breakdown and generate silanol groups ($-\text{Si}-\text{OH}$) and non-bridging oxygen groups ($-\text{Si}-\text{O}-$). This implies gradual destruction of the glass network, which starts on superficial small defects, giving

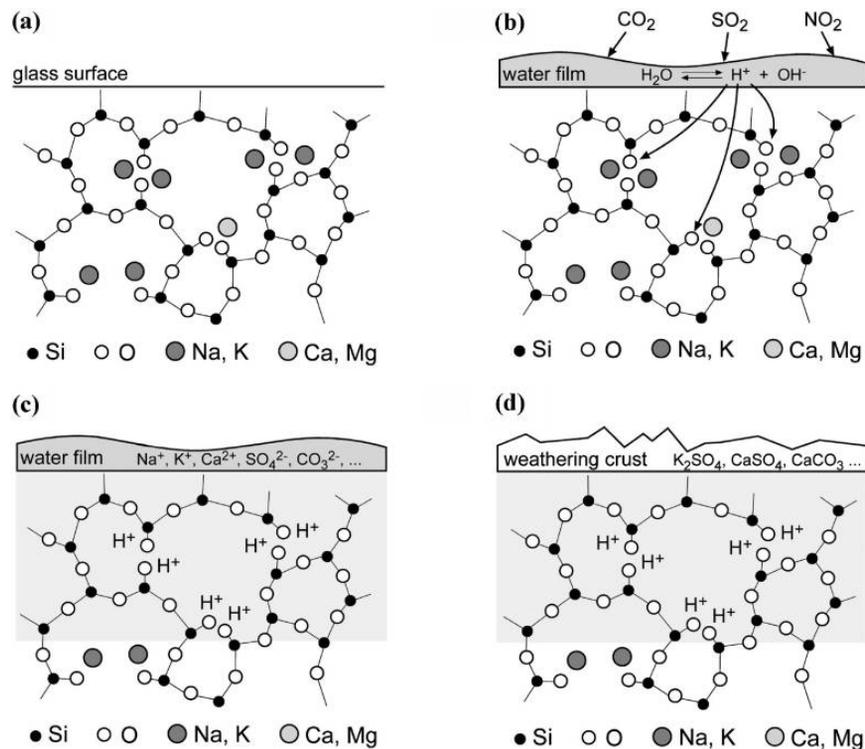
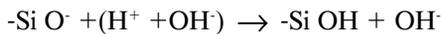


Fig. 6. Glass weathering process starting from a clean surface (a), a formation of a water film (b), a leached layer containing hydrogen (c) and crystalline weathering products on the glass surface [5].

rise then to pits and craters. In a latter stage ($-\text{Si O}^-$) groups may react with other water molecules following the equation:



giving rise to more silanol groups and hydroxyl ions which make, turns, the aqueous medium increasingly basic. Thus, the pH of water increases considerably because of the high concentration of OH^- ions and the water attack starting at neutral pH (pH = 7) becomes a more aggressive attack in a basic medium (pH > 7). For this reason, the initial pH of the aqueous medium as well as its dynamic evolution are key factors to determine both the type of attack suffered by glasses and the chemical damage produced.

When such a kind of chemical degradation occurs, the glass surface appears covered by pits and craters of different size, depth and interconnection degree. In addition, insoluble deposits from corrosion products are filling the craters and/or are extended throughout the whole glass surface, forming a more or less thick crust that decrease the original transparency of the glass piece or change its original colouring. Along the centuries the stained glasses have suffered deep alterations, which always start on their surface due to the interaction with

the environment. For this reason the characterisation of such alterations and their correlation with the originating mechanism are essential.

The hydrolysis of SiO_2 -rich materials as a function of temperature, pH, and time has been the subject of considerable research. In most cases the entire reaction is presumed to be surface controlled. One possible description of the respective steps is already $\text{SiO}_2 + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 2\text{H}_2\text{O}^*$ activated complex $\pi 1$ or $(\text{SiO}_2 \cdot 2\text{H}_2\text{O})^* \rightarrow \text{Si}(\text{OH})_4$

The dissolution behaviour of various SiO_2 -modified materials has been investigated over the last years, e.g. quartz in water, amorphous silica in water and chloride solution or in highly alkaline environment, silica nanoparticles and silica glasses.

This phenomenon can also affect protected with coatings glasses. The importance of SiO_2 -coatings has recently grown for a wide range of optical, photovoltaic, and pharmaceutical products. During a product's lifetime these coatings interact with water intermittently (weathering, cleaning cycles) or continuously (chemical reactors, containers). Therefore, the hydrolytic resistance is an important issue and respective investiga-

tions are necessary, as the hydrolytic resistance of coatings is supposed to be significantly different from the corresponding solid or grain material (e.g. the surface to volume ratio and morphology) [1, 4-6,10,14].

