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Study of a surface treatment based on zinc salts to protect glasses from atmospheric alteration: Mechanisms and application to ancient glass objects in museum

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Résumé

En s'inspirant d'un procédé industriel employé pour protéger les verres de vitrage durant leur stockage et leur transport, cette étude vise à évaluer la potentialité de faibles quantités de sels de zinc pour réduire efficacement la cinétique d'altération de certains verres du patrimoine peu durables (silicates riches en alcalins). Pour cela, l'action protectrice de sels de zinc a été évaluée par la conduite d'expériences de vieillissement (contrôle de la température et de l'hygrométrie) sur une composition de verre réplique, représentative de compositions chimiquement instables du patrimoine. Nos résultats montrent l'effet bénéfique des sels de zinc déposés en faible teneur (de l'ordre du $\mu\text{g}/\text{cm}^2$ de zinc) sur la diminution des cinétiques d'hydratation à 80 °C ou à 40 °C (85 % HR), lorsque le traitement est réalisé sur une surface non préalablement altérée. De plus, le traitement modifie la nature des sels formés à la surface du verre altéré. Différentes espèces de zinc (II) sont identifiées à la surface du verre avant ou après les essais de vieillissement. Notamment, l'étude de la spéciation des ions Zn^{2+} par GI-XAS (spectroscopie d'absorption X en incidence rasante) montre leur insertion progressive au sein du réseau silicaté au cours du vieillissement. Plusieurs hypothèses sur l'origine de l'action protectrice des sels de zinc sont avancées. Elles mettent en avant le rôle prédominant des espèces de zinc chimisorbées dont la formation est thermiquement activée dans les mécanismes de protection. Aussi, ce type de traitement ne pourrait être envisagé qu'avec une étape de chauffage modéré du verre. De plus, sur la base de résultats préliminaires, les performances du traitement apparaissent fortement dépendantes du degré d'altération de la surface avant le dépôt. Ce point est déterminant pour l'application visée et doit être approfondi.

Abstract

Inspired by an industrial process to protect manufactured glass windows against atmospheric alteration during their storage and transport, the current research is focused on the potentiality that a surface deposit of a small amount of zinc salts may efficiently reduce the alteration kinetics of chemically unstable ancient glass (alkali (Na,K)-rich silicate). To this purpose, the protective action of zinc salts was investigated by the mean of ageing experiments (temperature and humidity control) on a relevant ancient glass composition replica. When the treatment was performed on pristine glass (about $1 \mu\text{g}/\text{cm}^2$ of deposited Zn^{2+} ions), treated glass plates developed a significantly thinner hydrated layer than the untreated one at 80°C or 40°C (85 RH%). Furthermore, the zinc salts treatment modifies the nature of salts on glass surface. Different Zn(II)

species were identified on the glass surface prior to or after the ageing. The study of the Zn(II) speciation on glass surface by grazing incidence GI-XAS (Grazing Incidence-X-ray Absorption Spectroscopy) showed the insertion of Zn(II) into the silicate network with the ageing. Several hypotheses about the protective action of Zn(II) against glass atmospheric alteration are formulated. They highlight the predominant role of the chemisorbed zinc species in the protective action. Because these chemisorbed species are formed by thermal activation, a moderate heating step in the treatment protocol is necessary. From preliminary results, the glass surface state prior to the zinc treatment appears critical regarding its efficiency and should be investigated deeper in view of the application.

1. Introduction

Until now the best protective measure applied by conservators and curators to slow down the atmospheric alteration of ancient glass objects is the control of the environment (temperature, relative humidity, pollutants) within suitable museum display cases (Bailly, 2008). Nevertheless, by acting directly on the glass surface, more efficient and less costly protective methods could be proposed. In accordance with the museum context, such a method must be:

- Non-toxic,
- Respectful of the mechanical, chemical and esthetical integrity of the glass object,
- Reversible as far as possible,
- With a small amount of applied material,
- Of easy-handling with a manageable frequency for the museums,
- Not expensive and readily available.

