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Efficiency of cleaning solutions to remove difficult contamination
on weathered float glass exposed in an urban environment

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Abstract

This study investigates the removal of different contaminants on soda-lime float glass weathered artificially and naturally. Organic, inorganic non-metallic, metallic, and saline contaminants were selected to evaluate the degradation of float glass in contact with them. Bird droppings, cement dust, aluminum particles, and sodium chloride were deposited on the glass surface. The four contaminants altered the glass surface to varying degrees. Glass samples were weathered in a climate chamber for one and seven days. Another set of glass samples was exposed outdoors in Ilmenau, Germany, for 50 days (20 days unsheltered and 30 days sheltered). Before and after the weathering, the glass samples were cleaned with three cleaning agents (DI water, citric acid, and a commercial glass cleaner). The chosen cleaning solutions provided different cleaning results for the glass surfaces. Depending on weathering exposure (artificial or natural), contaminants seem to affect glass surfaces differently. During outdoor weathering, deposits adhere differently to the glass surface treated with different cleaning solutions. In addition, the effectiveness of a commercial protective agent is compared with the chosen cleaning agents. Optical microscopy was used to localize weathering products and evaluate glass surface degradation. Energy-dispersive X-ray spectroscopy (EDX) and Auger electron spectroscopy (AES) were used to identify chemically the unremoved weathering products. Surface analysis indicated the presence of chlorides and carbonates on the weathering products and more considerable delamination effects on glass naturally exposed under shelter conditions. It has been evaluated that the cleaning agents have influenced the removal of contaminants and the glass durability differently.

Resumen

Este estudio investiga la remoción de diferentes contaminantes en el vidrio flotado soda-lime envejecido artificial y naturalmente. Se seleccionaron contaminantes orgánicos, inorgánicos no metálicos, metálicos y salinos para evaluar la degradación del vidrio flotado en contacto con ellos. Se depositaron en la superficie del vidrio excrementos de aves, polvo de cemento, partículas de aluminio y cloruro de sodio. Los cuatro contaminantes alteraron la superficie del vidrio en distintos grados. Las muestras de vidrio se envejecieron en una cámara climática durante uno y siete días. Otro grupo de muestras de vidrio se expusieron al aire libre en Ilmenau (Alemania) durante 50 días (20 días sin protección y 30 días con protección). Antes y después de la exposición, las muestras de vidrio se limpiaron con tres agentes de limpieza (agua destilada, ácido cítrico y un limpiador comercial). Las soluciones de limpieza elegidas proporcionaron diferentes resultados de limpieza para las superficies de vidrio. Dependiendo de la exposición (artificial o natural), los contaminantes parecen afectar a las superficies de vidrio de manera diferente. Durante la exposición a la intemperie, los depósitos se adhieren de manera diferente a la superficie del vidrio tratado con diferentes soluciones de limpieza. Adicionalmente, se compara la eficacia de un agente protector comercial con los agentes de limpieza elegidos. Se utilizó la microscopía óptica para localizar los productos del envejecimiento y evaluar la degradación de la superficie del vidrio. Se utilizó la espectroscopia de Rayos X de energía dispersiva (EDX) y la espectroscopia de electrones Auger (AES) para identificar químicamente los productos de meteorización no eliminados. El análisis de la superficie indicó la presencia de cloruros y carbonatos en los productos de meteorización y efectos de delaminación más considerables en el vidrio expuesto de forma natural en condiciones de refugio. Se ha evaluado que los agentes de limpieza han influido de forma diferente en la eliminación de los contaminantes y en la durabilidad del vidrio.

Zusammenfassung

In dieser Studie wird die Reinigung verschiedener Verunreinigungen auf künstlich und natürlich verwittertem Kalk-Natron-Floatglas untersucht. Es wurden organische, anorganische nicht-metallische, metallische und salzhaltige Verunreinigungen ausgewählt, um mögliche Schäden an Floatglas bei Kontakt mit diesen zu untersuchen. Vogelkot, Zementstaub, Aluminiumpartikel und Natriumchlorid wurden auf der Glasoberfläche aufgebracht. Die vier Verunreinigungen veränderten die Glasoberfläche in unterschiedlichem Maße. Die Glasproben wurden in einer Klimakammer einen und sieben Tage lang bewittert. Eine andere Gruppe von Glasproben wurde in Ilmenau, Deutschland, 50 Tage lang im Freien gelagert (20 Tage ungeschützt und 30 Tage geschützt). Vor und nach der Bewitterung wurden die Glasproben mit drei Reinigungsmitteln gereinigt (DI-Wasser, Zitronensäure und ein handelsübliches Glas reinigungsmittel). Die gewählten Reinigungslösungen lieferten unterschiedliche Reinigungsergebnisse für die Glasoberflächen. Je nach Bewitterungseinwirkung (künstlich oder natürlich) scheinen sich die Verunreinigungen unterschiedlich auf die Glasoberflächen auszuwirken. Bei der Bewitterung im Freien haften Ablagerungen unterschiedlich auf der mit verschiedenen Reinigungslösungen behandelten Glasoberfläche. Darüber hinaus wird die Wirksamkeit eines handelsüblichen Schutzmittels mit den gewählten Reinigungsmitteln verglichen. Die optische Mikroskopie wurde genutzt, um Bewitterungsprodukte zu lokalisieren und die Veränderung der Glasoberfläche zu bewerten. Energiedispersive Röntgenspektroskopie (EDX) und Auger-Elektronen-Spektroskopie (AES) wurden zur chemischen Identifizierung der nicht entfernten Verwitterungsprodukte eingesetzt. Die Oberflächenanalyse wies auf das Vorhandensein von Chloriden und Karbonaten aus den Verwitterungsprodukten hin und auf größere Delaminierungseffekte bei Glas, das unter einer Schutzabdeckung dem Wetter ausgesetzt war. Es wurde festgestellt, dass die Reinigungsmittel die Entfernung von Verunreinigungen und die Haltbarkeit des Glases unterschiedlich beeinflusst haben.

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1   Introduction

Glass is a durable non-crystalline material that exhibits a near-range order. Float glass is broadly used in architecture, automotive, and photovoltaic industries due to its optical, mechanical, and chemical properties. "Float" refers to the glass manufacturing process, where liquid glass floats on a long molten tin bath under controlled heating and cooling. The main components of soda-lime glass are silicon dioxide, sodium oxide, calcium oxide, aluminum oxide, and magnesium oxide. Soda-lime glass is stable to environmental influences because it has a good network arrangement [1,2]. Despite its high chemical resistance, soda-lime float glass can be compromised when exposed to liquid media.

Glass corrosion mechanisms are based on the interaction between the glass surface and water [3,4]. Before glass corrodes, two main mechanisms occur: gel layer formation (ion exchange) and network dissolution. During ion exchange, cations are replaced by hydrogen (H^+) ions [5,6]. After ion exchange, a hydrated surface layer (gel layer) is formed, protecting the glass from further corrosion [7,8]. Network dissolution occurs in solutions with high pH (pH > 9). Hydroxide ions (OH^-) present in the solution break the Si-O-Si bonds, causing the glass to dissolve [9].

Glass degradation studies usually involve outdoor exposure or weathering experiments under climatic chamber parameters [10,11]. In artificial weathering, float glass is mainly exposed to certain well-defined types of sand, such as Sahara dust, at a specific temperature and humidity [12–14]. In natural weathering, glass alteration is caused by the interaction between environmental conditions and the glass surface [15]. Factors affecting glass weathering include temperature, humidity, pH, rain, and pollutants.

High temperatures accelerate corrosion mechanisms [16], and temperature variations also alter glass structure [17]. Water molecules enter the glass faster when exposed to a humid environment [18,19]. More alkali ions are leached from the glass surface, and the thickness of the leached layer increases with increasing humidity [20]. At a low pH of less than nine, the leaching of ions predominates; therefore, a gel layer is formed, and network dissolution is enhanced at a high pH of more than nine. Rain washes away some contaminants leading to a prevention to further reactions on the glass surface, but self-cleaning is insufficient to remove all contaminants.

In a humid environment, a thin water film forms on the glass surface. Atmospheric gases such as SO_2, CO_2, and NO_2, as well as particles present in the air, can deposit and dissolve in the water film reacting with the leached ions, K^+, Na^+, Ca^{2+}, coming from the glass, forming weathering products such as carbonates, sulfates, nitrates, and chlorides on the glass surface [21–23]. After the water film evaporates, a weathering crust is observed on the glass surface. The most common weathering products include salt deposits, delamination, color alteration, iridescent films, and dried water droplets [24–26]. From which, delamination is a very severe effect that is irreversible.

This study focuses on four contaminants commonly found in rural and urban environments: bird droppings, cement dust, aluminum particles, and sea salt. They are deposited on the glass surface, and glass samples are exposed in a climate chamber (80 °C, 80 % R.H) and outdoors (unsheltered and sheltered) to compare the chemical attack on the float glass. For comparative purposes, the cleaning agents have also been applied on glass exposed for a much longer time than this study duration. Atmospheric contamination cannot be avoided; therefore, cleaning is required to slow down or reduce glass degradation. It has been shown that cleaning before weathering reduces degradation, and cleaning after weathering can restore the surface [27].

Three cleaning solutions were selected to compare their effect on the cleanliness of glass surfaces. However, cleaning agents do not always remove difficult contaminants; one option is to protect the glass surface with a protective agent before exposure. A commercially available protector containing zinc, potassium, and bismuth oxides was investigated to evaluate its benefits on cleaning float glass [28,29]. The role of zinc as a glass protector has been investigated in previous studies [30,31], but only for weathered glass in a climate chamber.

This study aims to determine which cleaning agent removes contaminants more effectively and protects the glass surface without damaging the glass surface. In comparison to former studies [12–14,32,33] on outdoor and contaminant-induced exposure, model particles were chosen to pinpoint typical effects of the site-specific mixture of aerosols and other contaminants. It also aims to understand the role of the protector on naturally weathered glass better.

2   State of art

2.1   Pollutants inducing glass corrosion and alteration

One factor that strongly influences (accelerate) the kinetics and mechanisms of glass corrosion is atmospheric pollutants originating from industry, traffic, agriculture, and nature [34]. Air pollution damages all materials, including glass, by depositing impurities on the surface, causing surface degradation. When the pollutants reach the glass surface, they can either settle or be removed by rain or air. Their deposition or accumulation depends on the environment and weather conditions [35]. The degree of alteration on the glass surface is influenced by the type of contaminant, composition, and size [36].

Some airborne contaminants include sea salt, volcanic ash, minerals, and desert dust. Pollutants such as soot and smoke originate from fossil fuel combustion and biogenic combustion processes such as wood and vegetation fires [32]. Surface deposits on glass are a mixture of insoluble and soluble particles [37]. Insoluble particles include metal particles, black carbon [38], and insoluble soil aerosols such as feldspar and quartz. Soluble particles include salts such as sulfates, carbonates, nitrates, and chlorides [39], and particulate organic matter (POM) [40]. Most silica, aluminosilicate, and carbonate particles originate from natural soil dust or other products such as cement and concrete dust [41]. In climate chamber experiments, simulating fast degradation under extreme conditions, extra carbonate and sulfate particles did not alter the principles of float glass degradation. Sodium carbonate just enhanced the number of reaction products. Sodium sulfate particles dissolved within the gel layer and delayed the formation of typical reaction products by some days [42,43].

The pollutants effect, the amount, and the morphology of the deposits is influenced by the exposure site. Rural areas are characterized by agriculture and low emission industrial activities and therefore have low concentrations of industrial pollutants (SO_2 and NO_2). The aerosols in a rural area consist mainly of particles from wood combustion, pollen, spores, pollen, bacteria, plant debris, or organic fragments containing sulfur and phosphorus [39]. Aerosols in urban areas are mainly from engine combustion, tire and brake wear, road dust, coal combustion, and emissions from industry [44]. Four contaminants found in rural and urban environments are discussed next.

2.1.1 Cement dust

Glass can be exposed to cement dust when it is located near cement plants or construction activities. Cement is a hygroscopic material [45]. Hydration of cement depends on temperature, humidity, time of exposure, and particle size. At higher ambient temperatures, humidity increases; thus, more water vapor is present in the air [46]. Smaller cement particles result in smaller spaces between them; thus, water vapor cannot penetrate through the cement layer. When the cement is exposed to the environment for a longer time, it has more time to absorb water vapor.

The interactions between water vapor and cement particles are shown in Figure 1. Cement particles can adsorb water vapor from the atmosphere on their surface. The water bonds to the surface of cement particles by Van der Waals forces (Figure 1A). At higher humidity, capillary condensation occurs between cement particles (Figure 1B). Alkali sulfates present in the cement can dissolve in the presence of water (Figure 1C). Moreover, water can react with the cement components to form crystalline hydration products that can adsorb additional water molecules on their surface (Figure 1D). Additionally, the cement can also absorb water vapor into the bulk of the particles.
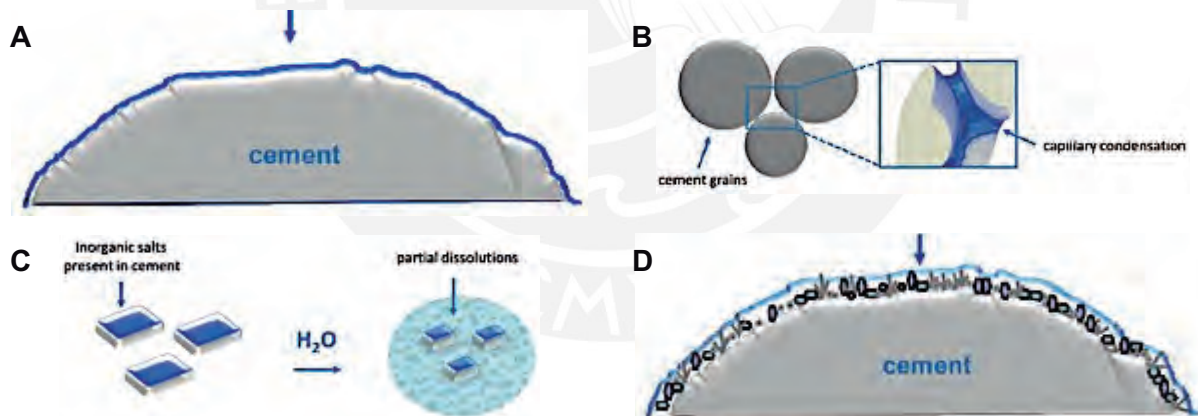

Figure 1. Schematic of the interactions between water vapor and cement particles [45]. **A)** Adsorption of water on the surface of cement particles. **B)** Capillary condensation between cement grains. **C)** Partial dissolution of inorganic salts present in cement. **D)** Adsorption of water on the surface of hydration products.

The interactions mentioned above between cement and water can lead to the hydration of the cement on the glass surface. The cement is dissolved, and ions from the cement constituents are released, leaving a hydrated layer of dissolved alkali hydroxides on the glass. The high

concentration of OH⁻ ions in the hydrated cement layer attacks the glass surface. The pH of the solution ranges from 12.7 for low alkali cement to 13.9 for high alkali cement [47]. Even the Portland cement with lower pH of 11 [48] is high enough to corrode glass because glass dissolution increases rapidly at pH above 9 (see Figure 2).
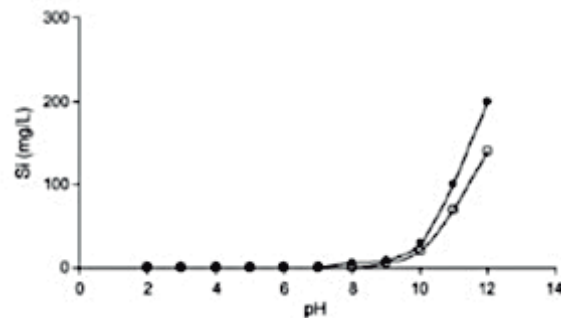

Figure 2. Exponential increase in silica dissolution when pH is higher than 9 [17].

The presence of cement on the glass surface increases the initial pH and accelerates the corrosion of glass. At high pH, the break-down of the silicate network is expected because the predominant mechanism is dissolution. The breakage of the Si-O-Si bonds is enhanced. As the glass dissolves, the pH increases, enhancing more and more network dissolution.

In addition, the layer formed by the deposition of dry cement dust on the glass surface reduces the transmittance of the glass [49]. Consequently, the efficiency of PV modules decreases when the density of the cement dust deposited on the glass surface increases [50]. Less solar radiation reaches the solar cells [51]. After the settlement of cement dust over some time, it becomes more difficult to be removed. It is recommendable not to let the cement dust settle for a long time; the glass surface must be cleaned regularly.

2.1.2 Aluminum particles

Aluminum come into contact with the glass surface because it is found mainly in the soil as oxide or silicate components like feldspar and as metallic particles from the metal frames of PV modules. There are three soiling mechanisms that increase particle adhesion to the glass surface: cementation, particle caking, and capillary aging [52]. These mechanisms occur when there is an interaction between water and particles (see Figure 3).
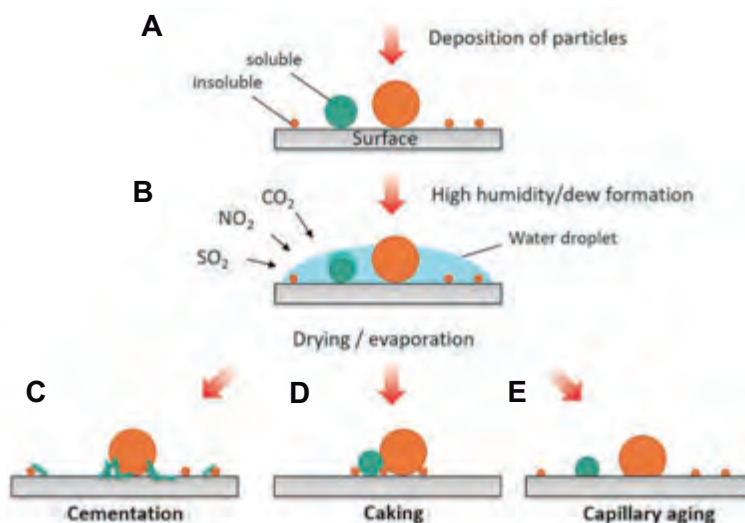
Figure 3. Schematic representation of soiling mechanisms that increase particle adhesion [53]. **A)** Deposition of particles on glass surface. **B)** Water droplet formation in contact with soluble and insoluble particles. **C)** Cementation by formation of solid bridges. **D)** Caking by agglomeration of particles. **E)** Capillary aging by increasing contact area between particles and surface.

Outdoors, soluble and insoluble particles deposit on the glass surface (Figure 3A). In humid environments, water droplets are formed. The soluble particles like salts (NaCl and gypsum) and atmospheric gases such as SO_2, CO_2, and NO_2 dissolve in the water droplets (Figure 3B). After water evaporation, precipitation of the soluble particles occurs, forming solid bridges between the insoluble particles and the glass surface [54]; this is called cementation (Figure 3C and Figure 4). This process also includes the formation of chemical bonds.
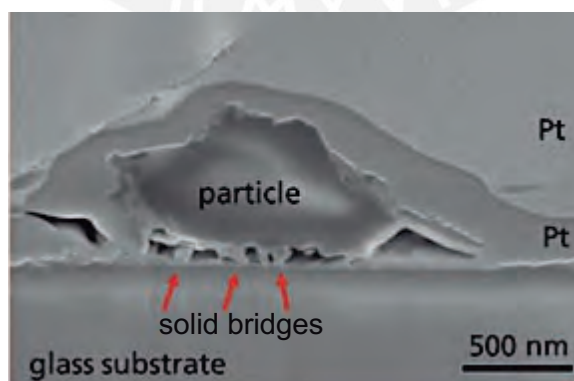

Figure 4. Solid bridges between a cemented insoluble particle on the glass surface [55].

The other process that increases particle adhesion is particle caking, caused by rearrangement, agglomeration, and compaction of particles. There is a small suspension of the particles in the water droplets, and after the droplet dries, the bigger particles settle first, and the small particles fill the spaces between larger particles and the glass surface [56]. The particles become agglomerated in a smaller volume (Figure 3D). The contact area increases, and so do the adhesion forces such as the Van der Waals forces.

The third mechanism that increases particle adhesion is capillary aging. As the liquid bridges between the particles and the glass surface begin to dry, the capillary forces press the particles against the surface (Figure 3E), increasing the contact area [57]. These mechanisms can occur simultaneously; thus, aluminum particles can adhere to and alter the glass surface generating weathering products.

Feldspar bearing sands as models for soil dust have been investigated [13,14]. Feldspars are much more likely to cement. During cementation, some chemical reactions take place, or the crystal changes its structure. Feldspar-like compositions are formed when pure silica sand is applied to the glass surface. Pure silica sand on the surface removes components from the glass, creating feldspar-like components around the sand grain.

Aluminum may cement somewhat to the glass surface due to the oxide layer on the metal particle. However, the adhesion of the aluminum metal particles to the glass surface is more likely due to caking. This study did not investigate whether there was a crystallographic change or a chemical reaction between the glass and particles. The small particles have a high contact area to volume ratio, and the ratio is enhanced by the movement of the larger flat side of these small particles after some events of water condensation; this increases the adhesion to the surface. The larger particles are removed by wind or cleaning, and the small ones find a place with much adhesion.

2.1.3 Bird droppings

The glass surface in an outdoor environment is exposed to many types of contaminants, such as bird droppings. This contaminant is one of the main sources of soiling on PV modules. Bird droppings are composed of three constituents: 1) liquid urine, which consists of uric acid ($C_5H_4N_4O_3$); 2) a semi-solid green component that depends on the bird seed-eating; 3) a semi-solid whitish component [58]. In addition, bird-dropping particles are mainly composed of quartz

(SiO$_2$), aluminum phosphate (AlPO$_4$), sodium aluminum silicate (AlNaO$_6$Si$_2$), and aluminum calcium sodium silicate (AlCaNaO$_4$Si) [59].