Analytical techniques

Rapid developments in the fields of microelectronics and computer sciences, however, have contributed to the development of a variety of non-destructive, surface analytical techniques for the scientific investigation and material characterization of these unique and valuable objects. These methods include scanning electron microscopy in combination with energy or wavelength-dispersive spectrometry (SEM/EDX or SEM/WDX), secondary ion mass spectrometry (SIMS), and atomic force microscopy (AFM). In this account, we address glass analysis and weathering mechanisms, exploring the possibilities (and limitations) of modern analytical techniques.

Atomic Force Microscopy (AFM)

AFM is a non-destructive and non-invasive direct observation technique in which previous preparation and handling of the sample is not required. It investigates the possibilities to point out the pathologies derived from different corrosion and weathering processes. The results to be obtained will be the first approach to build further a data base about the interrelation between topography, morphological microstructure, chemical composition of glasses and their degradation mechanisms.

Up to now this technique has been moderately used in the study of historical glasses, whereas its powerful possibilities have been proved in the last years for a wide variety of materials [3,5].

Scanning Electron Microscopy (SEM)

SEM images from the external surface of a glass can show the deep craters sometimes interconnected upon a stratified surface. EDX analyses can determine the element content. If a silica decreasing is observed, compared with the percentage found in the bulk glass then relative high amounts of calcium and sulphur might be detected, which could indicate the formation and precipitation of calcium sulphate. Probably, this is the result of the interaction between the environmental SO_2 with the calcium ions leached from the glass network during a degradation process occurred under the

sequence of acid and alkaline pH. Firstly SO_2 and/or SO_3 are combined with humidity to form H_2SO_4 , which start the acid attack to the glass network.

As a consequence the ion-exchange between H^+ from the acid environment and alkaline ions (e.g. Na^+ or K^+) from the glass takes place, and silanol groups Si-OH are generated in the glass surface. This causes the local increasing of the pH in the glass surface due to the presence of OH^- ions from dissociated water and alkaline ions leached. These chemical species are the responsible for the attack under alkaline conditions, in the sequence of acid and alkaline pH, which occurs breaking down siloxane bonds Si-O-Si and $\text{Si-O-} \dots \text{Ca}^{2+} \dots \text{O-Si}$ links. The result is the leaching of Ca^{2+} ions towards the glass surface where, once combined with atmospheric CO_2 , precipitates as a carbonate, which is further displaced by sulphate ions forming calcium sulphate. If EDX analyses demonstrate a decreasing in the Na_2O and K_2O percentages, related to such contents in the bulk glass a surface dealcalinisation took place, while the relative amount of silica increased [5].

Secondary Ion Mass Spectrometry (SIMS)

SIMS is based on the bombardment of a sample surface with a high energy ion beam of, for example, Ar^+ , Ga^+ , O_2^+ , Cs^+ , or O and the subsequent detection of the eroded material ions accelerated into a mass spectrometer. This technique is especially suitable for measurements of depth profiles of certain elements/masses (e.g., detection of hydrogen, alkali, or alkaline earth ions in corroded or weathered glasses). Outstanding features of SIMS are the capability of detecting all elements of the periodic table and the very low detection limits in the nanogram per gram region. [5]

A nuclear reaction analysis (NRA)

NRA technique is used to measure the hydrogen concentration as a function of depth and the hydration rate is determined from these measurements. Rutherford Backscattering Spectrometry (RBS) was used to measure alkali ion profiles. Combining these two techniques gives valuable insight into the mechanism behind glass decay.

Examples of corrosion of various types of glasses

Lead crystal glasses experience an intense decay process, which becomes more acute when the per-

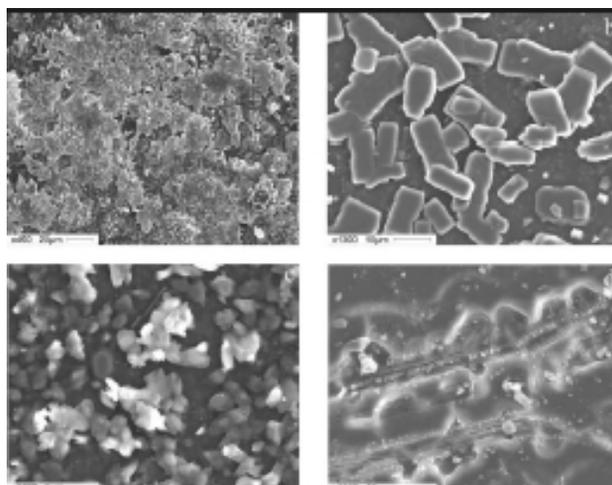
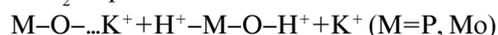


Fig. 7. SEM images of weathering phenomena of glasses after exposure to ambient conditions [5].

centage of PbO increases. The higher the content of PbO, higher is the amount of Pb^{2+} ions leached from the glass network. The leached Pb^{2+} ions could form firstly lead hydroxide, which, in fact, is a non-stoichiometric hydrated oxide. Then, due to the high concentration of salts into the bath, lead salts or plumbates can be formed since they are soluble in the simulated marine medium when pH has raised up to basic values after the ageing cycles. Plumbates of alkaline metals, such as sodium or potassium (highly abundant in the salts bath), are stable and there could exist into the bath, thereby stabilising the lead ions in the solution. This is a typical example of the Congruent dissolution by simple dissociation mentioned at the beginning of this presentation.