External chemical treatments which have been investigated in the past for the protection of museum glass objects mainly consisted in more or less strongly adherent coatings to act as a protective barrier against moisture (Dal Bianco *et al.*, 2008 ; Oakley, 2001 ; Koob, 2006). But for reasons of limited performances and lack of reversibility, they were eventually abandoned. In this study, we focus on the potentiality of a protective treatment based on the deposit of a very small amount of zinc salts on glass surface in order to slow down the alteration of chemically unstable ancient glass (alkali (Na,K)-rich silicate).

The idea of this treatment stems from industrial applications, namely the use of small amounts of zinc salts to protect soda-lime silicate glass in an industrial context, either against the atmospheric alteration of flat glass during their transport and storage (Rullier, 1975 ; Lewchuk *et al.*, 1967), or against the silicate network dissolution of glassware during their washing in dishwasher (Berger *et al.*, 2006 ; Caravajal, 1990 ; Keyes *et al.*, 2002 ; Eiting *et al.*, 2012). A very few hypothesis are formulated in the literature regarding the origin of the zinc salts protective action: the chemisorption of Zn²⁺ ions on glass surface would make it less attractive for water (Nunes de Carvalho *et al.*, 2014), the diffusion and the insertion of Zn²⁺ ions into the silicate network would enhance the chemical durability of glass (Lewchuk *et al.*, 1967 ; Berger *et al.*, 2006). However, the insertion of zinc as network former, subsequent to a zinc salt treatment, has not been demonstrated to the best of our knowledge.

Our experimental approach is based on a treatment method adapted to the museum context and applied on glass replicas, the composition of which is representative of chemically unstable ancient glass (alkali (Na,K)-rich silicate). Effects of the zinc treatment on the phenomenology of atmospheric alteration are evaluated by performing comparative accelerated ageing tests (temperature and humidity control in neutral atmosphere) on untreated and treated glass samples. These effects on freshly polished glass surfaces are the main subject of this communication. Preliminary results dealing with these effects, when the treatment is performed on previously altered surfaces, will be introduced to draw up the perspectives for this research.

2. Experimental

Experiments were performed on one glass composition replica: a mixed-alkali silicate glass, named glass **A** ((wt%) SiO₂ 71%, Na₂O 11%, K₂O 11%, CaO 5%, MgO 1%, Al₂O₃ 1%), representative of several chemically unstable productions of the Middle-Age (Biron, 2015). Details regarding the fabrication of the glass replica, the preparation of samples (polished plates and powder) and the cleaning procedure of glass plates are described elsewhere (Alloteau *et al.*, 2017).

2.1. Zinc salts deposits on glass surface

Spraying treatment

In view of the application in the museum context, a zinc salt spraying treatment was carried out at room temperature on glass plates. Reagent grade zinc nitrate hexahydrate (Sigma-Aldrich) was diluted in absolute ethanol at room temperature to obtain Zn²⁺ ion concentrations in solution of 40 ppm up to 600 ppm. Pluronic F-127 (BASF), a low-foaming non-ionic surfactant, was added to the solutions for its wetting action. By the mean of a commercial sprayer, this zinc salt ethanolic solution is manually sprayed on the polished face of glass plates: a continuous film is observed on surface that evaporates very fastly in laboratory atmosphere at room temperature.

Alternative treatment: treatment by immersion

To compare with the spraying treatment, a treatment by immersion in a zinc salt solution adapted from Réf. (Nunes de Carvalho *et al.*, 2014) was achieved for a second batch of glass plates. Aqueous solution containing 80 ppm of Zn²⁺ ions was prepared by diluting reagent grade zinc nitrate hexahydrate (Sigma-Aldrich) in milliQ water and heated at 60 °C using a stirring hot plate. Glass plates were then immersed during 15 s in the hot Zn²⁺ bearing solution, then rinsed during 10 s with a continuous flow of cold milliQ water, and finally dried during 10 s with an air flux (T ≤ 40 °C).