The pH of bird droppings is between 3.0 and 4.5 due to the high uric acid content [60]. In a humid environment in the presence of water vapor, the low pH of bird droppings enhances the ion-exchange mechanism on the glass surface [61]. As long as it is acid, the leaching of ions from the glass predominates [62,63]. The glass surface remains smooth at low pH because only ions are leached from the glass and nothing from the matrix structure.

Usually, the green component of the bird droppings is washed away by low rainfall. However, the white component, which strongly adheres to the glass surface, often remains even after heavy rainfall. Moisture in the air increases the strong adhesion of the bird droppings to the glass surface [59]. The liquid component (uric acid) of bird droppings forms capillary bridges that increase adhesion and lead to cementation on glass surfaces [64].
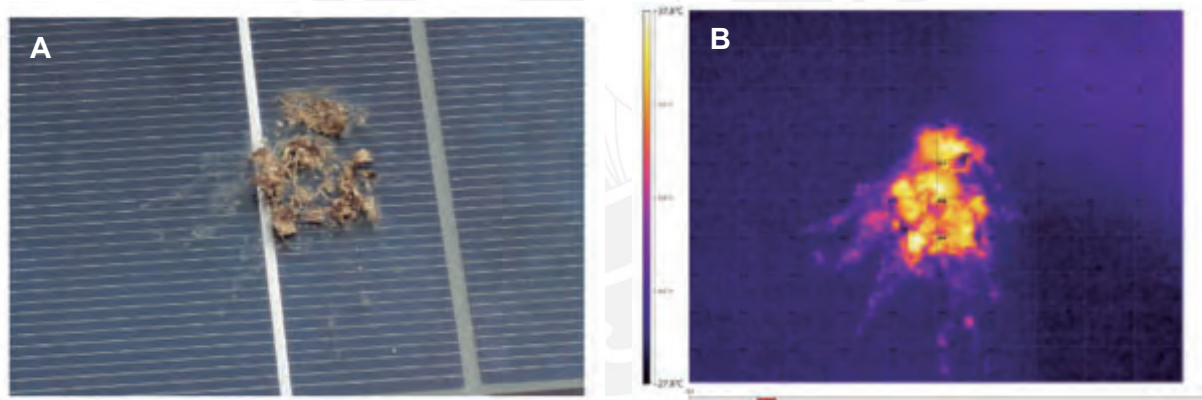

Figure 5. A) Real image of bird dropping deposition on a PV module. **B)** Deposition endorses higher temperature on the deposit area compared to the clean area around it [65].

In addition, when a deposit covers parts of the cell, the temperature in that area increases [66] (see Figure 5), resulting in energy losses. Dorobantu et al. [67] found that the temperature of the area covered with bird droppings was 10 ºC higher than the clean area around the deposit. Thus, to avoid these losses, cleaning is necessary.

2.1.4 Sodium chloride

Over 85% of the composition of sea salt is sodium chloride [68]. This salt is a common contaminant found in the atmosphere. Sodium chloride can be transported by the wind from the

sea to the glass surface [64]. Significant amounts of sea salt are also found in the aerosols more than 400 km away from the coast [69]. Sodium chloride is a hygroscopic compound that becomes liquid at 76% relative humidity [70]. McCormick et al. found that sodium chloride particles have an excellent ability to adsorb water, which in contact with other insoluble particles, droplets are formed only on the sodium chloride particles [71]. This phenomenon is observed on the glass surface at high humidity, where water-soluble particles like sodium chloride form microscopic droplets of salt solution that retain insoluble particles (see Figure 6B). As humidity decreases, the droplets of salt solution dries out, leaving a precipitated salt that forms a solid bridge between the insoluble particle and the glass surface (see Figure 6C).

Figure 6. Cementation process [72]. **A)** Deposition of an inorganic particle that contains water-soluble and insoluble salts. **B)** Formation of salt solution retaining insoluble particles at high humidity. **C)** Formation of precipitated salt, keeping the insoluble particle attached to the glass surface after drying.

Salts can indirectly enhance the weathering of glass surfaces [73]. Due to its hygroscopic property, sodium chloride on the glass surface can increase glass degradation by attracting water molecules from the air and keeping a water film on the surface for a longer time, enhancing the leaching mechanism [74]. In addition, salts as condensation nuclei can enhance the deposition of other particles (soiling) [72,75].

In a study [76], it was observed that the area of a glass cup containing fingerprints altered with different rates after dishwashing. EDX analysis revealed that the fingerprints consisted of thin porous layers enriched with NaCl. The fat and salt components of the fingerprint lead to differences in local alteration, which was enhanced by dishwashing and not removed. Porous layers formed on the glass as soon as it was severely damaged. The cavities in the porous layers can uptake impurities from the outside, which recrystallize inside and never come out. After repeated washing, salt crystals were captured in the pores of the corroded layers. The salt most likely did not come from the fingerprint. These crystals reprecipitated in the pores and could not

be rinsed out. Even after many cleaning attempts, the fingerprint could not be removed, and the salt crystals continued to be in the porous layers. They were protected against enough water to be rinsed away. The "protection" might reduce local leaching during washing due to the locally high Na concentrations in the NaCl-rich pores.

2.2 Surface wettability

One factor that influences the soiling of pollutants on the glass surface is surface wettability. The water contact angle can characterize the surface wettability. A surface can be either hydrophilic or hydrophobic, depending on how it interacts with water droplets; a water drop wets a surface with high surface energy, such as glass, and beads up on a surface with low surface energy. The surface is hydrophobic if the water droplet has a contact angle greater than 90° and is hydrophilic if the droplet has a contact angle lower than 90° (see Figure 7).
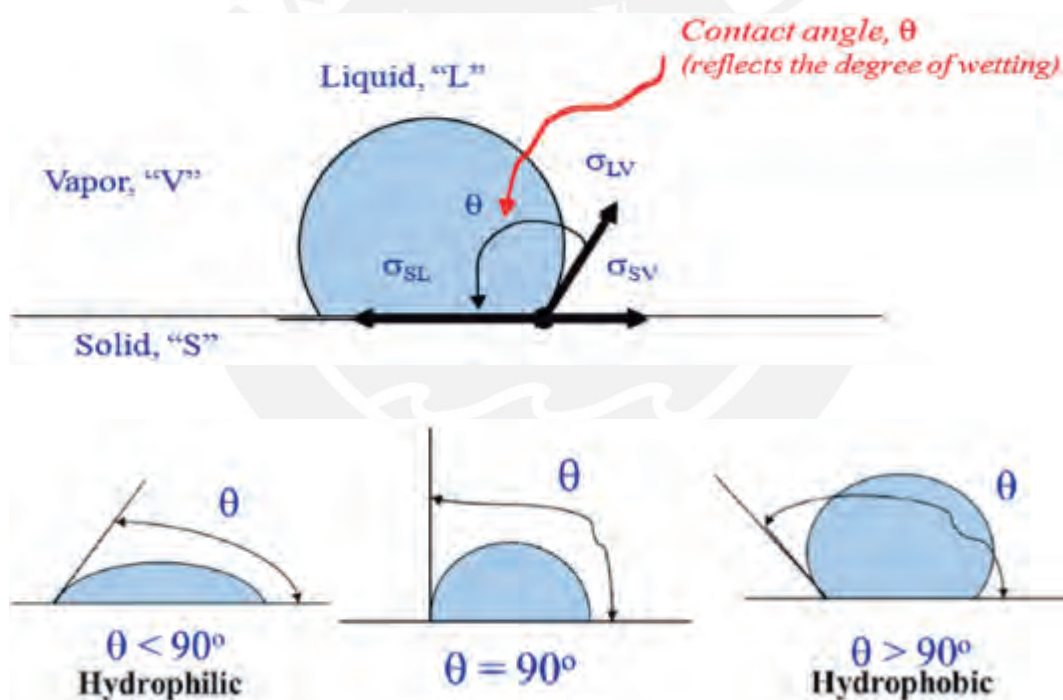
Figure 7. Schematic representation of hydrophilic and hydrophobic wetting conditions in relation to the contact angle [77].

A hydrophilic surface of a clean glass has hydroxyl groups (–OH) which are polar and form hydrogen bonds with water molecules [78]. The function of hydrophobic coatings is to cover these hydroxyls with non-polar molecules. The capillary adhesion of particles on the glass surface is greater on hydrophilic surfaces and lower on hydrophobic surfaces and increases with humidity

on hydrophilic glass, while on hydrophobic glass, the increase of capillary force is independent of humidity [79] [80]. Hydrophobic coatings repel liquid water but not water vapor [77]. Microdroplets can form on hydrophobic surfaces [81], but stable liquid bridges between particles and surfaces cannot form [82]. As humidity increases, a water film gradually accumulates on hydrophilic surfaces by condensation [83], while hydrophobic surfaces prevent the formation of the water film instead promote water beading, leading to self-cleaning [84,85].

When a drop of water is applied to a flat, smooth, homogeneous surface, such as glass, the contact angle will depend on the surface tension of the liquid and the chemistry of the surface (surface energy) and the atmosphere. The cleanliness of the glass can be assessed by measuring the contact angle. Effective cleaning methods result in a hydrophilic surface with a low contact angle [86], the concentration of hydroxyl groups increases after the cleaning process.

Uncleaned surfaces enhance corrosion because their topography is not homogeneous. The inhomogeneous alteration over the entire surface originates from the different wettability. The inhomogeneities on the glass surface serve as starting points for corrosion at high relative humidity [27]. In contrast, a clean surface is smooth and has a homogeneous surface; thus, a clean surface helps to maintain a glass surface with minor alterations after weathering. All glass surfaces alter with time. As contaminants with different wettabilities change the alteration rates locally, they can affect the homogeneous appearance. Thus, unavoidable alteration is much more probable to irremovable visible effects, i.e., corrosion.

2.3 Weathering products

When the glass deteriorates, its composition alters, and a weathered layer forms on its surface [87]. This altered layer changes the glass appearance by forming a cloudy layer or cracks [88]. Other weathering products discussed in this investigation include bulges and iridescent films that can lead to delamination.

2.3.1 Bulges

Humidity induces the aging of glass surfaces, which yields various weathering products on the sub-µm scale. One of these intrinsic glass features is the bubble-like structure called bulges (see Figure 8). The bubble effect is caused by the formation of local corrosion centers [89]. These gel-like bubbles are stable and can remain on the glass surface over time. They are found occasionally and are randomly distributed over the glass surface. Two effects are assumed to be

inducing the bubble formation: a locally increasing swelling of the gel layer and a recondensed silica layer on top of the gel layer.
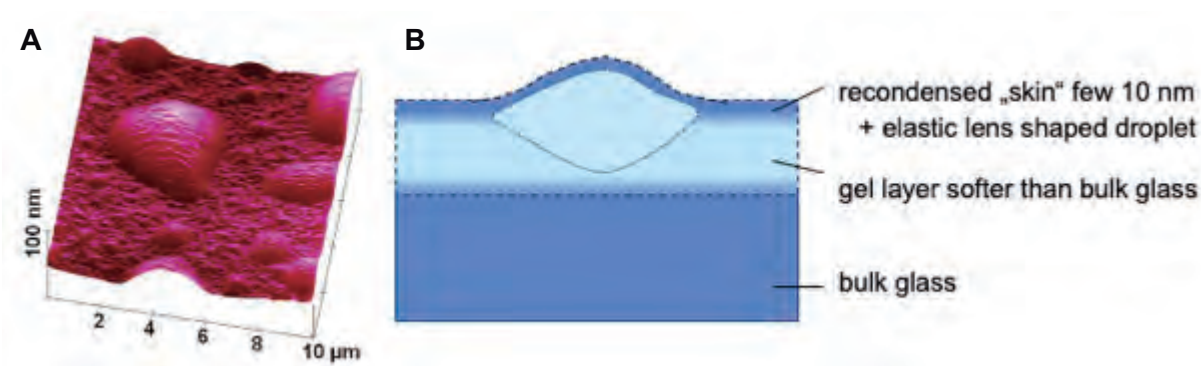

Figure 8. A) AFM image of bulges on the glass surface. **B)** Schematic representation of a droplet formation on the glass surface [90].

The swelling gel layer has a condensed "skin" on it (Figure 8B), and in this "skin," certain regions swell faster than the rest (Figure 8A) due to the high concentration of sodium carbonates and sodium hydroxides that attracts water to be better dissolved. Bulges are an intrinsic part of the gel layer; they do not lie on the surface.

In a study, the AFM profiles of weathered glass show uniformly distributed bulges on the glass surface after weathering in a climate chamber at high humidity and temperature (80% RH and 80 °C) [12]. It was assumed that carbonates precipitate in them. In another study, it was also observed that bubble-like structures formed under the glass surface. A hydroxide solution (NaOH) accumulates in the glass surface due to the leaching process during weathering. Therefore, it was assumed that these bubbles possibly contained concentrated NaOH solution from which sodium carbonate crystallized under the glass in contact with CO_2 from the air [91].

2.3.2 Iridescence effect

As an optical phenomenon, iridescence depends on the diffraction of light at thin layers with differences in optical density. This effect is observed due to the different refractive indexes of layers on or in the glass. Environmental factors like soluble salts, carbonates, and humidity favor the formation of iridescent films [92]. The iridescence effect can be observed in a circular shape formed by the evaporation of water drops. In a high humidity environment, more circular alteration marks are formed on the glass due to the high presence of water drops [93]. The water drops

hold moisture on the glass surface, leading to hydration and ions' leaching. The static condition of water drops can accelerate the alteration mechanisms; thus, circular alteration layers are formed. The alteration layers are fragile and can break, creating a hole in the glass surface where water can deposit, enhancing network dissolution. The iridescent colors indicate that a hydration layer has formed, which is the initial stage of the alteration layer. The iridescent effect is attributed to the leaching of Ca ions, as the weathering crust formed on the glass surface was found to be enriched in calcium carbonates [25,94]. However, this might not be the only possible reason. Repeated condensation cycles and drying of water droplets on the glass surface enhance the iridescent effect [95].

In harsh environments, weathered glass can also develop thin layers of transparent material that produce iridescent films over the glass surface [96]. The iridescent thin surface layer of silica has a different structure than the glass [91]. The iridescent color is created by interference effects caused by the light rays reflected from the thin films [97]. The iridescent film is composed of alternating layers of air and weathered glass crusts and can develop over time into a thick layer that can flake off, resulting in delamination of the glass surface. Iridescence is an irreversible effect.

2.4 Cleaning agents for glass

There are different cleaning methods for closed and open systems. In closed systems, reusable glass bottles are cleaned with sodium hydroxide [98]. The glass is dissolved from the inside to the outside. This method is the best way to sterilize it and create a new surface inside. A high pH is used in the dishwasher, but citric acid and other components are always added in the final step to restore the acidic surface and restore the neutral pH of the water before it goes into the wastewater. For float glass cleaning in washing machines, many people only use DI water. Another cleaning option is polishing with cerium oxide or aluminum oxide as a mechanical wiping process with brushes [99]. In contrast to household dishwashing and commercial container or flat glass washing machines with closed cycles and wastewater treatment, outdoor cleaning is subjected to stricter restrictions regarding wastewater. In closed systems, more aggressive agents can be used than in outdoor.

A wide range of cleaning agents is available for glass cleaning, including water, commercial products, chelating agents, acids, and organic solvents. Tap-water and deionized water are commonly used for outdoor cleaning flat glass. However, tap water contains salts such as

carbonates, chlorides, and sulfates [100] that can deposit on the glass surface and enhance the formation of weathering products that later are difficult to remove. Deionized water is used to prevent those deposits on the glass. Ion-exchange resins treat deionized water to remove the impurities from tap water [101].

Commercially available cleaning agents act in a solvent to remove contaminants from the glass surface. These agents are designed to be dissolved in water (tap water, deionized water, or distilled water). These commercial cleaners are only non-hazardous in the typical low concentration released with other wastewater. A commercial cleaner contains a mixture of chemicals; some may include alkali, surface-active chemicals, and chelating agents [97]. Some of the chemical components can damage the glass surface, but the exact composition is not known.

A chelating agent reacts with metal ions such as calcium or magnesium ions. It forms multiple bonds around the metal ion and locks it into a protective complex [102]. The cleaning target is the weathering crust which usually consists of calcium carbonates and sulfates. This cleaning agent can attack the glass surface under the weathering crust because it also contains calcium and magnesium ions in its structure. This agent increases the leaching of alkaline earth modifiers.

Toxic acids must not be used for cleaning float glass. Hydroxycarboxylic acids, also called organic acids, such as citric acid, form weak complexes with alkaline earth ions [97]. Therefore, a larger amount of this cleaning agent is required to ensure the dissolution and removal of calcium ions present in weathering products. Cleaning solutions containing a small amount of organic acid can be used as cleaning agents because their low pH reduces the dissolution of silicate [103]. Some research has been conducted to find the best cleaning agent for glass, in which citric acid shows moderate to good effect in cleaning weathered glass [104,105].

2.5 Protective agent containing zinc, and bismuth

The commercial protector called Finish Protector was developed to prevent glass corrosion during dishwashing [106]. This protector is a phosphate glass that dissolves in water which contains zinc and bismuth as protective agents. A previous study in 2014 [28] showed that bismuth and zinc deposit on the glass surface during the dishwashing process and formed a protective layer. The smaller zinc ions (Zn^{2+}) penetrate the glass structure at the surface, and the bigger bismuth ions (Bi^{3+}) remain on top protecting the gel (hydrated) layer. Figure 9 illustrates the idea that a

monomolecular phosphate layer containing Zn and Bi adheres to the silicate surface. However, a later study in 2017 [29] was conducted with the same commercial protector agent to better understand the protective action mechanisms on float glass surfaces.
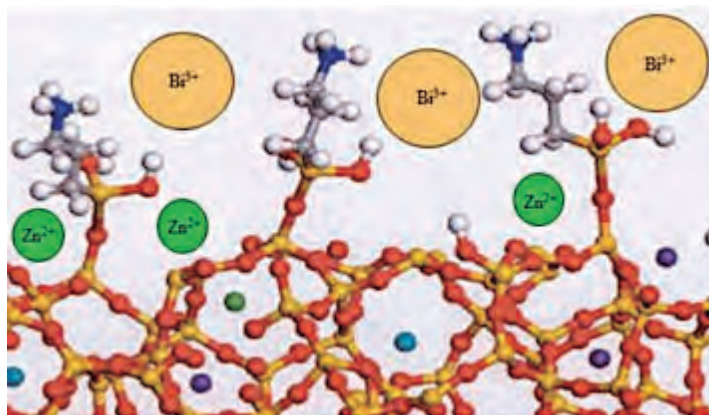

Figure 9. Schematic representation of the glass surface structure forming a protective monolayer containing zinc, bismuth ions and phosphate groups (grey) [28,106].

The chemical depth profiles showed the presence of two layers: a zinc-rich phosphate layer on the glass surface containing Zn, P, Bi, and K and a Na-depleted subsurface layer (see Figure 10). The phosphate layer also contains Na and a small amount of Ca coming from the glass. Zinc and phosphorus diffuse into the glass, but only a small amount of potassium and bismuth diffuse into the glass surface. The diffusion of zinc ions into the glass surface stabilizes it and delays further chemical attacks. The thickness of the layers in this study is to be assumed much higher than in normal use. The float glass samples were exposed to the protector longer than during normal cleaning to clarify basic mechanisms.
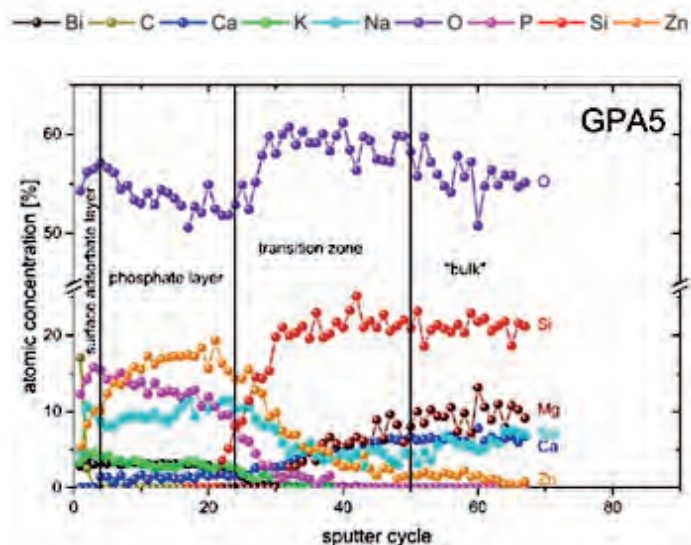
Figure 10. Depth profile of glass immersed in a protector solution for five days, where the phosphate layer has a thickness of ~6 nm and the transition zone a thickness of ~8 nm [29].

The main processes for the formation of the protective layer on soda-lime glass are diffusion and precipitation. Transition elements such as zinc improve the linkages between the atoms within the glass network [107], thus protecting the glass surface by increasing its corrosion resistance. In addition, the presence of Zn, P, Bi, and K in the gel layer leads to a gel layer with a higher mass than the typical gel layer, which could result in a layer with a higher refractive index. The glass samples immersed in the protective solution showed no degradation effects such as clouding or iridescence; instead, they had the same optical appearance and clarity as the untreated glass. Nevertheless, further experiments are needed to prove the effectiveness of the protector under natural weathering.