Phosphate glasses frequently have poor chemical durability in aqueous solutions. The molybdenum is potentially of greater interest as it can occupy both octahedral and tetrahedral sites, and is susceptible to exhibit different oxidation states. MoO_3 oxide is able to participate to the formation of material's network either in crystalline or vitreous states. Molybdophosphate glasses ensue since it forms water soluble, but otherwise stable, glasses over a wide and continuous compositional range. Although work on phosphate glasses has been reported in recent years, specific information pertaining to the mechanism of glass dissolution and other glass properties are lacking. Among the numerous previous investigations of molybdophosphate glasses we may cite the study of molybdenum phosphate glasses containing Ag_2O or K_2O . The mechanism of the dissolution $\text{K}_2\text{O}-\text{MoO}_3-\text{P}_2\text{O}_5$ glasses can be described in a two-

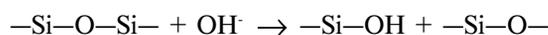
stage process: at first, an ion-exchange between the network modifier K^+ ions in the glass and H^+ , H_3O^+ and/or H_2O species from the solution can be observed:



The ions are diffusing in opposite directions, leading to the formation of a so-called leached or gel layer in the glass, which is depleted in potassium and enriched in hydrogen bearing species. In the second stage of the dissolution process the former network breaks down. From the determination of the concentrations of P_2O_5 and MoO_3 in the leachate solution it is indicated that leaching of the ternary glasses is selective rather than congruent dissolution.

Referring to **glass fiber** reinforced composites, they are frequently subjected to corrosive media. Such situations arise during application of these composites in sewage pipes, structural components in chemical plants, boats, and others. In the case of structural elements of glass fiber reinforced concrete, the matrix itself presents a corrosive environment (pH-value >12.5). Therefore, the high demands on reinforcing glass fibers require detailed knowledge about quality regarding chemical resistance and strength. The long term chemical resistance of glass and mineral fibers cannot be explicitly measured or determined. For this reason, glasses are generally compared to each other after accelerated aging at fixed or at least comparable experimental conditions. The rate of corrosion depends on numerous parameters such as temperature, aging time, chemical constitution of the glass, but also on the chemical composition of the aging solution. Furthermore, the glass fiber sizing applied during spinning influences the corrosion process by forming a protective coverage on the surface. This thin sizing film, which is typically a few tens of nanometers in average thickness, basically consists of an organo-silane coupling agent, a polymer film former and a lubricant. These influencing factors lead to variable properties of the final glass fibre. Unfortunately, a major problem exists with respect to the discrepancy between estimated and predicted fiber properties. It is well-known that the measured tensile strength of glass fibres is significantly lower than its theoretical value. This is evidently due to pre-existing defects, which show multiple populations with varying depth. Besides protection from moisture attack sizing treatment is believed to improve the mechanical properties due to the formation of a three dimensional network of

polysiloxane. Obviously, this healing effect is associated with a disappearance of the population of severe surface flaws by blunting the crack tips. The corrosion in alkaline media is mainly controlled by the dissolving of the SiO₂-network, and not by diffusion like in acid media. The hydroxyl ions of the solution disrupt the siloxane bonds in the glass and, as a consequence, silicates migrate into solution



Alkali silicate glasses belong to a family of materials that have seen wide use in applications that include the production of ceramics, constituents in paints, sealing pipes and other systems with fluid flow and even as an egg preservation agent. These materials have not seen wider use in electronics because they tend to have high ionic mobility that would lead to corrosion. ASG materials are water based (dissolved in aqueous solutions); they look like water and cure when water is removed by evaporation, leaving a solid glass material. Thus, they can be applied under atmospheric pressure, in a variety of methods, and processing temperatures can be as low, or lower than, the cure temperature of many conventional organic materials. Once cured, the glass layer can be quite robust as well as impermeable to moisture. It is well known that diffusion and ionic conductivity of binary alkali silicate glasses increases with increasing ion concentration. For this reason, high alkali containing glasses are generally avoided for use in electrically insulating applications. However, ion mobility can be drastically reduced by exploiting the "mixed alkali effect". While there is no universally accepted theory that explains the mixed alkali effect, it is recognized that the use of multiple alkali, especially those with a larger mismatch such as potassium and lithium, can reduce the ionic mobility of alkali silicate glasses by five orders of magnitude or more.

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