Glass powders have also undergone an immersion treatment: after 15 s of immersion in the hot Zn²⁺ bearing solution, glass powders were vacuum filtered on a Buchner funnel. The filtered glass particles, which were collected by deposition on a filter paper, were rinsed with a controlled amount of milliQ water (about 20 mL) and then dried at 50 °C during 24 h.

Glass surface characterization

After surface treatment, the visual aspect of the zinc salt deposits on glass plate surfaces was studied by optical microscopy. In order to quantify the amount of Zn²⁺ deposited on the surfaces, sensitive and accurate methods were selected: either spatially unresolved (PIXE¹, EDXRF², XPS³) or spatially resolved (SEM-EDX⁴). Details about the apparatus and the optimized operating conditions are given in Réf. (Alloteau, 2017). For glass powders, the mean concentration of Zn²⁺ ions deposited after the immersion treatment is controlled by wet dosage: after desorbing the Zn²⁺ ions from glass surface with an acidic solution (diluted HCl in milliQ water), the solution was sampled and analyzed by ICP-AES⁵. In this paper, the quantity of zinc on glass surface is systematically expressed in weight concentration per unit area (µg/cm²) of Zn²⁺ ions. With our spraying treatment, the concentration of Zn²⁺ ions on glass surface varied from about 0.1 µg/cm² to about 1.5 µg/cm², depending of the concentration of the spraying solution. With our immersion treatment, the concentration of Zn²⁺ ions on glass surface was evaluated close to 0.1 µg/cm². In this paper, we focus in particular on the effect of the spraying treatment of lowest and highest concentration, named **ZP0.1** and **ZP1.5** respectively. The immersion treatment is named **ZN0.1**.

2.2. Evaluation of the Zn(II) action against glass atmospheric alteration

¹ Particle induced X-ray emission

² Energy dispersive X-ray fluorescence spectroscopy

³ X-ray photoelectron spectroscopy

⁴ Scanning electron microscopy – Energy dispersive X-ray

⁵ Inductively coupled plasma-atomic emission spectroscopy

Effects of the zinc salt treatments on the glass atmospheric alteration were studied by ageing simultaneously untreated and treated glass plates at 80 °C or 40 °C, 85 RH% over various time periods (V tests), or during 2 years in ambient atmosphere. The subsequent surface and near-surface modifications were compared in terms of morphology (surface state, nature of the precipitates, altered layer thickness) and chemical composition. Zinc treatments were performed shortly before a V test, either on non-altered and freshly cleaned glass plates, or on pre-altered glass plates. Details regarding the V tests and the characterization methods are given in Ref. (Alloteau *et al.*, 2018).

2.3. Study of the Zn(II) speciation on glass surface

Zn(II) speciation was studied for treated glass plates, before and after ageing tests, to follow its chemical evolution over time. The nature of the precipitates that eventually formed consecutively to a zinc treatment was studied by XRD⁶ with a X'Pert PRO PANalytical instrument using Cu-K α radiation, and by micro-Raman spectroscopy with a Renishaw Invia spectrometer with a 532 nm solid-state laser as excitation source.

To investigate the chemical environment of the Zn²⁺ ions which were potentially adsorbed on glass surface, GI-XAS⁷ experiments were carried out at the Zn-K edge (9660.8 eV). These measurements were performed at an incident angle close to 1° (grazing incidence) to only probe a thin surface layer, in fluorescence mode. In addition to the treated glass plates, XANES⁸ spectra of Zn(II) reference compounds were also collected. These compounds were solid standards that could be present in our samples (having coordination number 4 or a mixture of 4 and 6 for the Zn(II)), and a liquid standard solution of Zn²⁺ (coordination number 6). The six solid standards, either commercial or synthesized in the laboratory, were: zinc oxide (ZnO), zinc hydroxide (Zn(OH)₂), willemite (Zn₂SiO₄), zinc hydroxide nitrate (Zn₅(OH)₈(NO₃)₂·H₂O), hydrozincite (Zn₅(CO₃)₂(OH)₆) and a glass sample (named glass **A**+Zn) specially prepared for this XANES study with composition similar to that of glass **A** to which 2 wt% ZnO was added in substitution of SiO₂.