Based on the idea that zinc diffuses into the glass surface to protect it from degradation, the deposition of zinc salts on the glass surface as a protective treatment was investigated. The treatment reduces the hydration kinetics, forms a thinner hydrated layer, and reduces the formation of carbonates on the glass surface compared to untreated glass at 40°C or 80°C and 85 RH% [30]. In addition, further investigation of the salt-zinc treatments observed that the chemisorbed zinc ions on the glass surface and the ions diffused on the glass surface provided better protection than the physisorbed ions. Alloteau et al. stated that the formation of the zinc-rich surface layer could act as a diffusion barrier [31].

3   Experimental Method

The experimental section includes glass selection, sample preparation, and glass exposure in the climate chamber and outdoors. A more detailed explanation of the test specimens, sample preparation, cleaning methods, inspection, and analytical methods follows below.

3.1   Test specimens, pollutants and cleaning solutions

3.1.1   Soda-lime float glass

The glass samples used for this study were greenish soda-lime float glasses. The greenish color comes from the iron content in the glass. Glass samples were 10×10 cm^2 in size and 0.3 cm thick. The calculated content of the glass constituents in weight percent (wt%) is given in Table 1.

Table 1. Calculated chemical composition of greenish soda-lime float glass according to the X-ray fluorescence analysis of the Zentrum für Glas- und Umweltanalytik GmbH [33].

Component	SiO_2	Na_2O	CaO	MgO	Al_2O_3	K_2O	Fe_2O_3	SO_3	TiO_2
Content by weight %	72.80	13.07	8.80	4.21	0.48	0.28	0.066	0.24	0.018

3.1.2   Selected contaminants

Four specific types of contaminants were selected and applied to the surface of glass samples. Bird droppings (BD), cement dust (CD), aluminum particles (AP), and sodium chloride (SS) were selected because they represent organic, inorganic-nonmetallic, metallic, and saline components (see Figure 11). The specific properties are summarized in the following paragraph. Apart from the lack of information on these pollutants, they belong to the most common pollutants found on float glass when exposed to the environment. Therefore, further investigation is required. In addition, these pollutants were selected to allow a comparison between organic and inorganic pollutants. Thereby, it can be investigated which type of defects on the surface is related to which pollutant. The contaminants were dissolved in DI water and the pH was measured with pH indicator strips.

Bird droppings (pH~5) are found in all environments and are a potential source of sulfur and phosphorus on the glass surface [108,109]. The fence from where the bird droppings were taken was galvanized: additional zinc could not be excluded from the collection of bird droppings.

Nevertheless, if the bird droppings were collected in the garden, other traces from the ground and trees would be even less well defined. **Sodium chloride** (pH~5) is derived from sea salt spray and is found primarily in places near the ocean but can also be transported over the low mountain ranges in central Germany [69]. The sea salt is not pure as an air pollutant, but pure sodium chloride was selected to understand its effect on the glass surface. **Cement dust** (pH~9) is an air pollutant found near buildings and construction activities and is a source of calcium [110]. The selected cement was Portland cement, according to DIN 1164 [111]. It was chosen because of the $Ca(OH)_2$ dissociation in water would favor high pH. **Aluminum** (pH~5) particles are found in the metal frames of PV modules. Aluminum was chosen as an example of a metallic contaminant. The aluminum was obtained by scratching the PV modules' frame with a glass nail file not to contaminate the collection of aluminum with other metal particles.

Figure 11. Four types of contaminants applied to the glass surface before artificial and natural weathering.

3.1.3 Cleaning solutions and Protector

Three cleaning solutions were chosen for the investigation. In addition to the cleaning solutions, a commercial protector was used in the investigation. The solutions were used to understand how the glass surface changes after cleaning or after using the protector. Furthermore, comparing cleaning solutions with the protective agent is important to understand if any of the selected cleaners can be effective without additional usage of protector. pH indicator strips were used to measure the pH of each solution.

Deionized water is the most common cleaning solution for glass, as it has a pH of 5 to 7[1] and should not damage the glass surface as much while cleaning. **Schukolin**® SolarSoft is a commercial cleaner specifically designed for cleaning photovoltaic modules. This cleaner is presented as highly biodegradable and environmentally friendly [112]. However, the chemical composition of this cleaning solution remains unknown. Five milliliters of Schukolin were diluted in one liter of DI water (pH~6). **Citric acid** monohydrate ($C_6H_8O_7 \cdot H_2O$) is a solid white crystalline compound. Six grams of citric acid were dissolved in one liter of DI water (pH~2). This solution is not hazardous to the environment [113,114] and is used in household cleaning products. A cheap, nontoxic solution such as citric acid, with poor previous investigations, is considered necessary for this study.

Glass protector is a solid and water-soluble commercial product produced by Reckitt Benckiser GmbH, Mannheim, distributed via supermarkets (see Figure 12). It is a phosphate glass containing zinc oxide, potassium oxide, and bismuth oxide. It is used in dishwashers to protect glass from corrosion. The protector was crushed in a mortar. A saturated solution was prepared by dissolving 100 g of the protector in 1 L of DI water. The saturated solution has a whitish color and a pH of 1.
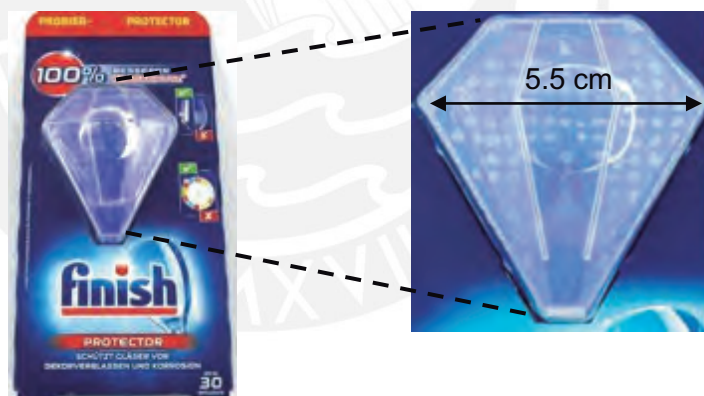
Figure 12. Water-soluble glass protector containing zinc, potassium, and bismuth oxides.

3.2   Glass sample preparation prior to weathering

Glass samples were cleaned with three different cleaning agents (DI water, citric acid and, Schukolin) before the exposure to remove storage-related contaminants. The reason for this was observing whether the cleaning agents influence surface properties (such as wettability and

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[1] Different pH indicator strips measured different values then cannot be excluded the possibility that pH changed over time due to CO_2 uptake.

chemical resistance) prior to weathering. After cleaning with DI water, Finish Protector was also applied to another set of samples prior to weathering. The side that was cleaned in all the glass samples was the air side which was the exposed side. The immersing time of the samples in the cleaning and protector solutions was 5 minutes. After that, they were dried with compressed air, followed by the deposition of contaminants described below.

3.2.1 Preparation for climate chamber exposure

Cement dust, bird droppings, sodium chloride, and aluminum particles were deposited on the air side of the glass. Before deposition, the contaminants were weighted (see Table 2), but the differences in the weights were not part of the analysis in this study. The position of the contaminants on the glass is shown in Figure 13. Four glass samples were used for each exposure (1 day and 7 days), three of which were treated with the cleaning solutions and one with the protector.

Table 2. Amount of contaminants added to the glass surface for exposure in the climatic chamber.

	Weight (mg)	
Contaminants	**1 day**	**7 days**
Aluminum	4.0	2.0
Cement dust	33.5	30.5
Sodium chloride	26.5	26.3
Bird droppings	24.0	22.5
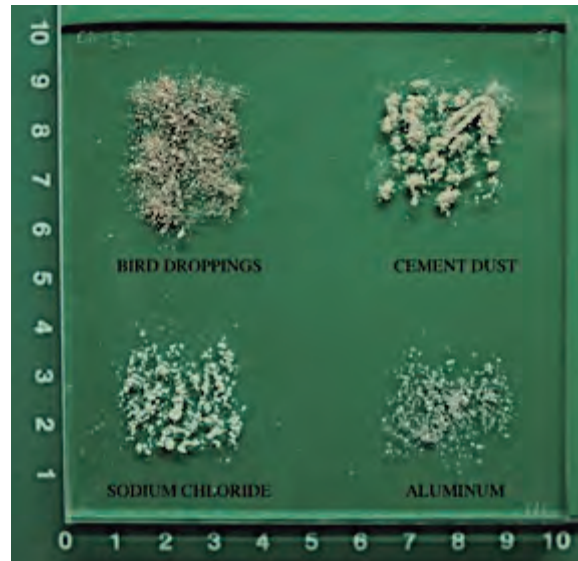
Figure 13. Position of contaminants on the glass surface treated with citric acid before artificial weathering in the climate chamber.

3.2.2 Preparation for outdoor exposure

Cement dust, bird droppings, sodium chloride, and aluminum particles were also deposited on the glass for the outdoor exposure samples. The position of the contaminants on the glass is shown in Figure 14. The contaminants had to be applied in such a way that they rested for a long time during exposure. Two types of contaminants were applied per glass sample to prevent them from mixing. The contaminants were weighted before deposition (see Table 3). After deposition, five raindrops were applied with a dropper to each contaminant to avoid being blown away with the air during transport. Raindrops were used because the contaminants were expected to come into contact with raindrops during the exposure period. After drying at room temperature (see Figure 15), the glass samples were transported to the exposure site. Eight glass samples were used for outdoor exposure, six of which were treated with the cleaning solutions and two with the protector.
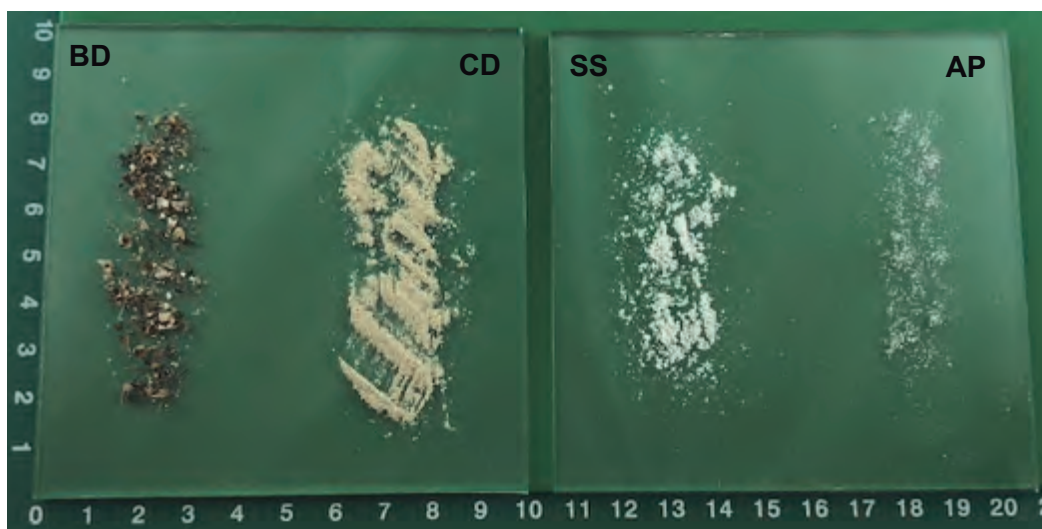
Figure 14. Position of contaminants on the glass surface treated with DI water before outdoor exposure.

Table 3. Amount of contaminants added to the glass surface for outdoor exposure.

Contaminants	Weight (mg)	
	20 days	30 days
Aluminum	4.2	5.4
Cement dust	188.5	100.3
Sodium chloride	86.5	80.0
Bird droppings	38.5	40.3
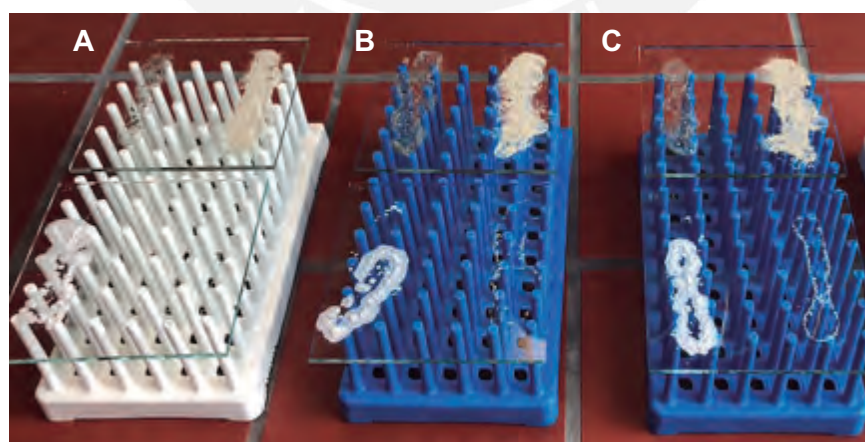
Figure 15. Glass samples prepared for natural weathering with applied contaminants on glass surface before exposure. **A)** Glasses treated with citric acid. **B)** Glasses treated with DI water. **C)** Glasses treated with Schukolin.

3.2.3 Preparing glass with protector

In addition to the cleaning with DI water for 5 minutes and drying with compressed air, the glass sample was immersed in the protector solution for an additional 5 minutes (see Figure 16A). It was then dried with compressed air. The protector left an inhomogeneous white layer after drying with compressed air (see Figure 16B). Then, the contaminants were deposited on the glass (Figure 16C) and exposed to natural and artificial weathering like the other glass samples.
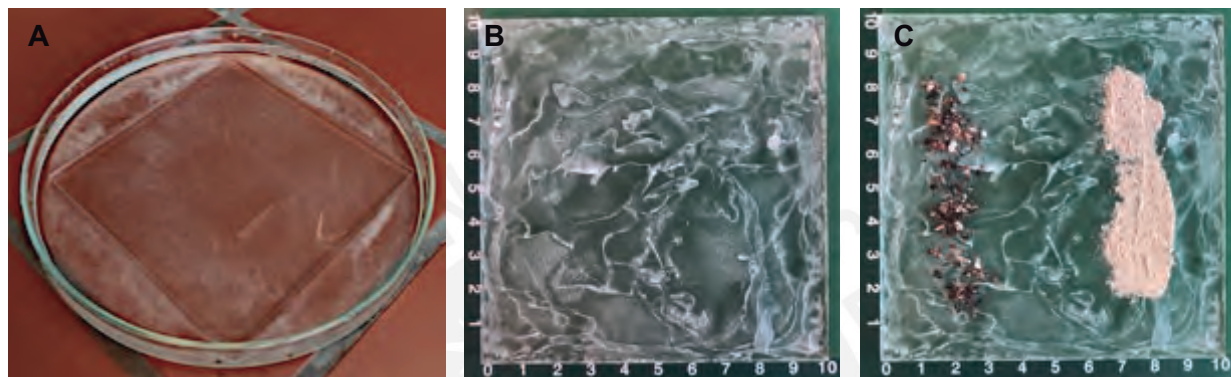
Figure 16. A) Clean float glass immersed in the protector solution for 5 minutes. **B)** Inhomogeneous white layer on glass surface after drying with compressed air. **C)** Glass with deposited contaminants (bird droppings and cement dust) before weathering.

3.3 Types of exposure

Different types of exposures were chosen to compare the different weathering degrees of the float glass. Artificial alteration in a climate chamber is an accelerated form of degradation and is often used to investigate alterations on glass surfaces at high temperatures and high humidity. Outdoor exposure investigations are a more reliable indicator of the real natural weathering of glass due to natural factors such as temperature and humidity variations, sunlight, air pollutants, rain, and wind.

3.3.1 Artificial alteration

The glass samples were exposed in a climatic chamber (Binder KF 240) at 80 °C and 80 % relative humidity. Glass samples were exposed first for 1-day in the climate chamber. Then a different set of glass samples were exposed for seven days to compare the degree of degradation between these two. Glass samples were on top of two holders in the middle of the climate chamber (see Figure 17).
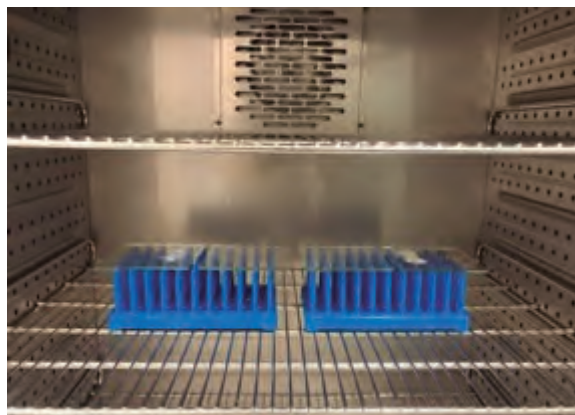
Figure 17. Position of glass samples inside the climate chamber with contaminants.

3.3.2 Natural weathering

The roof of a three-floor building in the Center for Micro- and Nanotechnologies at the Ilmenau University of Technology (50°40′32″ N 10°56′11″ E) served as the exposure site. The glass samples were initially exposed unsheltered for 20 days (see Figure 18A), but the samples were removed from the exposure site due to heavy rainfall for many days, which removed the contaminants. The first exposure period was from May 20 to June 9, 2021. The contaminants were reapplied, and the glass samples were exposed sheltered for another 30 days. A glass cover was placed 10 cm above the samples to prevent the contaminants from being washed off on rainy days (see Figure 18B). The samples were held in an aluminum frame positioned in a slope of around 15°. The second period was from July 19 to August 18, 2021.
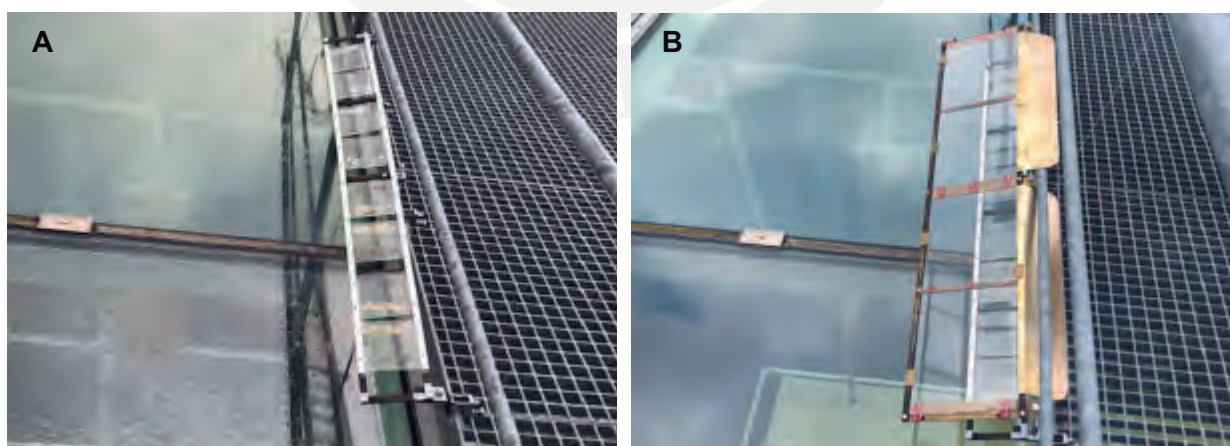
Figure 18. Exposure of 10x10 cm^2 glass samples on the roof of the Center for Micro- and Nanotechnologies in Ilmenau, Germany: **A)** unsheltered and **B)** sheltered with a glass cover.

3.3.3   Long-term exposure

Long time weathered glass of the same composition was investigated as a comparison to understand further weathering degree and cleaning efficiency on glass. Prior to weathering, the glass exposed in Erfurt was cleaned only with DI water. The investigated glass sample was exposed for 1.5 years near the Erfurt Airport (50°58′47″ N 10°57′29″ E, 316 m AMSL). The samples were held in a plastic frame positioned in a slope of around 20°. During weathering time, samples underwent no unnatural activity.

3.4   Cleaning after weathering

After weathering, the samples were removed from the climate chamber or exposure site and cleaned with the same cleaning agents used prior to weathering, either citric acid, deionized water, or Schukolin. The glass was immersed in the cleaning solution for 5 minutes. Afterwards, samples were taken to the mechanical cleaning machine. The air side was wiped with a microfiber cloth. Mechanical cleaning with a force of approx. 5 N was completed after four wipes. Subsequently, the microfiber residues and any loose residues were removed with compressed air. In addition, after weathering, the samples treated with the protector were cleaned with DI water. The glass sample exposed to long-term weathering was cut into three pieces, and each piece was cleaned with a different cleaning solution.

3.5   Analytical Methods

The analytical methods used provided information about weathered glass and are described in more detail below. The methods selected for the surface analysis were contact angle and transmission measurements, optical microscopy, Auger electron spectroscopy, energy-dispersive X-ray spectroscopy, and atomic force microscopy.

3.5.1   Contact angle measurement

The wettability of the glass surface was determined by measuring the contact angle to DI water. The change in wettability indicates how much the glass properties (e.g., surface tension, surface energy) have changed after different exposures and different treatments (cleaning and protector). The device used was the MobileDrop from Krüss. It is a semi-automatic system for measuring the contact angle on the glass surface. The contact angle method used was the circle-method. The

dosing step for each drop was 2 µl, and the diameter of the needle used was 0.77 mm [115]. The contact angle of three droplets was measured per average value in Table 4.

3.5.2 Transmission spectroscopy

Light transmission through the glass was measured using the UV-VIS-NIR scanning spectrophotometer UV-3101PC from Shimadzu. The data was acquired in wavelength scanning mode. The selected wavelength range was from 190 nm to 1100 nm, and the scanning speed was slow, 100 nm/min. This technique provides information on how clear the glass remains after weathering. One measurement per sample was taken in zones with few visible traces of contaminants. The measured area for each glass sample was 3.41 cm^2.

3.5.3 Optical microscopy

Optical microscopy is an important technique for the analysis of glass surfaces [116]. An optical light microscope, Carl Zeiss Axiotech with an Axiocam 305 digital camera, was used to observe and evaluate the glass surface. The microscopy images provide information on the contamination degree and the weathering products on the surface after weathering. After glass cleaning, optical microscopy can trace back unremoved weathering products and irreversible changes. Different magnification scales (5x, 10x, 20X) were used to capture contaminants and weathering products of different sizes. The exposure mode was bright field.

3.5.4 Auger electron spectroscopy (AES)

AES is a common analytical technique used, especially in the study of surfaces [117]. It measures within the first 2 nm of the glass surface. AES was used to identify the elements remaining on the glass surface after cleaning. It provides information about the composition of the weathering products that are difficult to remove. The instrument used is a Thermo VG Scientific Microlab 350. Measurements were made at two points, one on the weathering product and one outside the weathering product. The accelerating voltage was 10 keV, the current of the primary electron beam was approx. 15 nA and the angle of incidence was 80º [33]. The sample had to be tilted close to 0º to minimize the charging effects.

3.5.5   Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX)

The images of the weathering products after cleaning the glass surface were taken using SEM. In addition, EDX was used to determine the chemical elements present in the surface layer. The spectrum shows characteristic energies of elements [118]. The instrument used was SEM Hitachi S-4800 and a detector Thermo SDD NORAN7 [33]. The acceleration voltage used was 10 kV with a penetration depth of approx. 1 μm. Prior to the measurements, the samples were coated with a thin layer of platinum. Information on enrichment and depletion of the elements was obtained by doing EDX measurements at different positions on the glass surface. Measurements were made at five points, three on the weathering product and two outside the weathering product.

3.5.6   Focused ion beam (FIB) and transmission electron microscopy (TEM)

The images of the bulges were taken using FIB-TEM. TEM is an imaging technique with high resolution. An electron beam passes through the sample to produce an image [119]. FIB is used to prepare the samples for TEM. FIB bombarded the glass surface with accelerated heavy ions to remove material [120]. The device used was TEM Titan^3 G2 60-300. The electron energy was 300 keV, and the resolution was 0.136 nm [121]. TEM was used in the bright field mode.

3.5.7   Atomic force microscopy (AFM)

The AFM is used to observe the topography of the glass surface with almost atomic resolution in the nanometer range. The surface must be cleaned to avoid moving particles during scanning that could distort the images. It is possible to see how the glass surface changes after weathering, which gives an overview of the degree of the surface alteration. The measuring device was Dimension Edge with ScanAsyst® from Bruker. Peak force tapping mode was used, in which the tip oscillates up and down during its displacement. This mode allows for more accurate topographic measurements [122]. The tip used is made of silicon nitride (Si_3N_4) and has a radius of ≤ 12 nm [12]. The scan rate was 0.5 Hz, and the size of the investigated surface was 10 x 10 μm^2. The measurements were performed at four different positions on the surface, two near the weathering product and two far from the weathering product.

4   Results and Discussion

4.1   Contact angle measurement

Unweathered glass represents lower contact angles when compared to the weathered glass, independent of the cleaning treatment. The contact angle of glass weathered for one day under climate chamber show to be much higher than on the glass weathered outdoor (see Table 4). The increase in contact angle is the highest for glass weathered for seven days in the climate chamber. These values can indicate that the climate chamber is a harsher environment for float glass degradation. After cleaning, the glass surface exposed to natural weathering is restored but not after exposure in the climatic chamber. The contact angle sees only the first molecules on the glass surface, where a recondensed silica layer is formed after a long time at a high temperature, despite the high humidity outside. As soon as the OH- groups condense to siloxane bridges; they do not want to break away again; thus, a more alkali-free "skin" is formed on the surface.

Regarding cleaning solutions, citric acid provides the lowest contact angle before and after the weathering. The low contact angle of unweathered glass (38.4º) cleaned with citric acid indicates that citric acid provides OH⁻ groups on the surface by leaching sodium ions out and putting water on the surface. This information can indicate that citric acid forms a stable layer and does not compromise the glass surface. On the other hand, DI water records the highest contact angle in all cases and gives a hint in the influence of DI water in reducing the wettability of the glass surfaces. DI water is very effective in extracting alkalis in which in the following step also results in the formation of the recondensed silica layer. DI water is depleted of everything so the concentration radiant for alkalis to diffuse out is much stepper.

Table 4. Average water contact angles with standard deviations of unweathered and weathered glass after cleaning including the protector solution.

Cleaning agents	Unweathered	Natural weathering	Climate chamber 1 day	Climate chamber 7 days
DI water	43.7º ± 0.3	48.8º ± 0.1	60.0º ± 0.3	61.1º ± 0.8
Schukolin	41.3º ± 0.4	45.8º ± 0.1	57.9º ± 0.1	59.3º ± 0.7
Citric acid	38.4º ± 0.8	41.4º ± 0.1	52.3º ± 0.5	55.6º ± 0.3
Protector	--	42.0º ± 0.2	54.7º ± 0.2	57.1º ± 0.3

The contact angle of glass samples treated with protector solution and exposed to natural and artificial weathering was also measured after cleaning to see the difference with the other cleaning

solutions. Table 4 shows that the contact angles of the glass samples treated with protector were lower than the glass samples treated with DI water and Schukolin but not smaller than those treated with citric acid. The protector solution does not make the surface less hydrophilic. Samples treated with citric acid still have the smallest contact angles. This result emphasizes that glass cleaned with citric acid still has the smoothest surface and has the highest wettability. The acidic agents such as citric acid and the protector keep the surface more hydrophilic in all four cases.

On a hydrophobic surface, the droplets fall, and there is less exposure time to liquid water, but every droplet that is not strong enough to roll down and dries in makes a spot. On a hydrophilic surface, however, the water runs off in the form of a film. Thus, the rest of the water drying with the rest of the dirt makes a haze that gradually decreases. It is much better for windows and exterior mirrors of cars if they are hydrophilic because if droplets form on them, they disturb the image much more. In photovoltaic applications, these small droplets can increase the temperature locally, resulting in energy losses. However, when they are just new droplets, they do not do too much damage. Some people prefer to make the surface hydrophobic for easy to clean. Nevertheless, a hydrophilic surface is preferred for this study; therefore, the low contact angles obtained using citric acid or protector are emphasized.

4.2   Transmission measurement

The transmission percentages shown in Table 5 were obtained by finding the maximum value in the visible range (380-780 nm) of each spectrum. Measurements on unweathered glass showed that the transmission is around 91%. Naturally weathered glass and glass that has been weathered for one day in a climatic chamber also has a transmission of around 91% after cleaning because the surface has not been damaged, and it recovers its original transmittance. The percentage transmitted through the glass depends on the glass thickness and the refractive index [123]. In this case, all the glass samples have the same thickness; thus, it is expected that all the glass samples have the same transmittance. However, after seven days, the glass weathered in a climate chamber developed a cloudy surface, causing the transmission to drop to 88-89% (see Table 5). This again emphasizes that the 7-days exposure in the climate chamber is the harshest method for the glass. However, when comparing the three cleaning solutions on the 7-day weathered glass, the glass cleaned with the citric acid seems to maintain a higher transmission than Schukolin and DI water.

Table 5. Maximum transmission of unweathered and weathered glass after cleaning including the protector solution.

Cleaning agents	Unweathered	Natural weathering	Climate chamber 1 day	Climate chamber 7 days
DI water	90.8%	90.8%	90.9%	88.6%
Schukolin	90.8%	90.8%	90.9%	89.3%
Citric acid	90.6%	90.8%	90.9%	89.8%
Protector	--	90.4%	91.0%	89.8%
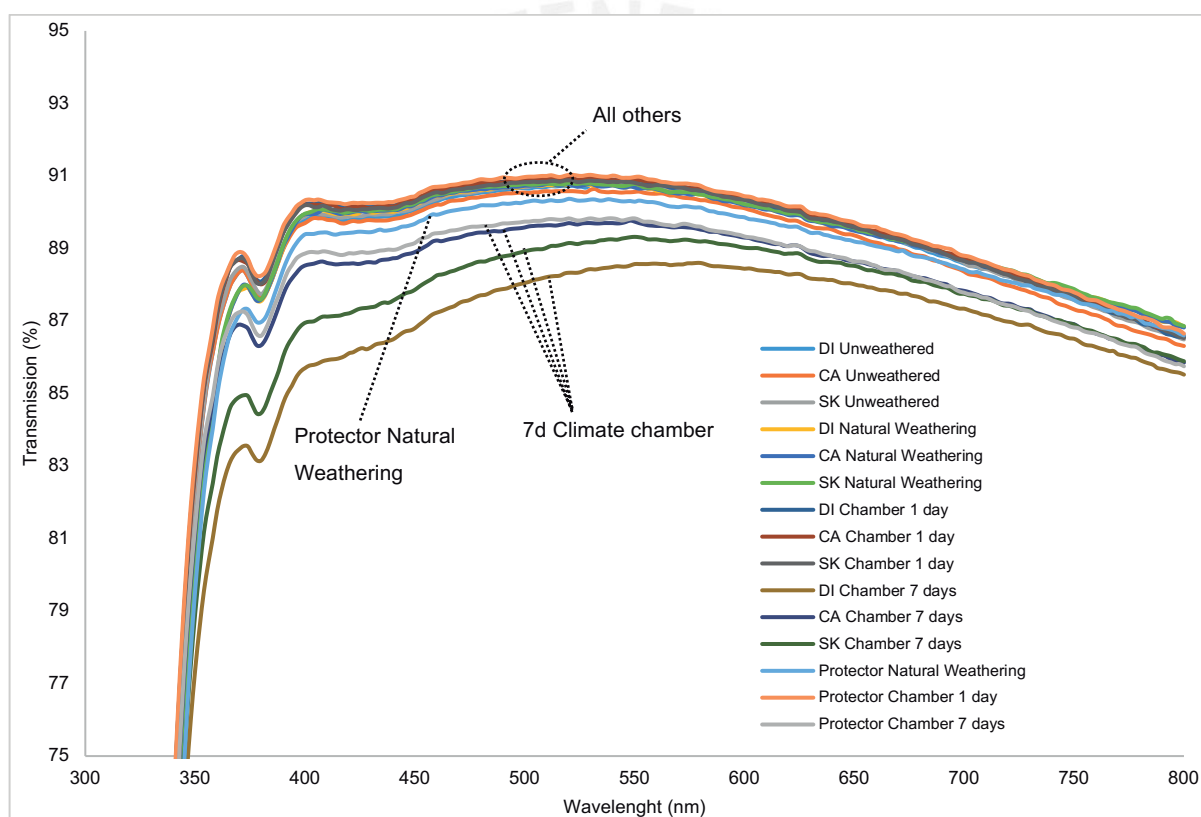
Figure 19. Optical transmission visible spectrum of unweathered and weathered glass after different exposures and treatments.

The percent transmission in the visible range (380-780 nm) of all the glass samples is shown in Figure 19. The lower value of 90.4% of natural weathered glass with protector could be due to the dry whitish protector layer on the glass surface, which was difficult to remove. Alternatively, another reason could be that the protector might enhance the reflectivity of the glass. Even though a big difference in reflection was not observed, it cannot be discarded. In addition, it can be observed that the glass weathered in a climate chamber for seven days and cleaned with DI water has the lowest maximum transmission of 88.6%, followed by the glass cleaned with Schukolin with 89.3%. The glass cleaned with citric acid has the highest maximum transmittance of 89.8%. There are no differences in all the other spectra; they show a normal variation within the measurements due to variations in the cleanliness of the samples. The higher the transmittance, the less altered and cleaner the surface. Citric acid has better performance in cleaning and protecting the glass surface. Most of the transmission loss could be due to straight light, which results from the different refractive indexes within surface layers. The whitish haze from the protector consists of micrometer-thick layers with different refractive indexes. A lot of highly refractive phosphate on the surface produces a lot of straight light in some places. Another point is that the refractive index changes when sodium is removed from the surface.

4.3 Light microscope images and analysis

4.3.1 Natural weathering in rural environment

4.3.1.1 20 days of exposition unsheltered

Glass samples exposed 20 days unsheltered underwent different weathering conditions. These included some days with moderate and heavy rain. The day with the highest precipitation was June 6th (see Figure 20), with a precipitation amount of 27 mm, i.e., 27 liters of rain per square meter. As a result, the contaminants (bird droppings, cement dust, aluminum particles, and sea salt) were removed and did not remain on the glass surface.
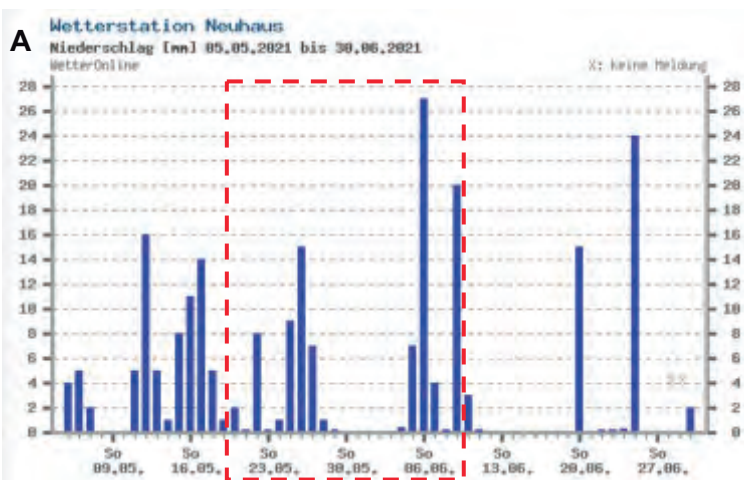
Figure 20. A) Precipitation during the first 20-days of exposition at the Neuhaus am Rennweg (50°30′36″ N 11°08′16″ E, 800 m AMSL) weather station [124]. **B)** Representation of the precipitation amount in mm per square meter [125].

At first glance, the glass samples appeared to have a clean surface. Although they did not appear damaged, the glass surface was evaluated under the light microscope to determine any microscopic degradation. Water rims predominate on all the glass samples. The small dust particles are completely removed with the three cleaning solutions.
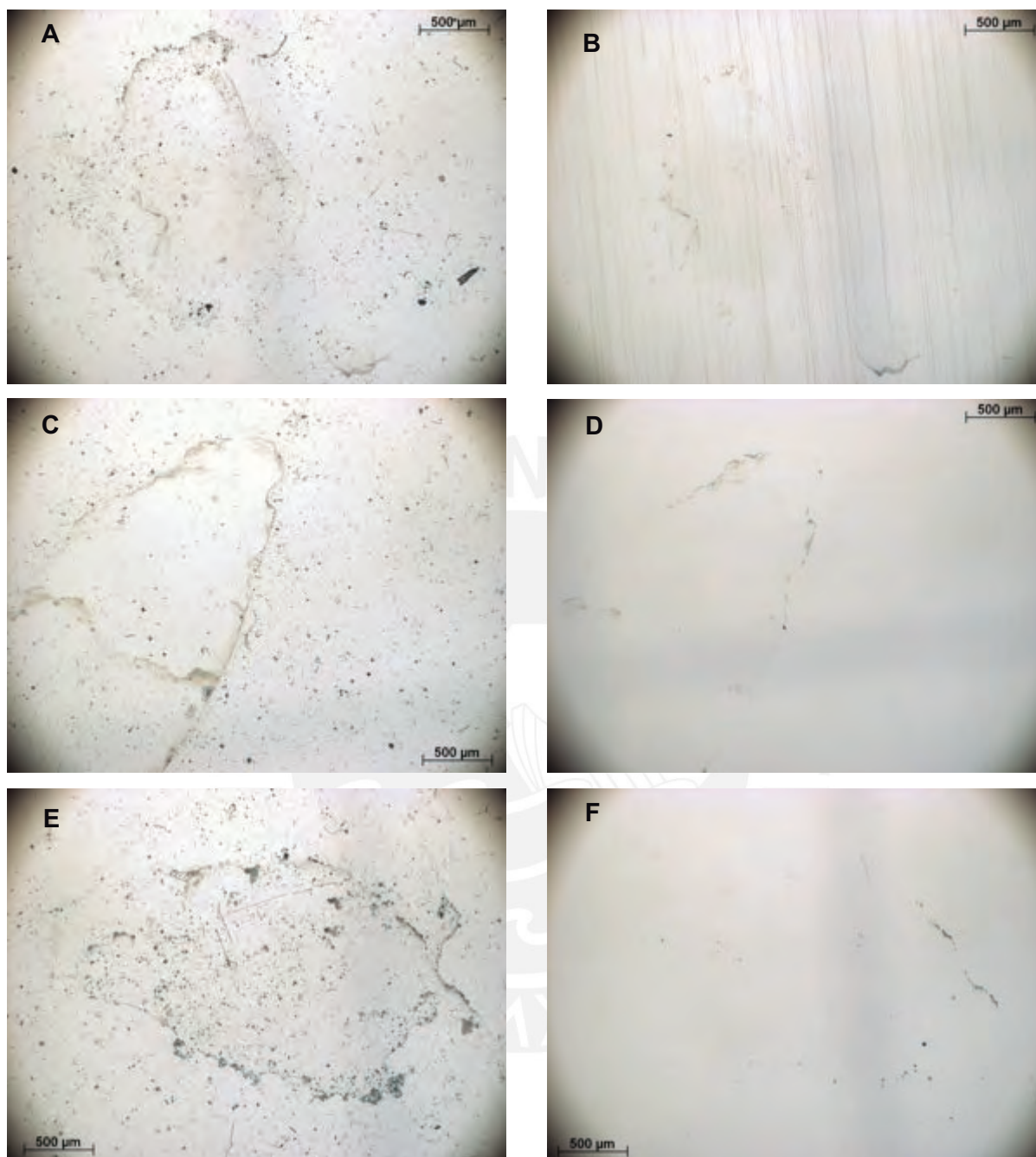
Figure 21. Water rims on glass weathered outdoors unsheltered for 20 days. **A)** Treated with citric acid before cleaning. **B)** Treated with citric acid after cleaning. **C)** Treated with DI water before cleaning. **D)** Treated with DI water after cleaning. **E)** Treated with Schukolin before cleaning. **F)** Treated with Schukolin after cleaning.

After noticing that the mechanical cleaning with citric acid left some traces on the glass surface, as seen in Figure 21B, manual cleaning with a cotton swab was performed to observe how the citric acid interacts with the glass surface in a small area. This cleaning was done next to the

microscope to immediately observe and capture the images of the process (see Figure 22). It was found that while cleaning, a sliding effect was created between the cotton swab and the glass surface, leaving some traces in the cleaning direction (see Figure 22C); however, these lines can be removed (see Figure 22D). The traces and their removal could mean that a few nanometers were removed from the surface, leaving behind a new surface. This sliding effect could prevent the glass surface from being scratched during cleaning. It is important to note that cleaning with citric acid can be time-consuming because it requires more time to obtain a better-cleaned surface. Further investigations are suggested in this context.
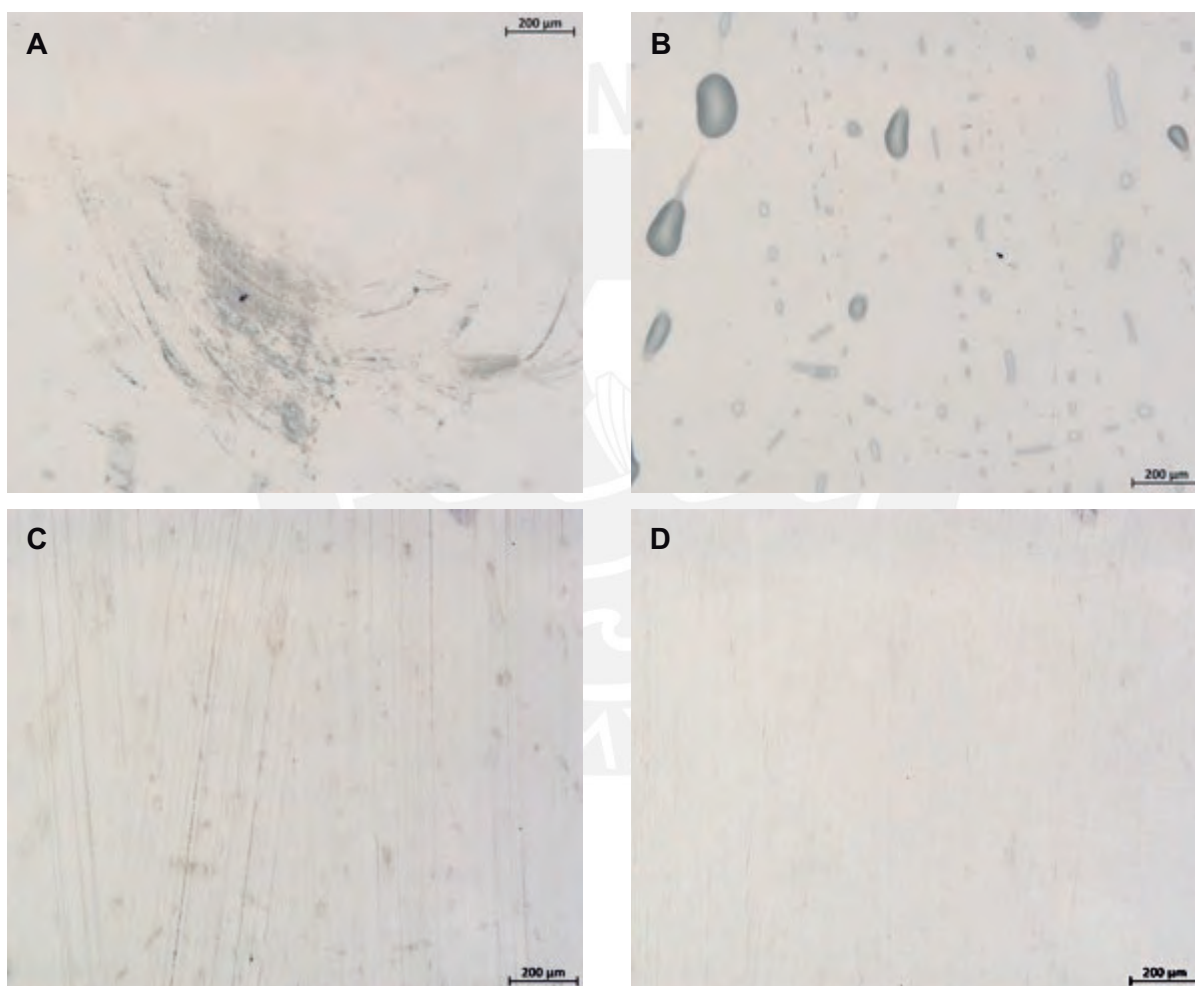
Figure 22. Glass sample during cleaning with citric acid using a cotton swab: **A)** Uncleaned, weathered glass outdoors unsheltered. **B)** Wetting the surface with citric acid, formation of droplets. **C)** Moving the cotton swab up and down four times to clean the surface leaves some traces. **D)** After 8 wipes, the traces are removed; clean surface.