2.4. Electroacoustic measurements to measure surface charges

Surface charges of glass powders, untreated or treated by immersion, were evaluated by electroacoustic measurements (Dukhin *et al.*, 1999), in order to assess the influence of the treatment on the nature of the glass surface. These measurements were carried out on a DT-300 equipment (Quantachrome/Dispersion Technology company), after calibration with colloidal silica (28 nm) dispersed in milliQ water (zeta potential = -38 mV).

3. Effects of the spraying treatment on a non-altered surface

3.1. Before ageing

To the naked eye, the spraying treatment did not modify the visual aspect of the glass plate surfaces, whatever the amount of Zn²⁺ ions that was deposited on surface (ranging from about 0.1 $\mu\text{g}/\text{cm}^2$ to 1.5 $\mu\text{g}/\text{cm}^2$).

At a smaller scale, an almost immediate surface precipitation was put in evidence (during the first hour after the treatment), the distribution of which appearing homogeneous on a 10 μm scale (figure 1). The morphology of precipitation is distinguished according to the amount of deposited Zn²⁺ ions:

- For the **ZP0.1** treatment, only Na and K nitrate salts were identified, numbered respectively

⁶ X-ray diffraction

⁷ Grazing incidence – X-ray absorption spectroscopy

- (1) and (2) in figure 1(b), but no zinc salt precipitated,
- For the spraying treatments of higher $[Zn^{2+}]$ concentrations (ranging from about 0.25 $\mu\text{g}/\text{cm}^2$ to 1.5 $\mu\text{g}/\text{cm}^2$), Na and K nitrate salts were also put in evidence (numbered respectively (3) and (4) in figure 1(d) for a **ZP1.5** treatment), together with zinc hydroxide nitrate ($Zn_5(OH)_8(NO_3)_2 \cdot H_2O$) (numbered (5) in figure 1(d)). The size of the latter phase crystals was all greater given the concentration of Zn^{2+} ions on surface.

The formation of Na and K nitrate salts on glass surface is related to the reaction of the Zn^{2+} counter-ion (NO_3^-) with alkalis coming from the outermost surface layer⁹ of glass plate. It is worth to notice that Zn^{2+} ions were systematically detected outside any Zn precipitates, at a concentration close to 0.1 $\mu\text{g}/\text{cm}^2$ ¹⁰. Furthermore, ToF-SIMS analysis of the **ZP0.1**-treated glass plates showed that adsorbed Zn^{2+} ions were mainly located at the outer surface (figure 4(a), purple curve).

3.2. After ageing

After a V test at 80 °C, 85 RH%, during 3 days, crizzling and flaking of the untreated glass surface occurred, as well as the progressive appearance of Na carbonates (figure 2(a)) (Alloteau *et al.*, 2018). Remarkably, with our **ZP1.5** treatment, these manifestations were suppressed after the V test (figure 2(b)). Only Na and K nitrate salts, and Zn, N, O, C-rich phases were identified on the treated and aged glass surfaces. Zinc precipitates likely evolved in terms of morphology and composition with the ageing and seemed less numerous on glass surface. The benefit of the **ZP1.5** treatment on the glass surface state is directly correlated to the considerable reduction of the alteration kinetics. Indeed, for the three durations of ageing (1 day, 3 days or 6 days), the altered layer thicknesses were reduced by a factor of about 10, 60 or 100 respectively with the treatment (figure 3(a) and table 1). Moreover, the alteration kinetics appeared linear for the treated glass plates, unlike the untreated ones for which an acceleration of the alteration kinetics was observed (Alloteau *et al.*, 2018).