The glass specimens exposed in Ilmenau show minor alterations that could lead to corrosion if the surface is not cleaned. More attention must be paid to the water rims and cement traces that are difficult to clean to avoid further corrosion (see Figure 23). The combination of rainwater and cement dust alters the glass surface, as iridescent effects can be observed in the weathering products.
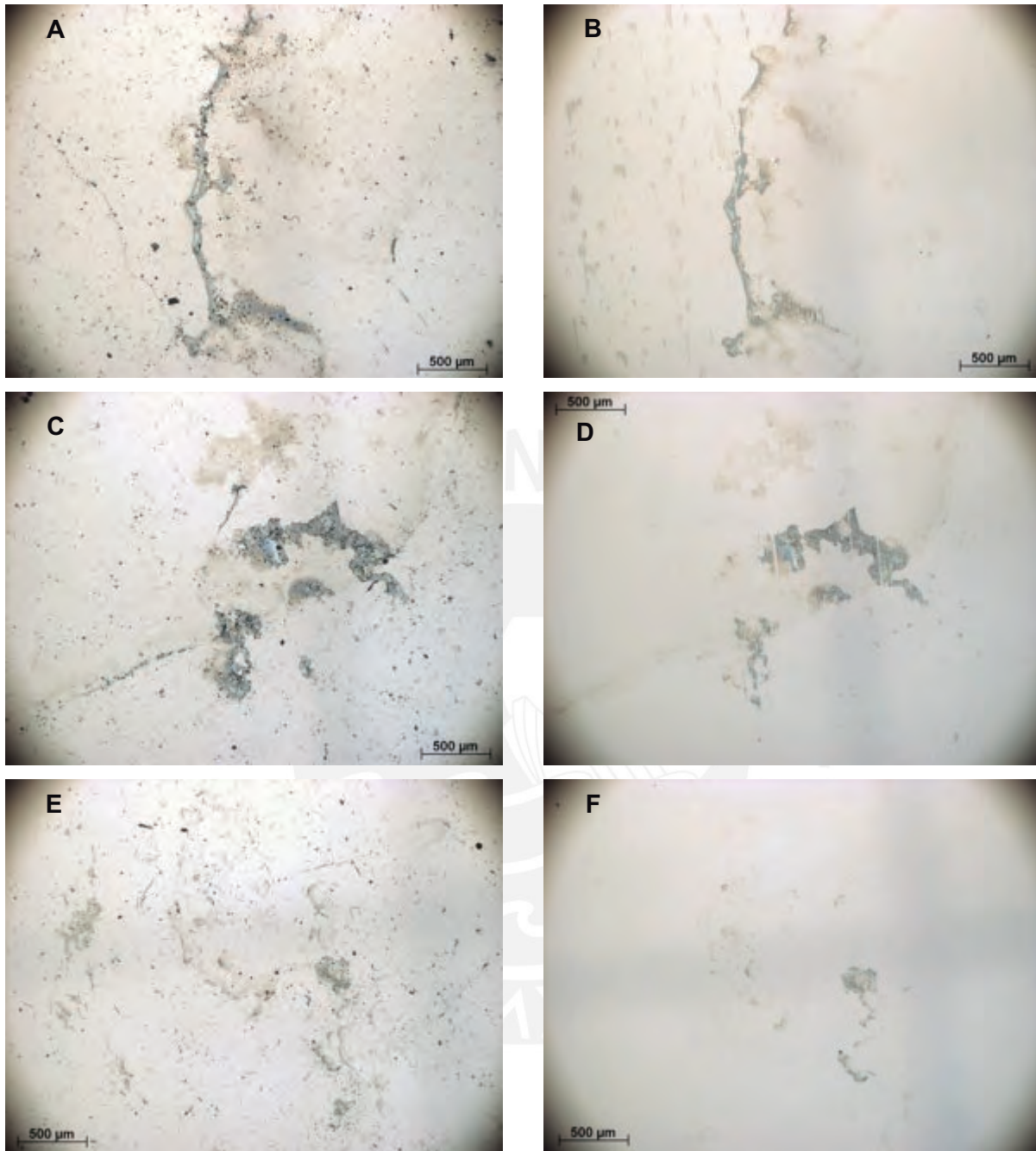
Figure 23. Traces of water rims and cement dust on the glass surface after 20 days unsheltered. **A)** Treated with citric acid before cleaning. **B)** Treated with citric acid after cleaning. **C)** Treated with DI water before cleaning. **D)** Treated with DI water after cleaning. **E)** Treated with Schukolin before cleaning. **F)** Treated with Schukolin after cleaning.

4.3.1.2 30 days of exposition with shelter conditions

This time, most contaminants remained on the glass throughout the exposure period (see Figure 24). More bird droppings and cement dust remained on the glass surface (Figure 24A) than sea salt and aluminum particles. Wind may also have contributed to removing some of the contaminants. Very few aluminum particles remained on the surface after exposure, and at first glance, no sea salt was visible on the surface (Figure 24B).
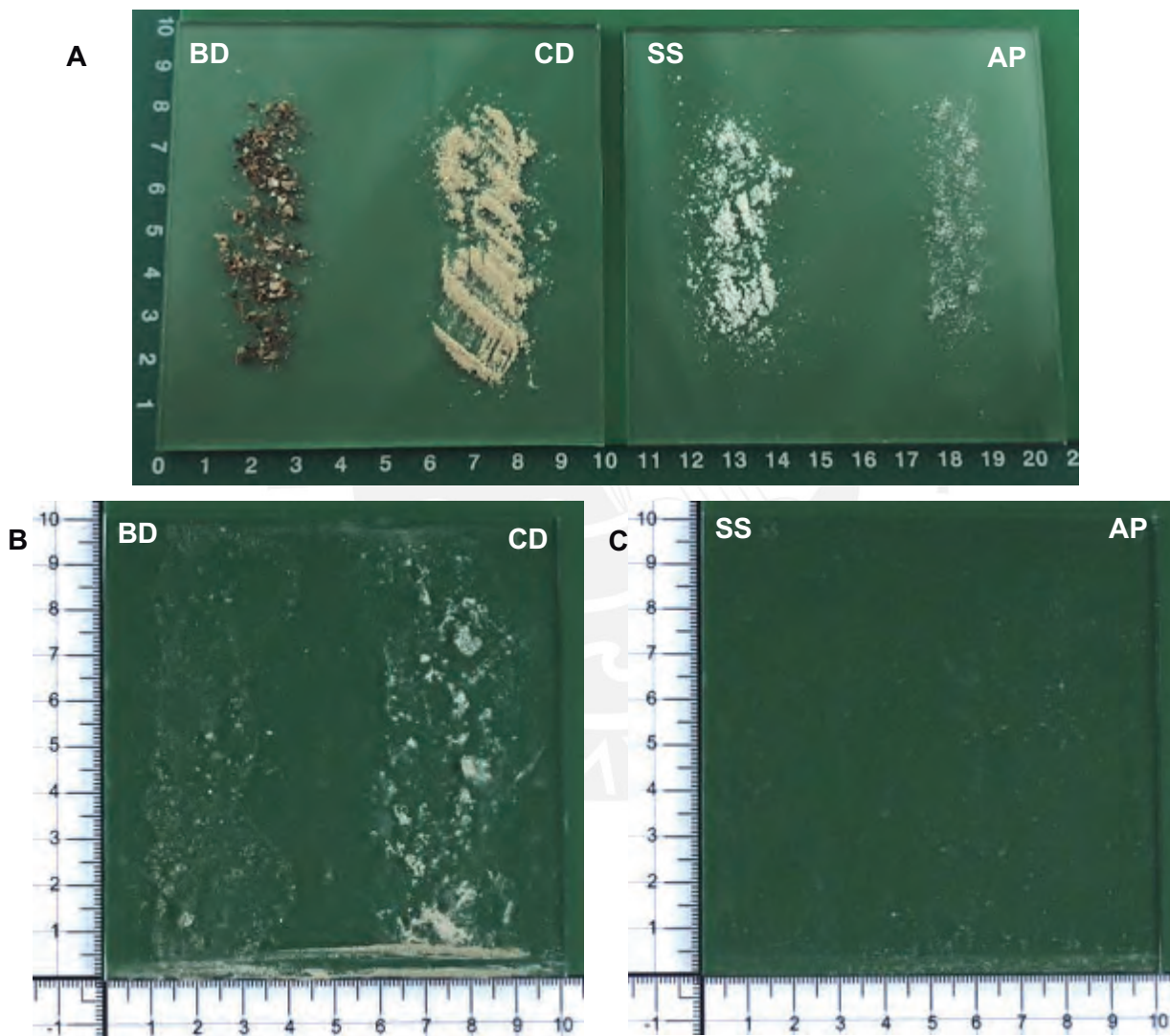
Figure 24. A) Glass samples with the four contaminants before weathering. **B)** Glass on which bird droppings and cement dust were deposited after 30 days of natural weathering before cleaning. **C)** Glass on which sea salt and aluminum particles were deposited after 30 days of natural weathering before cleaning.

The glass samples were cleaned, and the surface was examined with an optical microscope. The most common effects detected were delamination and iridescent spots of various sizes. These two are difficult to remove with the cleaning agents. Water rims were not found because the samples had not been in contact with rain. When glass is exposed to the natural environment, sunlight, temperature, and humidity fluctuations accelerate the alteration in the glass surface, leading to corrosion. The adhesion of particles to the glass surface also contributes to the deterioration of the surface, enhancing the formation of iridescent films (Figure 25C).

The adhesion of particles to the glass surface happens due to capillary forces and Van der Waals forces [53]. In capillary forces, liquid bridges are formed between the particle and the glass surface. Capillary forces increase when humidity increases. Van der Waals forces result from the direct contact of the particles with the surface; as the contact area increases, the Van der Waals forces increase. The particles are not easily removed from the surface when the capillary and Van der Waals forces increase.

The iridescent films indicate that a corrosive layer has formed due to the migration of alkali ions to the glass surface [94]. The alteration layer is fragile, and if moisture is maintained, it will eventually result in delamination of the surface (Figure 25F). Delamination and iridescent effects were observed in most glass samples, but after comparing the microscope images, the biggest and most frequent delamination effects were found in the glass samples treated with Schukolin (Figure 25E and 25F). However, since no chemical data is given from this cleaning solution, further interpretations cannot be made. For glass treated with DI water, the delamination effects are a bit smaller and less frequent. Furthermore, with citric acid, the effects are the smallest (Figure 25A and 25B); therefore, the citric acid solution with a low pH does not compromise the glass surface.
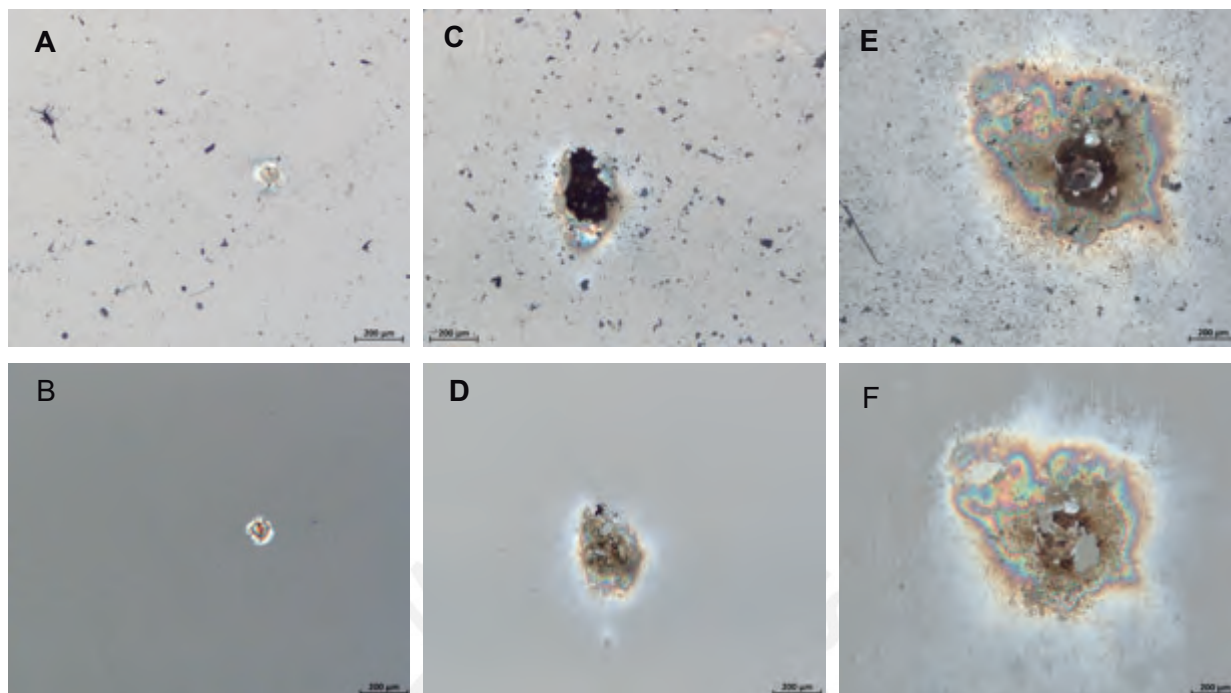
Figure 25. Iridescence and delamination effects after natural weathering under shelter conditions. **A)** Treated with citric acid before cleaning. **B)** Treated with citric acid after cleaning. **C)** Treated with DI water before cleaning. **D)** Treated with DI water after cleaning. **E)** Treated with Schukolin before cleaning. **F)** Treated with Schukolin after cleaning.

Other less common weathering products on glass surfaces include bulges (see Figure 26) found on samples treated with citric acid and DI water. In addition, the presence of aluminum particles on glass and the humidity of the environment cause cementation of this metal on the surface, which is difficult to remove with the cleaning agents.
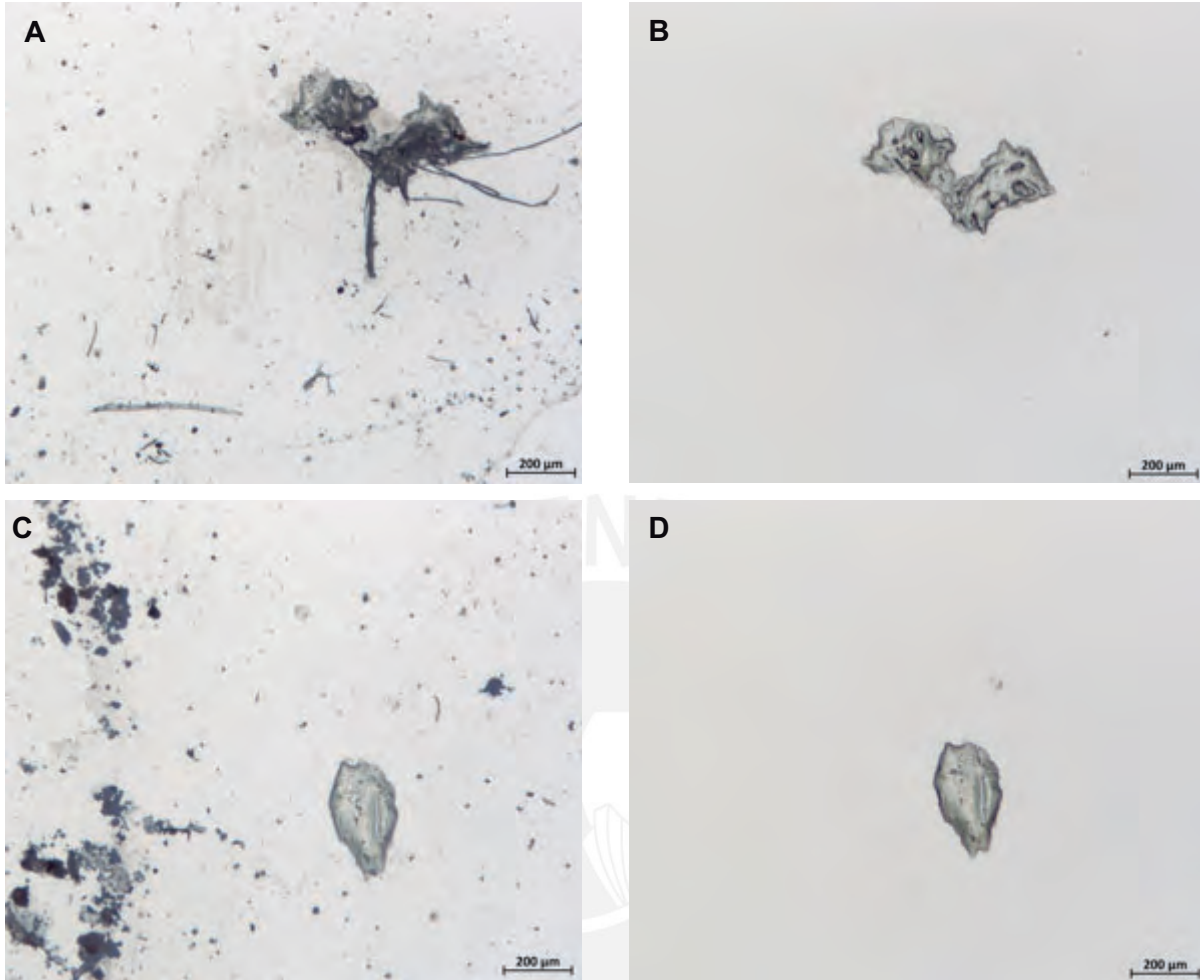
Figure 26. Bulges far from any contaminant after natural weathering under shelter conditions. **A)** Treated with citric acid before cleaning. **B)** Treated with citric acid after cleaning. **C)** Treated with DI water before cleaning. **D)** Treated with DI water after cleaning.

A solid bridge is formed after water from the environment evaporates, leaving behind the water-insoluble particle attached to the glass surface. After cleaning, the aluminum particles (Figure 27A and 27C) seem to have not been completely removed (Figure 27B and 27D). A thin cemented layer remains on the surface because solid bridge bonds are formed between the insoluble aluminum particle and the glass surface, increasing the particle adhesion to the surface, making it difficult to clean [53].
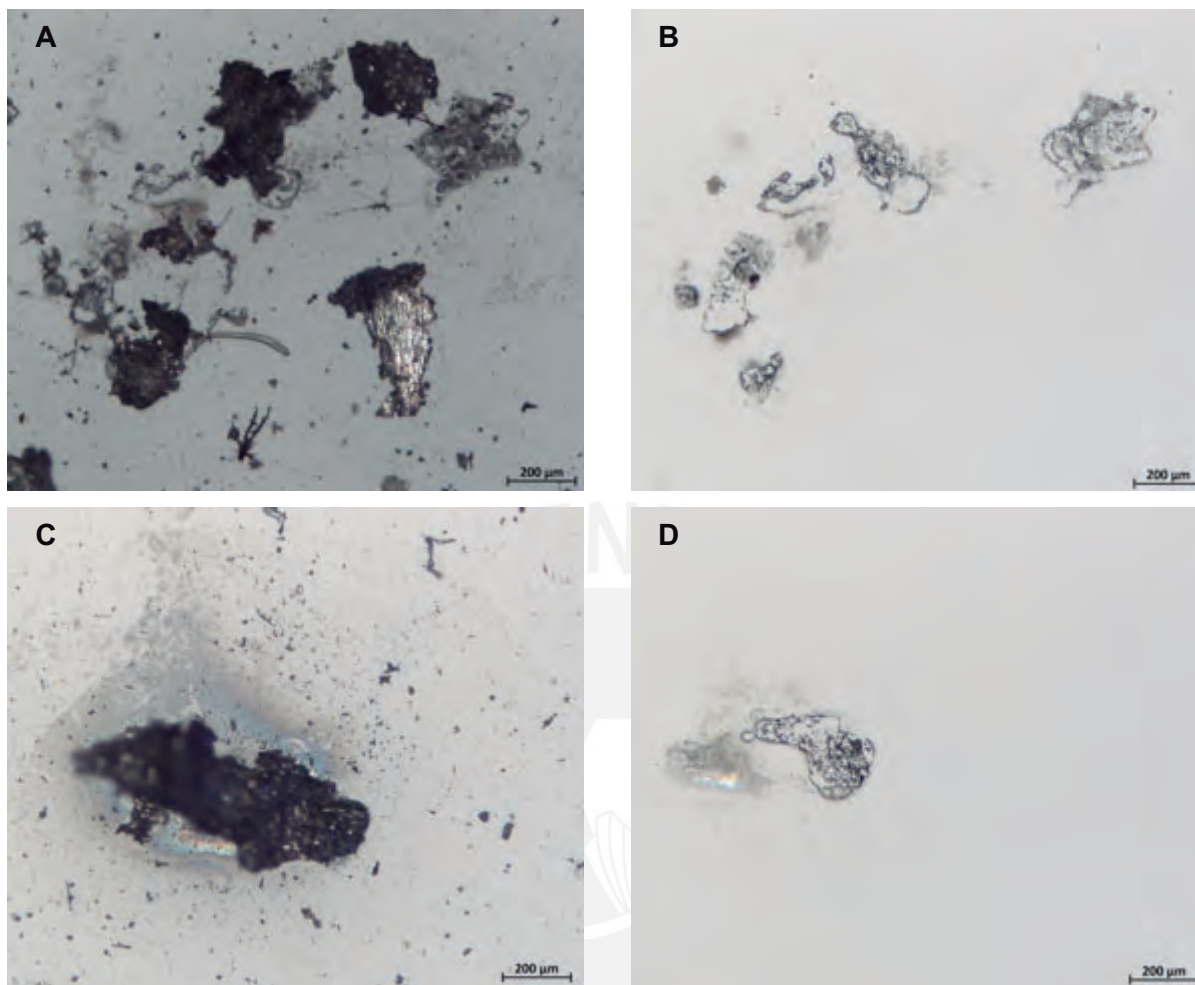
Figure 27. Aluminum particles forming a cemented layer on glass surface after natural weathering under shelter conditions. **A)** Treated with DI water before cleaning. **B)** Treated with DI water after cleaning. **C)** Treated with Schukolin before cleaning. **D)** Treated with Schukolin after cleaning.

Cement dust is a severe contaminant to the glass surface. The alteration in the surface is reflected in a change in the color of the surface (see Figure 28). Iridescent layers formed on almost the entire surface where cement dust is present. Before removal, it is observed that the iridescence color is less intense for glass treated with citric acid. Removing such a layer is difficult; however, citric acid seems to assist a faster and better removal of such layer. Perhaps, citric acid forms a more durable gel layer. This can be observed in Figure 28B, where scratches and layers are only present in few regions on the glass surface after cleaning.
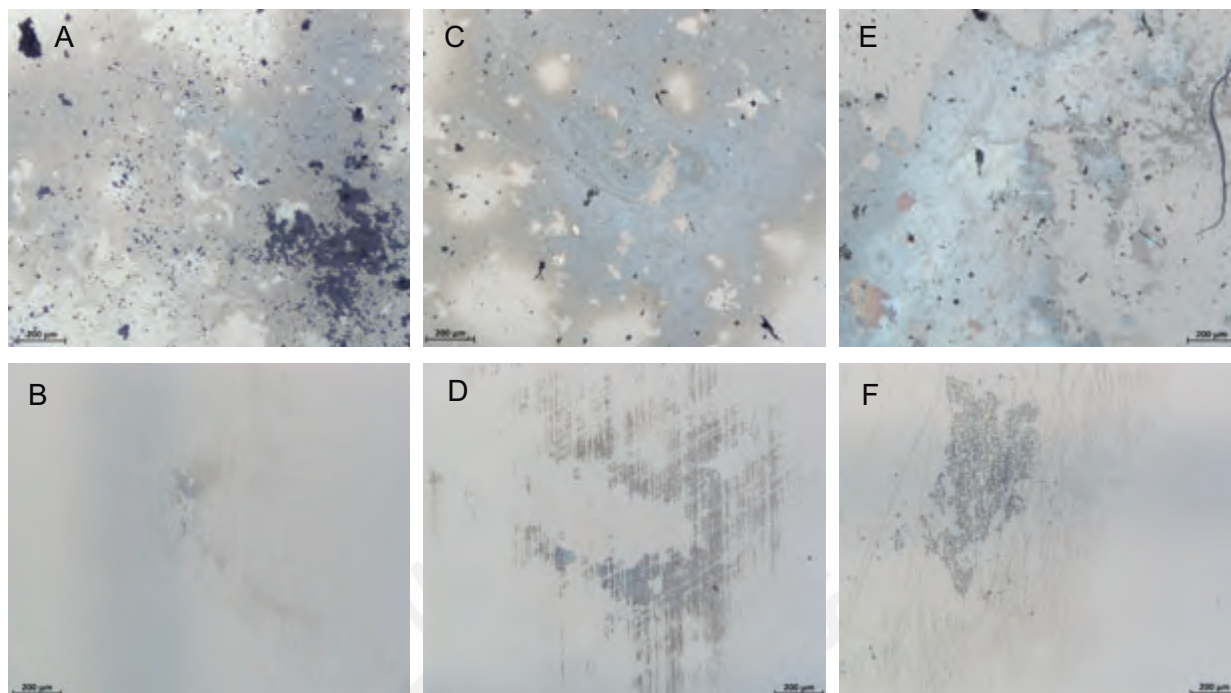
Figure 28. Cement dust alteration layer on glass surface after natural weathering under shelter conditions. **A)** Treated with citric acid before cleaning. **B)** Treated with citric acid after cleaning. **C)** Treated with DI water before cleaning. **D)** Treated with DI water after cleaning. **E)** Treated with Schukolin before cleaning. **F)** Treated with Schukolin after cleaning.

The glass samples treated with protector solution are shown in Figure 29. After cleaning with DI water, the protective layer is not entirely removed; some parts of the protector remain attached to the surface (see Figure 30B) because too much was applied. After weathering, alterations on the glass surface, such as iridescent films and thin cemented aluminum layers, are still visible (see Figure 30A). Bulges were not observed.
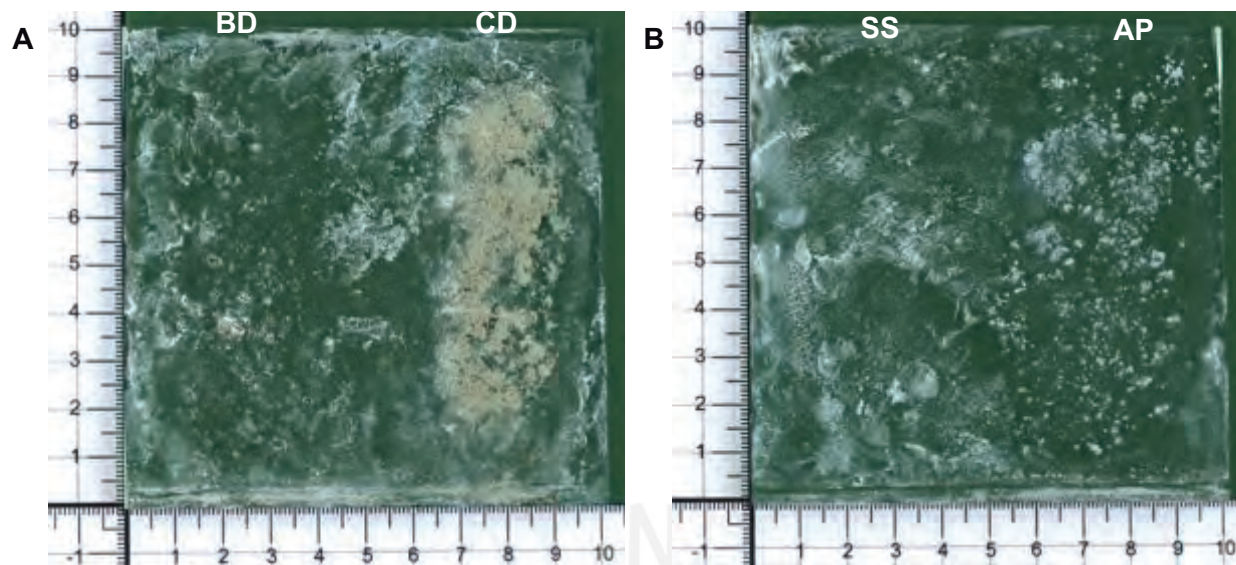
Figure 29. Glass samples treated with the protective agent after natural weathering. **A)** Glass on which bird droppings and cement dust were deposited. **B)** Glass on which sea salt and aluminum particles were deposited.
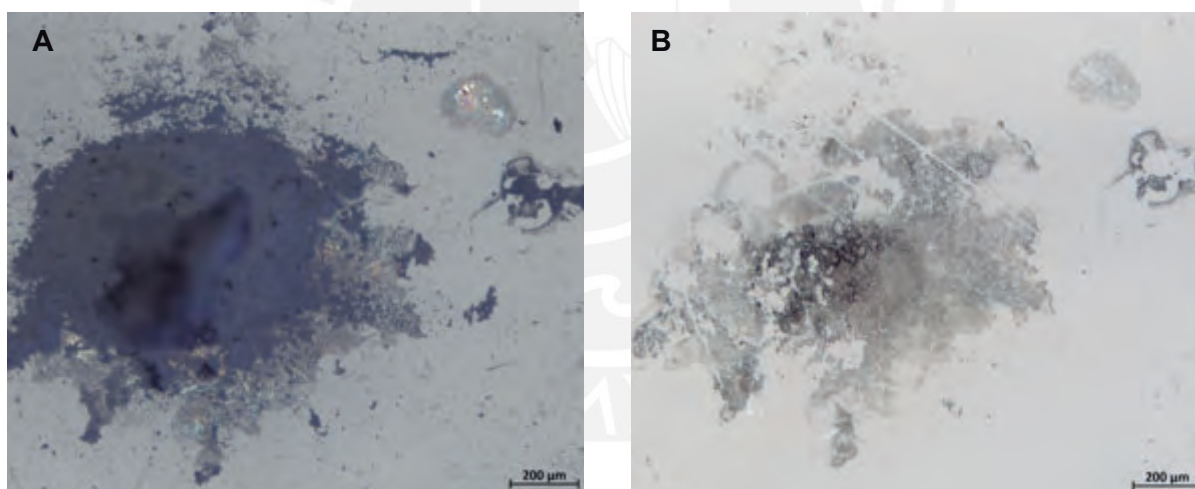
Figure 30. A) Protector, iridescent film and aluminum particle on glass surface after natural weathering, before cleaning. **B)** Remaining of protector and thin cemented aluminum layer after cleaning with DI water.

4.3.2 Long-term unsheltered exposure in urban environment

After long-term exposure, much dirt had accumulated over the years, but the surface was only moderately altered. Some physical similarities have been observed. Very few and small iridescence and delamination effects (Figure 31C), more small and large bulges (Figure 31A),

and few water rims (Figure 31E) were observed before cleaning. Small particles can be easily removed with the three cleaning solutions. After cleaning, similar weathering products such as delamination, iridescent effect, bulges, and water rims are still present. Differences on glass surfaces after different cleaning are small and difficult to interpret. The irreversible changes were minor when compared to the glass exposed in Ilmenau and the climate chamber. The adherence of atmospheric airborne has been lower in glass samples exposed in Erfurt; therefore, fewer weathering products are found on the glass surface during long-time exposure. Therefore, it can be said that natural activities such as rain, snow, and wind can maintain cleaner glass surfaces.
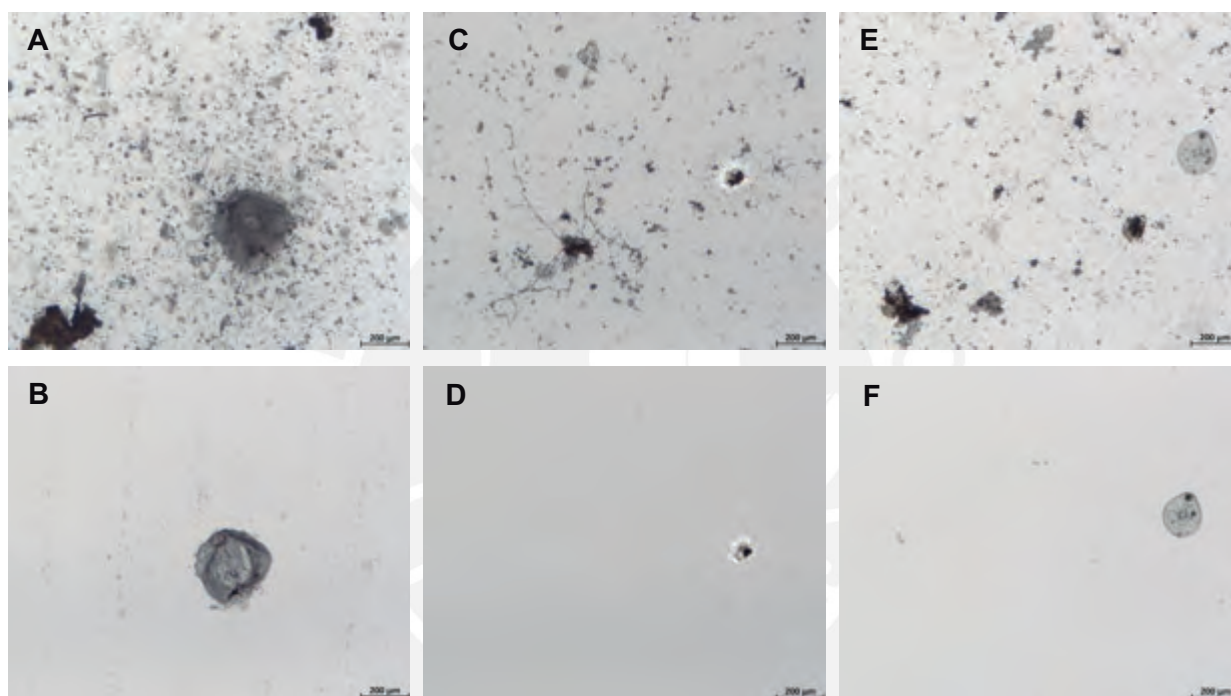
Figure 31. Weathering products on glass samples exposed for 1.5 years in Erfurt. **A)** Particles and bulges before cleaning with citric acid. **B)** Only bulges remain after cleaning with citric acid. **C)** Particles, weathering products and delamination effect before cleaning with DI water. **D)** Only delamination effects remain after cleaning with DI water. **E)** Particles and a water rim before cleaning with Schukolin. **F)** Water rim remain after cleaning with Schukolin.

4.3.3   Artificial alteration in climate chamber

4.3.3.1   Exposition for 1 day

Tests were carried out in the climatic chamber to compare the chemical attack on contaminated float glass with the natural weathering effect. The climate chamber parameters of 80 ºC and

80 %RH are very harsh for the glass because high temperature and high humidity increase the hydration rate and the leaching of ions from the glass surface. Therefore, it was decided first to expose it for twenty-four hours to see how the contaminants interact with the glass under these conditions. The glass was divided into four sections, one section for each contaminant. First, the contaminants were removed by running 150 ml of the cleaning solutions over the glass surface to see the alteration under each. After twenty-four hours, a non-homogeneous alteration is observed on the entire surface of the glass, which appears cloudy (see Figure 32A).
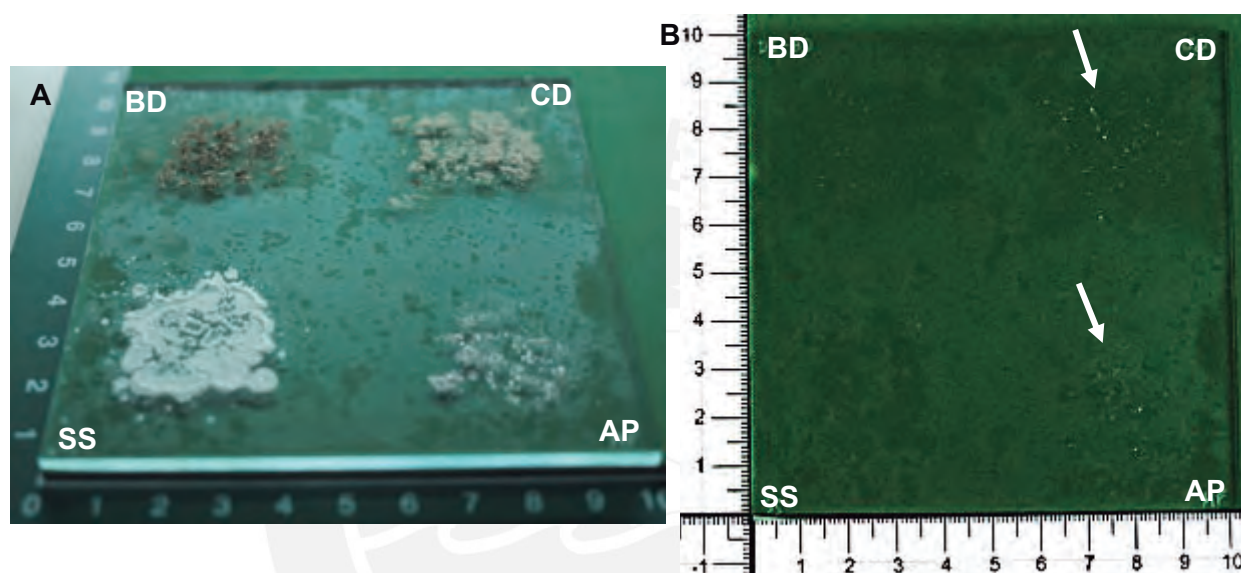
Figure 32. A) Bird droppings, cement dust, sea salt and aluminum particles on cloudy glass surface after 24 hours in the climate chamber (80 °C, 80 %RH). **B)** Glass surface after removal of contaminants by letting run 150 ml of DI water over it.

It appears that aluminum and cement are surface-active; some particles adhere to the surface and remain there even when 150 ml of deionized water is run over the surface (see Figure 32B- pointed with white arrows). At first glance, the surface does not appear to have changed much under the bird droppings and cement dust. Under sodium chloride (sea salt), the protection of the glass surface seems to be lower. In the climate chamber, sea salt changes from a solid to a liquid state and remains liquid until it is brought to ambient temperature, where it recrystallizes (see Figure 32A- SS section). In addition, the glass surface appears to have suffered some alteration under aluminum particles.

After mechanical cleaning, the glass surface was examined with an optical microscope, and it was found that the only contaminant that altered the glass surface was sea salt. Sea salt reacted

quickly with the glass because it is hygroscopic and agglomerates small particles on the rim after drying. The small amount of NaCl that remained on the rim dried as soon as the water dried. The rims of the salt after recrystallization were very difficult to remove (see Figure 33). None of the cleaning solutions can remove them completely. The strong interaction may be related to the chemical bonding of the salt to the glass surface. Twenty-four hours was not enough for contaminants such as bird droppings, cement dust, and aluminum particles to alter the glass surface in the climate chamber; these contaminants were easily removed with the three cleaning solutions.
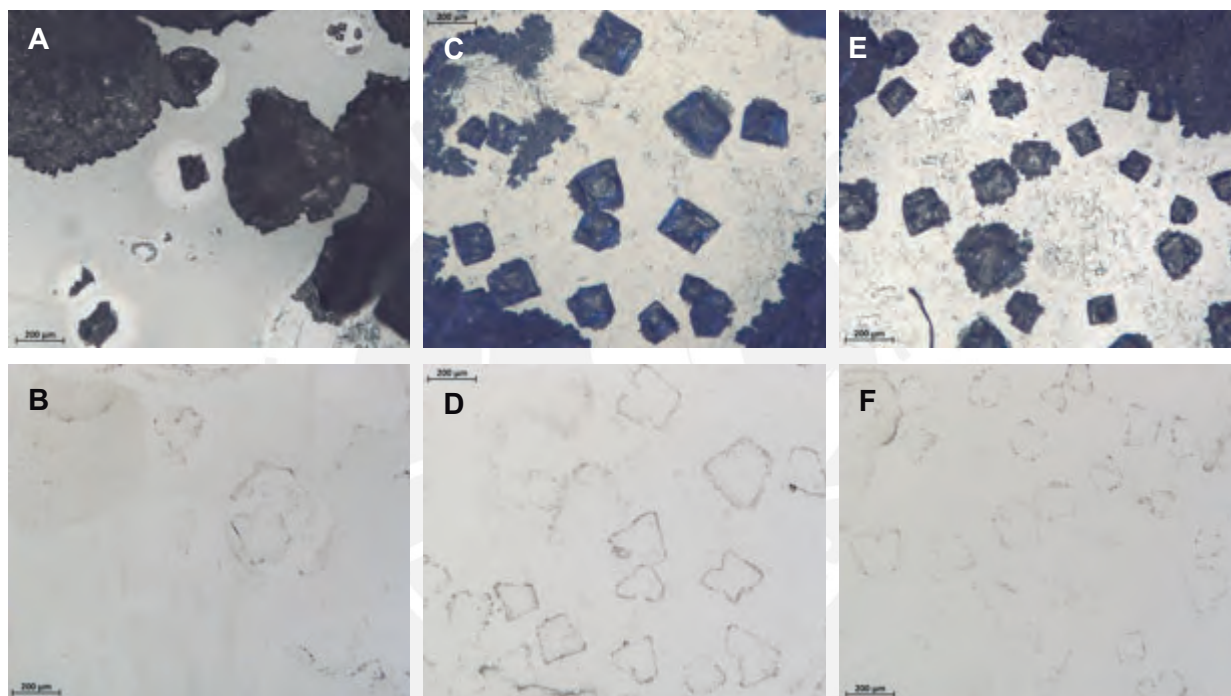
Figure 33. Weathered glass samples with sodium chloride in the climate chamber for 24 hours. A) Treated with citric acid before cleaning. B) Treated with citric acid after cleaning. C) Treated with DI water before cleaning. D) Treated with DI water after cleaning. E) Treated with Schukolin before cleaning. F) Treated with Schukolin after cleaning.