After V tests at 40°C, 85 RH% up to 6 months, by measuring the altered layer thickness (figure 3(b) and table 1) a strong diminution of the alteration kinetics with the **ZP1.5** treatment was demonstrated. However, the treatment appeared more efficient at 80 °C. Furthermore, based on the data at 40 °C, the alteration kinetics of the treated glass was slightly higher between 3 and 6 months than between 17 days and 3 months, which suggests the diminution of the treatment efficiency over time. For longer ageing times (up to 9 months), the formation of Na carbonate salts on the surface of the treated glass plates was put in evidence, but not that of Ca carbonate salts. It is a noticeable difference with the untreated glass plates that showed predominant precipitation of Ca-carbonates (Alloteau *et al.*, 2018).

By contrast, regarding the 2 years long ageing in ambient atmosphere, no positive effect of the **ZP1.5** treatment could be observed, neither on the surface state nor in terms of altered layer thickness.

Interestingly, a positive effect of our **ZP0.1** treatment on the reduction of the hydration kinetics was observed at 80°C over 1 day. This benefit was not observed for longer ageing durations at 80 °C, nor for ageing at 40 °C. Because this treatment corresponds to a low concentration for which all Zn^{2+} ions are adsorbed on glass surface, these results put in evidence the tangible and over time limited action of these adsorbed Zn^{2+} ions against the atmospheric alteration at 80 °C, 85 RH%.

The experimental results introduced in this section show the strong influence of the temperature on the performances of the spraying treatment, which suggests an evolutive and temperature-dependent Zn(II) speciation over time. A better understanding of the different Zn(II) species that form on glass surface in our experimental conditions, and their respective protective

⁹ A few tens of nanometers thick (according to ToF-SIMS analysis)

¹⁰ EDX analysis at 3 kV, after forcing Na migration

role against alteration, appears to be a pre-requisite to discuss the relevant conditions of use for a zinc salts treatment.

4. Study of the Zn(II) speciation on glass surface

4.1. Zn(II) species identified before ageing and their relative contribution to the protection

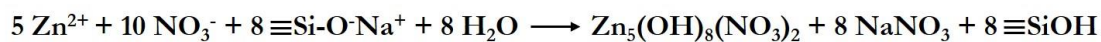
We consider the speciation of the adsorbed Zn^{2+} by focusing on the **ZP0.1** and **ZN0.1** treatments, for which no Zn-rich precipitates but only adsorbed Zn^{2+} ions were present on the glass surface. Note that for **ZN0.1** treatment, no Na nor K nitrate salts were observed, which suggests that Zn^{2+} ion was deposited on the surface without its counter-ion NO_3^- , unlike **ZP0.1** treatment.

For this last treatment, the comparison of the Zn profiles as obtained by ToF-SIMS, before and after a short rinse step (5 s) with milliQ water at ambient temperature, shows a significant decrease of the ionic intensity at the outer surface with the rinse operation (purple curve compared to blue curve in figure 4). Thus, Zn^{2+} ions appear weakly adsorbed on the glass surface after the spraying treatment. On the contrary, the Zn profile of a plate freshly treated by immersion (**ZN0.1**, orange curve) is very close to that of **ZP0.1** before any rinsing (purple curve), meaning that Zn^{2+} ions are more strongly adsorbed on the glass surface after the immersion treatment.