It was also noted that the glass sample treated with citric acid had no iridescent spots or bulges. However, five iridescent spots were observed in the sample treated with DI water and one bulge in the sample treated with Schukolin (see Figure 34).
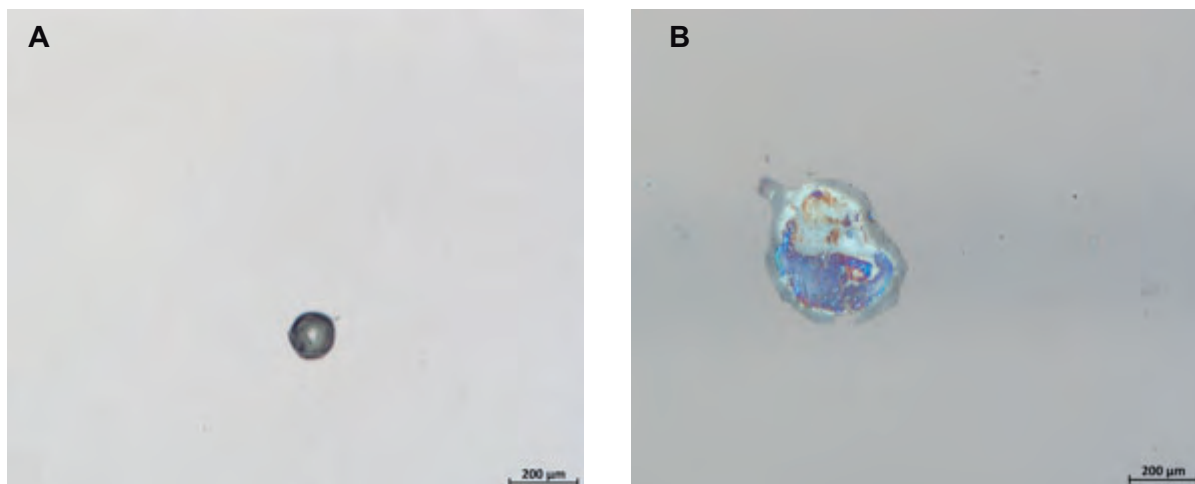
Figure 34. Glass weathered for 24 hours in the climate chamber. **A)** Bulge in glass treated and cleaned with Schukolin. **B)** Iridescent effects in glass treated and cleaned with DI water.

It was found that after cleaning, the rims of the recrystallized sea salt are fewer in the glass treated with the protector (see Figure 35D). However, the protective layer is not homogeneously distributed over the glass surface. After the protector is applied, the contaminants are added so that the contaminants are not in direct contact with the glass surface. Another problem with using the protector is that it sticks to the surface, and some spots are difficult to remove. Two bulges were observed, one in the bird droppings area and one in the sea salt area.
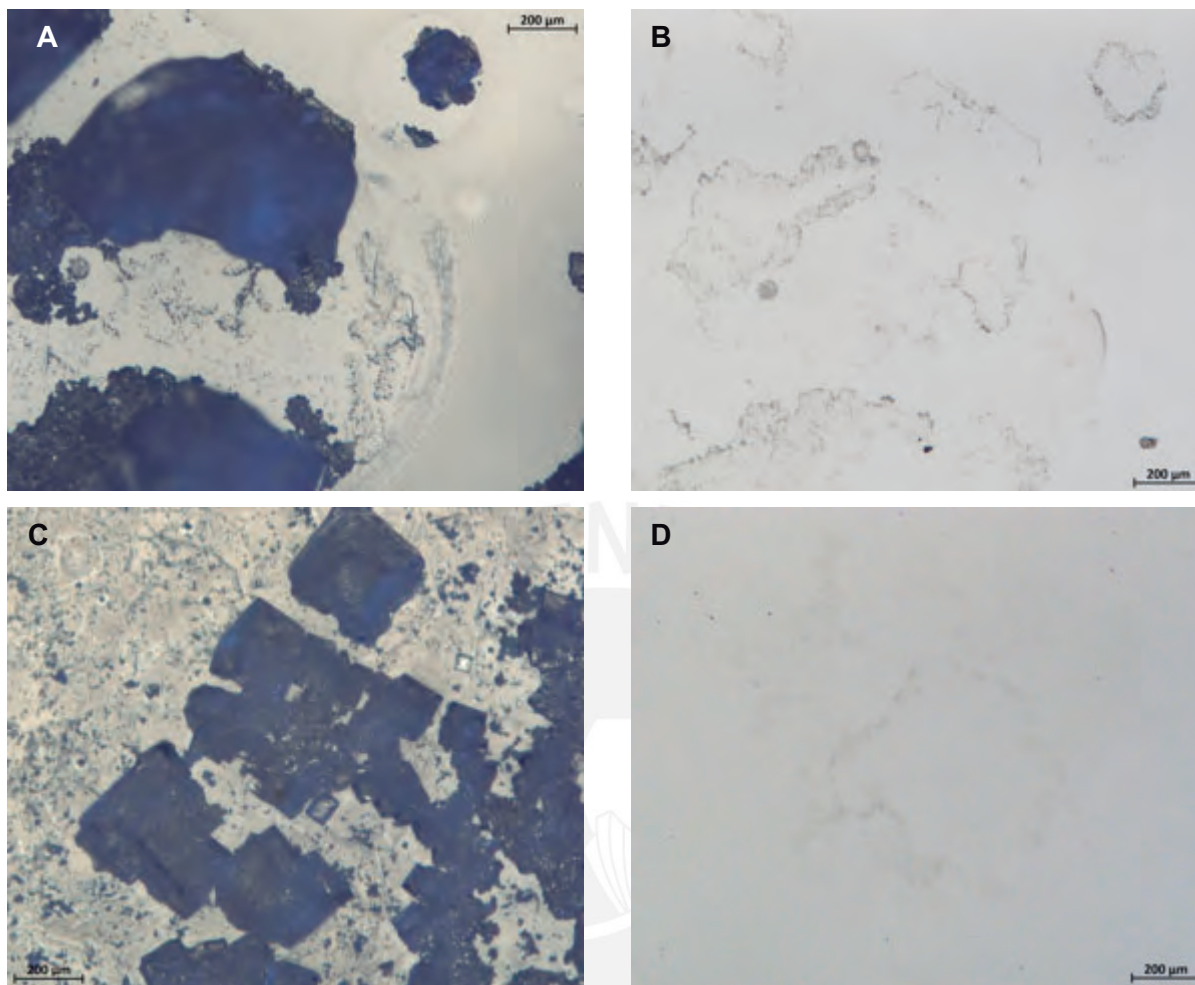
Figure 35. Glass weathered for 24 hours with sodium chloride in the climate chamber. **A)** Glass without protector before cleaning. **B)** Glass without protector after cleaning with DI water. **C)** Glass treated with protector before cleaning. **D)** Glass treated with protector after cleaning with DI water.

4.3.3.2   Exposition for 7 days

The experiment was repeated with new glasses, which remained in the climate chamber for seven days under the same conditions (80 ºC and 80 %RH). The longer the interaction between the contaminants and the glass surface lasted, the more damage occurred. A cloudier layer was formed on the surface compared to the glass exposed for one-day. The cloudy appearance originated from thick layers that developed with time in the climate chamber. After sodium ions were leached out and were not rinsed off, then layers built up. These layers did not develop homogeneously over the entire surface that is why the glass looks cloudy. After letting run 150 ml of the cleaning solutions over the surface, the observations from the one-day exposure in the

climate chamber were emphasized, where cement dust and aluminum particles remained even after letting run the cleaning solutions over it (see Figure 36). In addition, the areas where bird droppings were deposited and where sodium chloride (sea salt) recrystallized appeared to be less altered than their surroundings.
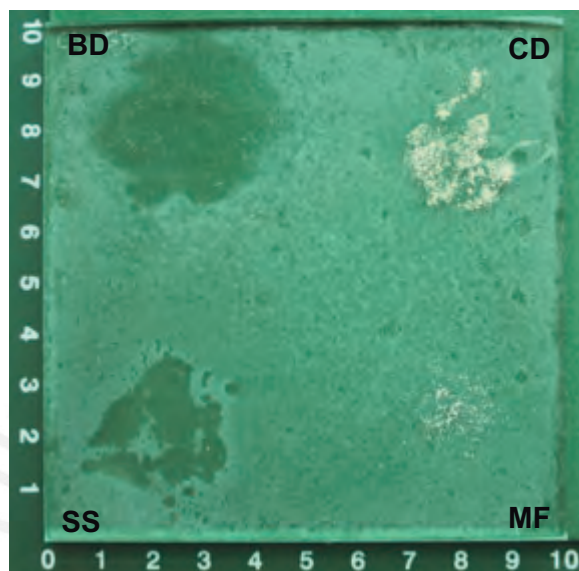
Figure 36. Cloudy glass surface after 7 days in the climate chamber (80 ºC, 80 %RH) and after removal of contaminants by letting run 150 ml of citric acid over it.

When viewed under the microscope, the contaminants that altered the glass surface were sea salt, aluminum particles, and cement dust. Each of these contaminants reacted with the surface in a specific way. There was minimal alteration on the surface that encountered bird droppings (see Figure 37D). In the bird droppings section, there were bigger particles that did not cling to the glass surface. The capillary forces between the particle and the glass surface could be small. The adhesion is low when the capillary force is low; thus, there is a low alteration on glass. Sea salt formed a rim after recrystallization that had an iridescent effect. It appears that the sea salt provided partial protection because the glass surface seemed to be much less altered inside the rims than outside the rims (see Figure 37A). The glass had a cloudy color outside the rim that could not be removed with three cleaning solutions. In addition, a definite contact rim was formed around the aluminum particle where it was deposited. The aluminum particle formed a solid bridge with the glass surface, and after the particle was removed, the solid bridge remained on the glass (see Figure 37B). An iridescent film was formed under or around the metal particle. Also, when cement dust was present, iridescent effects were produced (see Figure 37C). Below those iridescent films, the alteration was running faster. Some cement dust particles remained on the

surface after cleaning. These observations were repeated in the citric acid, DI water, and Schukolin samples.
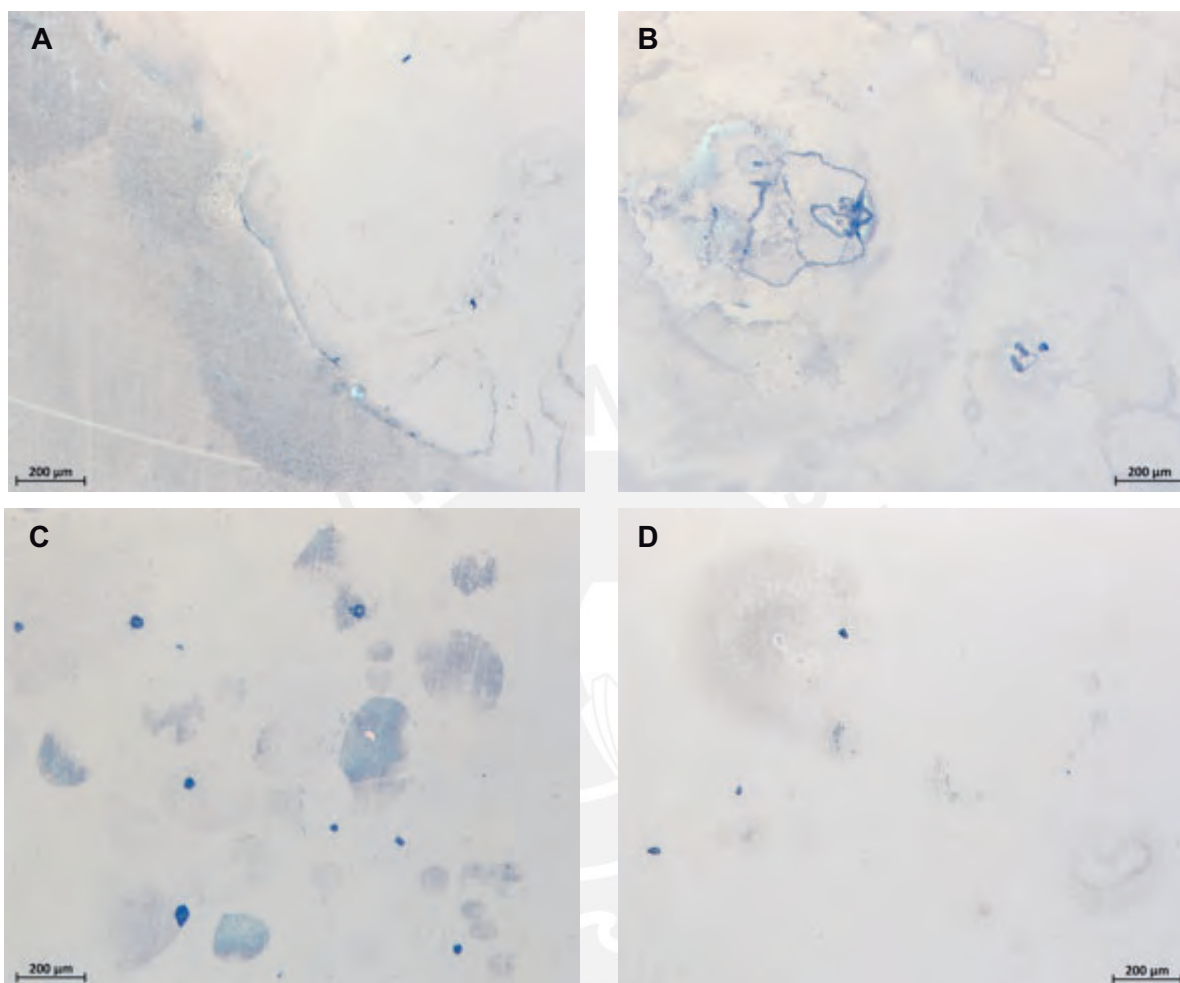
Figure 37. Weathering products on the glass surface after 7 days exposure in climate chamber. Glass samples were cleaned with DI water. **A)** Formation of water rim after removal of sea salt. **B)** Cemented part of aluminum particle and iridescent effect. **C)** Adhesion of cement particles and iridescent effect. **D)** Minor alteration in contact with bird droppings.

The glass without the protector formed a cloudy layer on the surface (see Figure 38A and 38C). Bulges were found on the glasses treated and cleaned with citric acid, DI water, and Schukolin. On the other hand, no bulges were found on the glass treated with the protector. However, cement particles adhering to the surface, solid aluminum bridges, and iridescent effects were still present in the glass with the protector (see Figure 38B and 38D). The protector prevented excessive surface degradation when exposed to a climatic chamber for seven days. However, it is not

recommended in the high concentration used here because it was difficult to remove after natural and artificial weathering (see Figure 39).
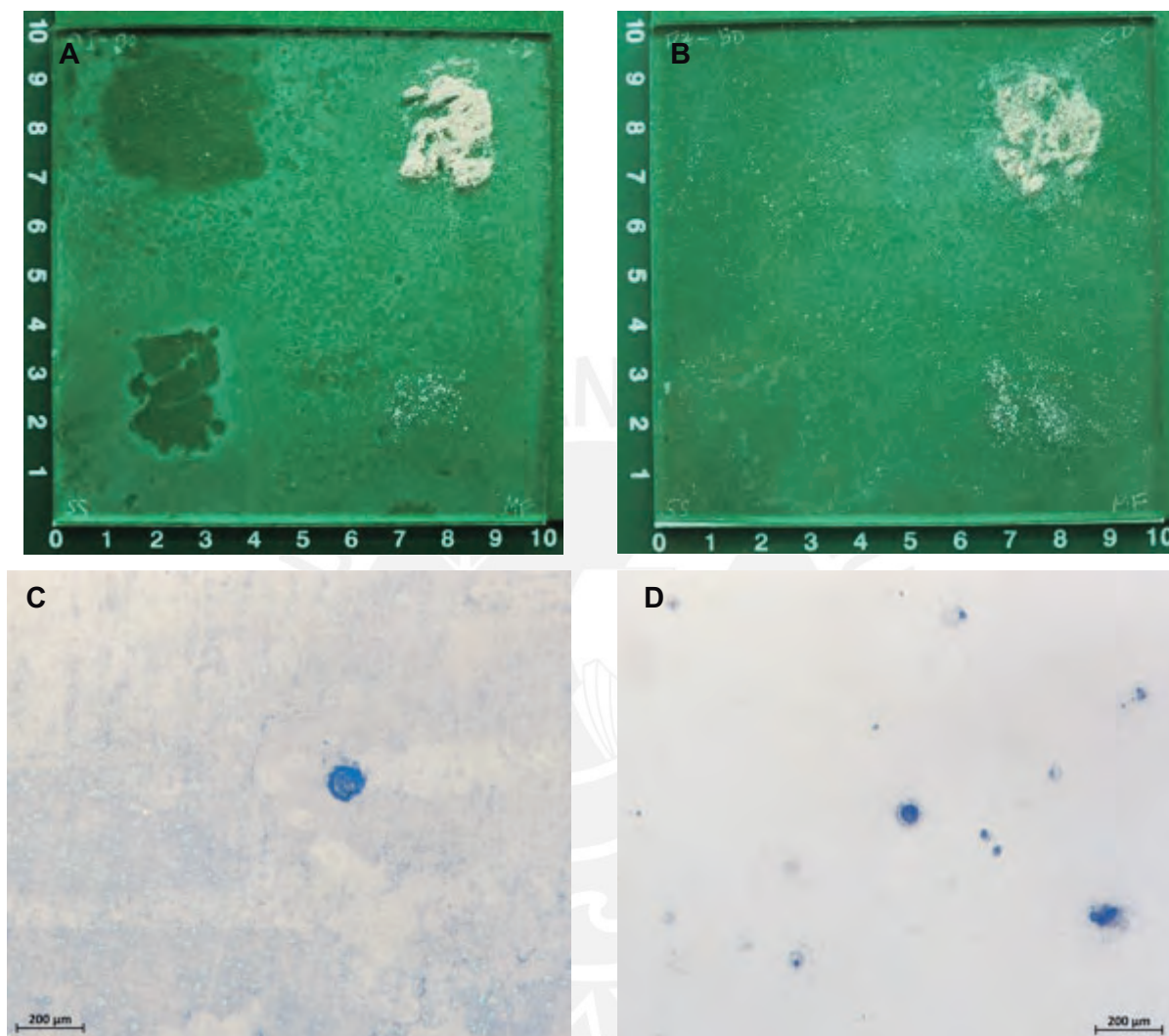
Figure 38. Glass samples weathered for 7 days in the climate chamber. **A)** Glass rinsed with 150 ml of DI water without protector. **B)** Glass rinsed with 150 ml of DI water with protector. **C)** Glass cleaned with DI water without protector. **D)** Glass cleaned with DI water with protector.
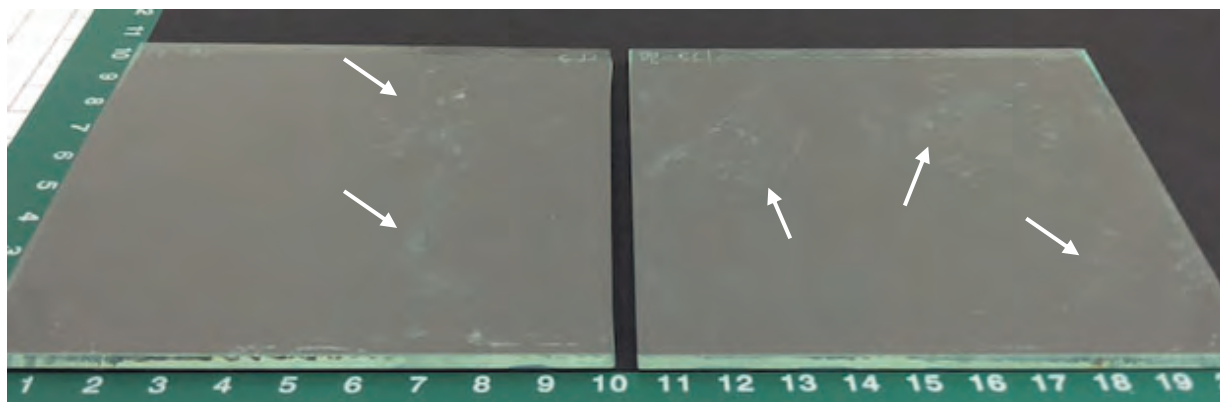
Figure 39. Remaining of dry protector after exposition and after cleaning with DI water (whitish spots pointed out with arrows).

4.4   AES images and analysis

The glass sample for this analysis was exposed for six months in an urban area on the sea coast (Durres, Albania), and after exposure, it was cleaned with DI water [33]. The weathering products to be analyzed are the water rim and the iridescent effect, which could not be removed after cleaning (see Figure 40B and 40C).
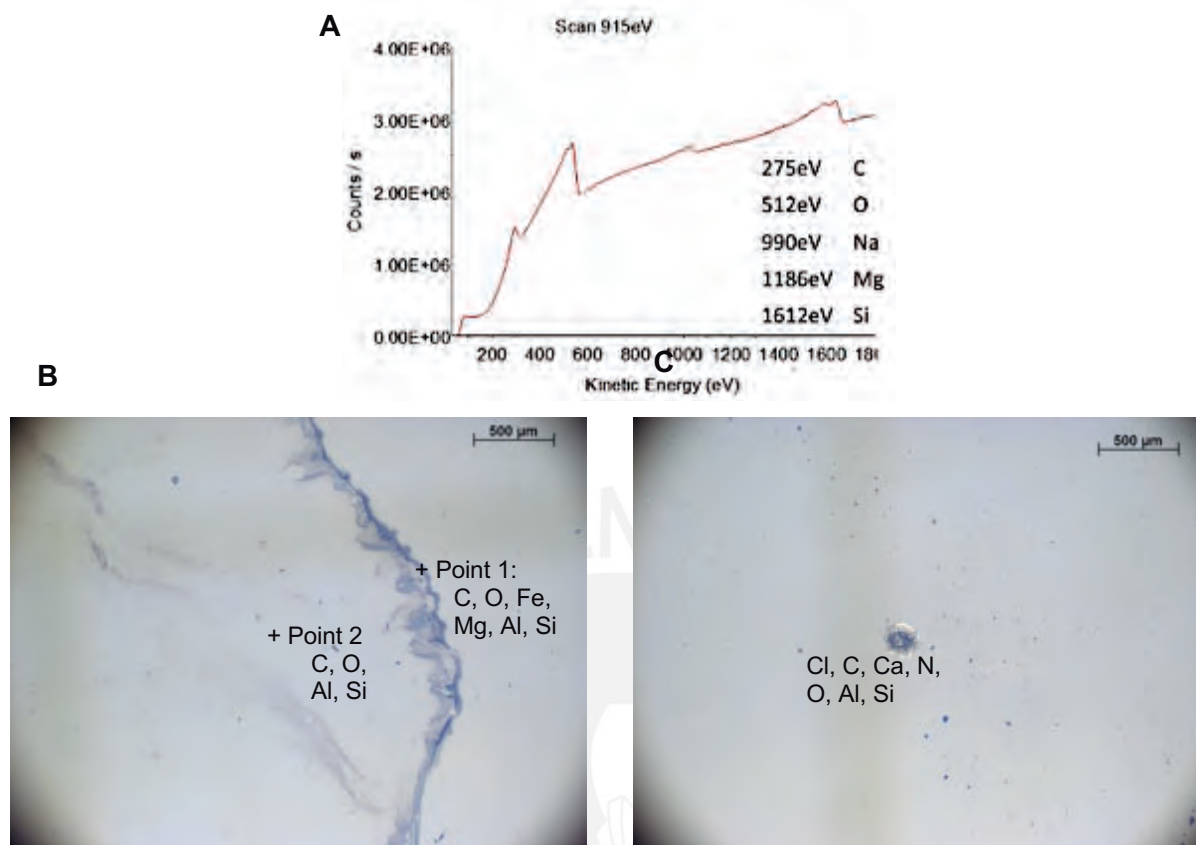
Figure 40. A) AES spectrum showing elements detected on an unweathered glass. Light microscope images of weathering products such as **B)** iridescence on a water rim and **C)** iridescent spot, after cleaning.

For the water rim (see Figure 40B): at point 1, carbon, oxygen, iron (very small), magnesium (very small), aluminum, and silicon were identified, and at point 2, away from the water rim, there was less carbon and no iron. For the iridescent effect (see Figure 40C): chlorine, carbon, calcium (small), nitrogen (small), oxygen, aluminum (very small), and silicon were identified. Carbon, oxygen, and nitrogen are elements found in the air and organic deposits. Silicon, sodium, and magnesium are elements also found on juvenile glass (see Figure 40A). Sodium, however, was not detected on the weathered glass. During weathering, sodium readily migrates from the bulk to the glass surface and forms a hydrated layer rich in sodium that is easily washed off by rain or snow or removed after cleaning.

The presence of iron in the water rim could come from mineral aerosols. Iron oxides are found in minerals such as hematite and magnetite [126]. Iron may also have originated from soil and desert dust [127]. Airborne iron may also originate from industrial and metallurgical plants, fossil fuel

combustion, traffic emissions, tire and brake wear, and road dust [128]. In the case of aluminum, it must be primally an external contaminant since glass contains a small amount of aluminum oxide and does not release it. Aluminum can come from airborne particles, the metal industry, or fuel combustion, depositing on the glass surface [129]. Inorganic dirt from the soil is predominantly aluminum. A high content of aluminum is found in sedimentary rocks, sandstones, and carbonates [130]. In the air, aluminum comes from the weathering of rocks and forms natural dust [131]. Feldspars, micas and, clay minerals contain aluminum [132]. Aluminum from soil and dust is found in air particles as aluminosilicates [133].

Chlorine can originate from natural emissions or human activities [134]. The primary natural source of chlorine is the evaporation of ocean spray as sea salt aerosol [135,136]. Deserts, dry salt-lakes, and saline soils of arid areas are sources of chlorine in dust storms [137]. Volcanoes release large amounts of hydrogen chloride [138]. Anthropogenic sources include biomass burning, coal combustion, and industrial emissions [139,140]. In addition, salts such as sodium chloride are used on roads and streets during wintertime.

Calcium ions in glass are bonded to two NBOs, they have low mobility, so it is less likely that calcium ions diffuse into the glass surface. Nevertheless, glass cannot be neglected as a source of calcium. Calcium is one of the major constituents of glass, but it was only detected on the glass surface of the weathered glass and not on the unweathered glass. Prolonged exposure time contributes to calcium ions migrating from the bulk to the surface, forming weathering products like $CaCO_3$. However, calcium could also come from the atmosphere, from cement plants, industrial plants, coal combustion, and construction [41]. Calcium and sodium are mainly coming from salts. Many Ca-salts are less water-soluble than Na-salt, so it is more likely to find them on rain-exposed surfaces. Calcium sulfates like gypsum $CaSO_4 \cdot 2H_2O$ are the most abundant salts detected on the glass surface after long-term exposition [87,141]. Calcium is abundant in soil, and it can be obtained from the weathering of the minerals like limestone, gypsum, and fluorite [142]. Calcium compounds are used in construction materials, like calcium carbonate, and calcium hydroxide is used to make cement [110].

4.5   SEM image and EDX analysis

The same sample used for Auger spectroscopy was also used for EDX analysis. EDX analysis was performed on the water rim as a weathering product (Pt3-Pt5) and on the glass surface next to the water rim (Pt1-Pt2) as a reference to compare composition and signal ratios (see Figure 41).
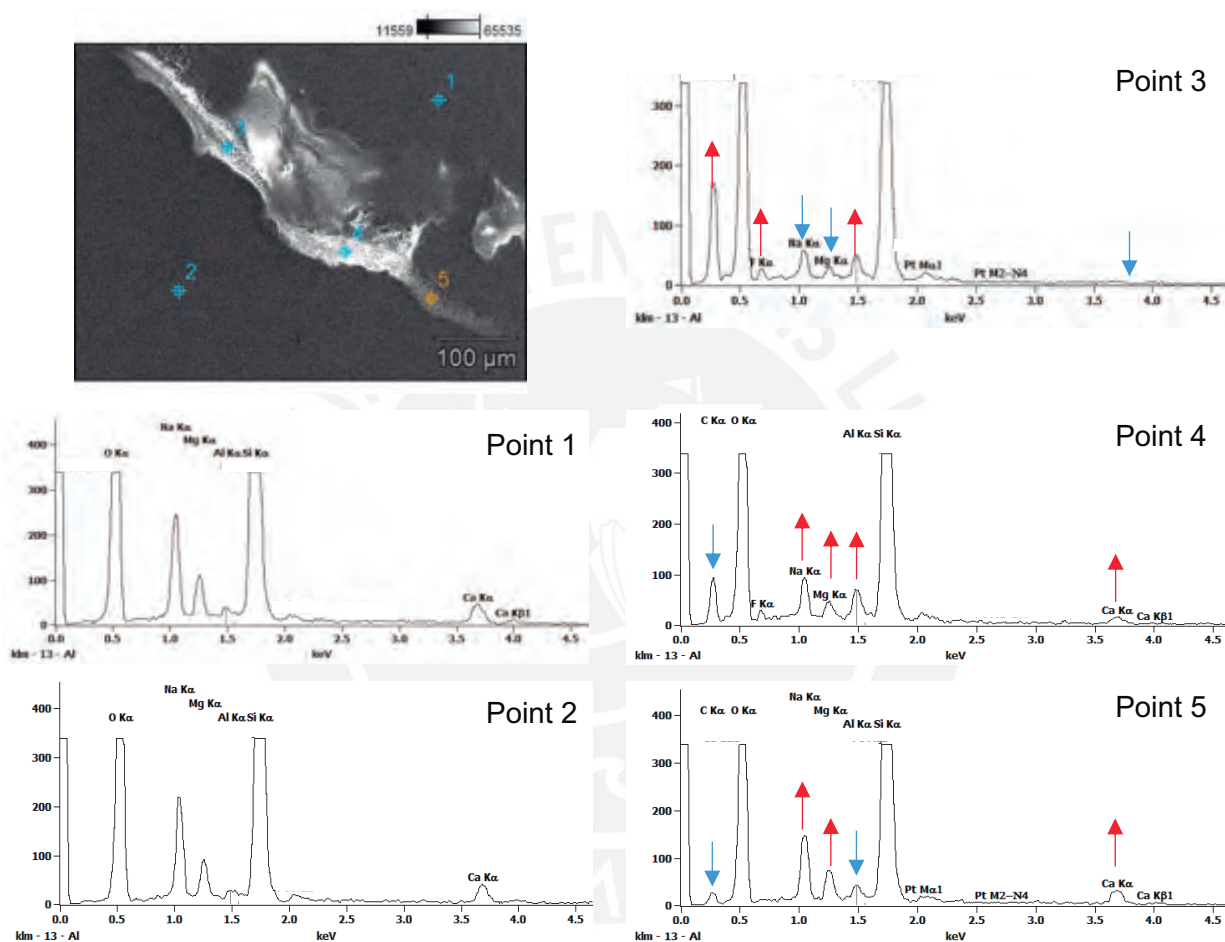
Figure 41. SEM image of the water rim and EDX spectra of three points on the water rim (points 3-5) and two points (points 1-2) outside the water rim as reference of the glass surface. Significant differences are marked by arrows.

The EDX spectra on the glass surface at points 1 and 2 seem similar; they show oxygen, sodium, magnesium signals and small peaks of aluminum and calcium. At points 3 and 4, carbon and fluorine signals appear in the spectra. In addition, the aluminum signal increases. Thus, the water rim contains traces of carbon, fluorine, and aluminum. Moreover, the peaks of sodium, calcium, and magnesium decrease at the water rim. The spectra of point 5, where the water rim fades, show that the signals of the elements approach the typical spectra of the glass composition: the

carbon signal decreases, the fluorine signal disappears, sodium, magnesium, and calcium increase, and the aluminum signal decreases. The aluminum and silicon signals on the water rim could be part of feldspar particles. The sodium signal on the water rim is not coming from the glass because it is low. Sodium could be coming from sea salt because there is also a fluorine signal on the spectrum. Moreover, it is typical for sea salt to contain a small amount of fluorine. Carbon might be coming from carbonates because of a high amount of oxygen on the water rim, but organic carbon cannot be entirely discarded as an also possible source of this element.

4.6   FIB-TEM images and analysis

The intrinsic glass features such as bulges were observed in this study. The glass samples were weathered for seven days in the climate chamber at high humidity and temperature (80% RH and 80 °C) and then cleaned with DI water and citric acid. The high humidity induced the formation of bulges in the gel layer of the glass. Prior to FIB-TEM, an approx. 5 nm carbon layer was deposited by sputtering on the glass samples. Two types of bulges were observed: hollow bulges (Figure 42A) and porous bulges (Figure 42B). Hollow bulges were swollen during electron beam irradiation. Some of them had solid bridges developed in the sub-glass surface, inside the bulge (Bulge 1- Figure 42A).
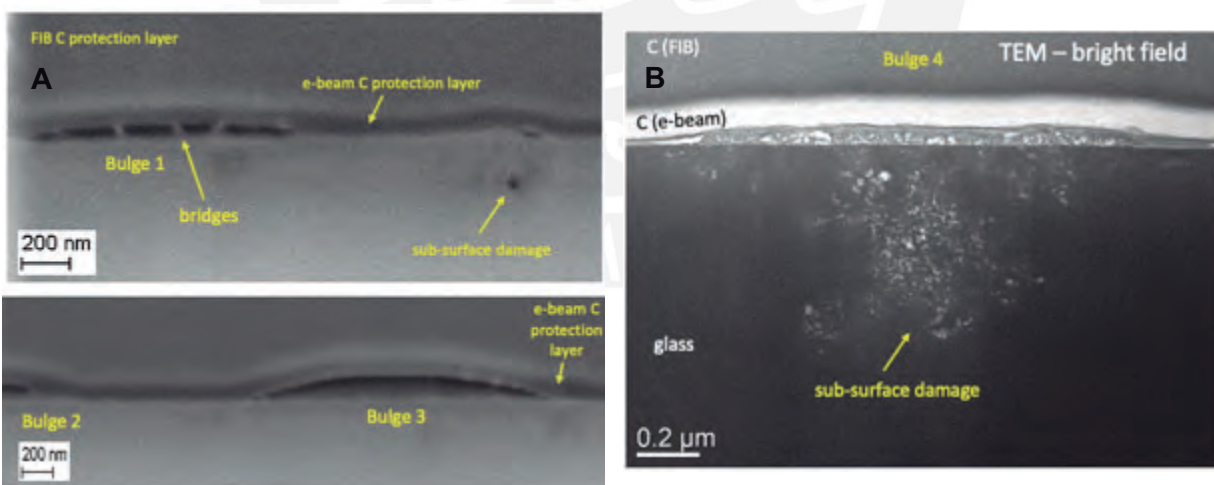
Figure 42. A) Glass cleaned with citric acid: Hollow bulges with and without solid bridges inside the bulge. **B)** Glass cleaned with DI water: Porous bulge on the glass surface with sub-surface damage.

The bulges were covered with a thin solid "skin" of approx. 10 nm in thickness. The bulge 4 in Figure 42B was approx. 50 nm high. The material inside the porous bulge was enriched with

sodium and also contained magnesium. The outer "skin" contained more calcium than the interior of the bulge. Silicon was not evenly distributed inside the bulge. Inhomogeneities were observed below the bulges up to 700 nm depth (Figure 42B) due to sodium, magnesium, and calcium depletion. These results showed that the bulges may be hollow with crystalline bridges or partially filled with Na- and Mg- enriched material and that the bulges originated from subsurface alteration underneath a well-connected glass "skin."

4.7 AFM images and analysis

The AFM images show the changes in the topography of the glass surface near and far from the weathering product, a bulge (see Figure 43). The glass sample was weathered in a climate chamber for seven days and then cleaned with citric acid.
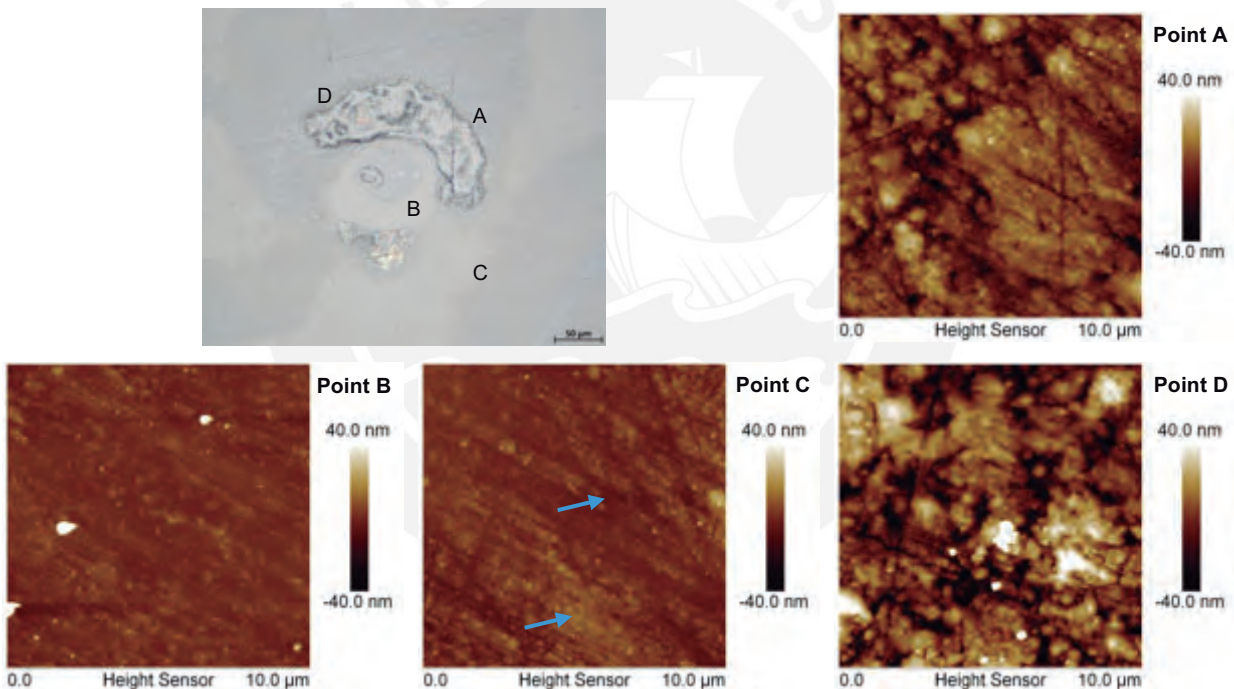
Figure 43. Optical microscope image of the weathering product and AFM images of four points near and far from the bulge (height sensor mode). Darker sections with more layers removed and brighter sections with fewer layers removed after cleaning marked with arrows.

Points A and D are located near the bulge; thus, the topography is more voluminous and looks like a cluster of particles around the weathering product with an approximate maximum height of 30 nm (Pt. A) and 40 nm (Pt. D). The surface at points B and C appears to be more homogenous; this topography is typical of cleaned glass. Point B appears to be slightly less altered than point

C. However, it is still a good glass surface. The line marks visible in the four images are from wiping. A typical characteristic of a cleaned glass is that height differences form between the layers on the surface after wiping. The darker sections show that altered layers have been removed, and the brighter sections show that fewer layers have been removed (see blue arrows). The step height between the darker and brighter sections is about 5 nm.

5   Summarizing Discussion and Conclusion

This study investigated the effectiveness of three cleaning solutions (citric acid, DI water, and commercial cleaner- Schukolin) and the interaction of four contaminants (cement dust, sea salt, aluminum particles, and bird droppings) with the glass surface under natural and artificial weathering conditions. For cement was expected more damages but the settling time on the surface was not long enough for cement to absorb water vapor to degrade the glass surface. Heavy rain during the exposition enhanced self-cleaning action, which reduced degradation. Another reason could be that the smaller cement particles result in smaller spaces between them; thus, water vapor could not penetrate the cement layer.

Low damage to the glass was expected for aluminum particles, but solid bridges formed beneath the metallic particle strongly adhered to the surface. The strong adhesion of the metal particles to the glass surface could be due to caking. The larger particles were removed by wind or cleaning, and the small ones found a place with high adhesion. For bird droppings, more damage was expected, but it was the contaminant with less alteration on the glass surface because they are acidic and contain a little bit of phosphate, which could probably act as the protector. For sodium chloride, some degradation was expected; however, salt increased the alteration on glass by attracting water molecules from the air and keeping a water film on the surface for a longer time, enhancing the leaching mechanism. Salts as condensation nuclei enhanced the deposition of other particles forming salt rims after condensation, which were difficult to remove. Optical microscopy shows that sea salt causes the most glass alteration when artificially weathered, while cement causes the most glass alteration when naturally weathered. The surface alterations are reflected in the formation of iridescent layers.

The formation of bulges was expected at high humidity. They were found occasionally and were distributed randomly on the glass surface. Iridescent and delamination effects were only found in the glass samples exposed outdoors with shelter conditions. Big delamination and iridescent effects are accelerated when the glass is exposed to temperature and humidity variations, but even more when exposed to sunlight, as these defects are not detected in glass exposed in the climate chamber. The absence of rain also intensifies these irreversible effects because when rain is present, it removes the contaminants maintaining a cleaner surface. Particles are local initiators for degradation producing iridescent and delamination effects; these effects were often found with sea salt particles.

The three cleaning agents removed small particles, but delamination, iridescent effects, and water drop rims were the most difficult defects to remove. It was expected for DI water to be much more effective, but DI was worse than the other cleaning solutions. However, when the protector was added to the DI water sample, it removed the bad action of the DI water. The contact angle of the glass surface with the protector was very similar to the citric acid. The Schukolin solution was expected to have a good effect, but higher delamination and iridescent films were found when using this solution in natural weathering under shelter conditions.

Citric acid was expected to have a good effect, and indeed, it was the cleaning solution with the lowest contact angles, which indicated that citric acid provides OH- groups on the surface by leaching sodium ions out and putting water on the surface. When cleaning with citric acid, a smooth layer is formed on the glass surface, preventing the glass surface from being scratched. The wettability of glass is higher when cleaning with citric acid. Glass cleaned with citric acid has the highest maximum transmittance after being exposed to the climate chamber for seven days. Citric acid shows to be more efficient in cleaning and protecting the glass surface. Citric acid seems to form a very stable gel layer that is difficult scratched. Citric acid promotes the durability of the glass surface during weathering. These results are supported by microscope observations, contact angle, and transmittance measurements.

The pH of the phosphate in the protector is so low that a large amount of protector applied on the surface could act as a low pH (acidic) buffer as soon as it becomes wet. The protector prevents excessive surface degradation when exposed to a climatic chamber for seven days. However, applying a high dose of it is not recommended because it is difficult to remove after natural and artificial weathering. The AES and EDX results indicate the presence of organic (carbon) and inorganic contaminants (chlorine, aluminum, iron, and calcium) on weathering products such as water rim and iridescent effect. EDX measurements indicate that a carbonate compound is present in the water rim. AFM images show that wiping creates a height difference between layers on the cleaned surface.

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<u>List of figures</u>

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<u>List of abbreviations</u>

AES - auger electron spectroscopy

AFM - atomic force microscopy

AMSL - above mean sea level

AP - aluminum particles

BD - bird droppings

CA - citric acid

CD - cement dust

DI - deionized Water

EDX - energy dispersive X-ray spectroscopy

LM - light microscopy

NIR - Near-infrared

POM - particulate organic matter

SEM - scanning electron microscopy

SK - Schukolin, commercial cleaner

SS - sea salt

UV - Ultraviolet

VIS - Visible

wt% - weight percent

Acknowledgments

<u>Statutory declaration</u>

I hereby declare that I have written this Master's Thesis on the topic of **"Efficiency of cleaning solutions to remove difficult contamination on weathered float glass exposed in an urban environment"** and have only used the sources given.

Ilmenau, November 12, 2021

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Elena Kristel Mendoza Carranza