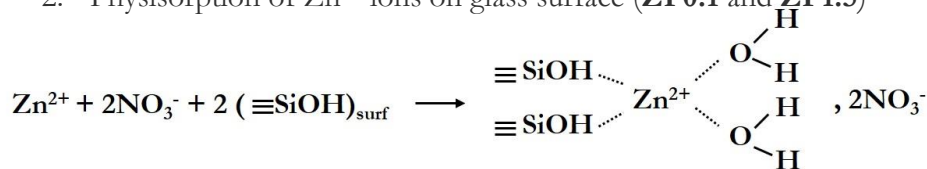
The determination of the charge surfaces by electroacoustic measurements is very interesting to corroborate the modification of the surface properties with the **ZN0.1** treatment and highlight the nature of the Zn^{2+} surface adsorption. For these measurements, calibrated glass powders, untreated or treated by immersion, were dispersed in an electrolyte of pH 10.3 (KCl 10^{-2} M for ionic force control). At this pH, the untreated glass surface was strongly charged (-23.8 mV, table 2). The treated glass had a very less negative charge (-3.9 mV). Considering that the zero charge point of ZnO is relatively high (between 8 and 10 (Marsalek, 2014)), these results indicate that the surface chemistry of the treated glass is dominated by the ZnOH bonds of chemisorbed species. Besides, successive acidifications of the powder suspensions with HCl caused the decrease of the surface charge for the untreated glass (-6.8 mV at pH 5), as expected for a silicate glass, while for the treated one, the surface charge decreased close to 0 at pH 8 and then became more negative consistently with the desorption of Zn^{2+} ions below pH 7¹¹.

To summarize, three different types of zinc speciation on glass surface were identified, after treatment and before ageing:

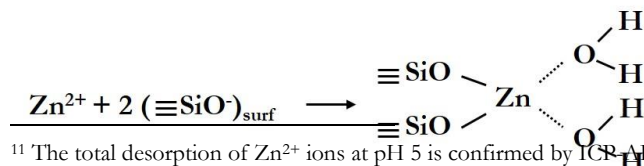
1. Formation of hydroxide nitrate by precipitation of Zn^{2+} ions with OH^- ions (**ZP1.5**)



2. Physisorption of Zn^{2+} ions on glass surface (**ZP0.1** and **ZP1.5**)



3. Chemisorption of Zn^{2+} ions on glass surface (**ZN0.1**)



¹¹ The total desorption of Zn^{2+} ions at pH 5 is confirmed by ICP-AES analysis of the filtered solution

It is worth to notice that a similar protection was given by the **ZN0.1** treatment and the **ZP1.5** treatment (15 times more concentrated in Zn^{2+} ions compared to **ZN0.1**), at 80 °C, 85 RH%, during 1 day, as evaluated by transmission FTIR. Indeed, in figure 5, the absorbance associated to the –OH groups appears very similar for these two treatments (orange and green curves), very slightly higher to that of the pristine glass (black curve), and significantly lower to that of the untreated glass (red curve). Furthermore, the protection by the chemisorbed Zn^{2+} ions (**ZN0.1** treatment) is better than by the physisorbed Zn^{2+} ions (**ZP0.1** spraying treatment), when comparing the FTIR signal of the two treatments of the same concentration (orange and purple curves).

However, for longer ageing durations at 80 °C, 85 RH%, the performances of the treatment by immersion were clearly reduced unlike the spraying treatment 15 times more concentrated.

4.2. Evolution of the Zn(II) speciation with the ageing

XANES spectra of reference compounds show qualitatively the influence of the composition and the structure of the Zn^{2+} bearing phase on Zn signal at the Zn K-edge (figure 6(a))¹². The peak position at the edge appears dependent on the coordination of Zn^{2+} ions (Waychunas *et al.*, 2003). For instance, when Zn^{2+} ions are 4-fold coordinated, the peak at the edge is located at around 9665 eV. When Zn^{2+} ions exist in a mixed 4-6 coordination, this peak is slightly shifted (2-3 eV) to higher energy and gets closer to the one of 6-fold coordinated Zn^{2+} ions (about 9668 eV).

XANES spectra of treated glass plates, before or after V tests, are reported in figure 6(b), for **ZP0.1** (purple curves) and **ZN0.1** (orange curves) treatments, to follow the evolution of the chemisorbed or physisorbed Zn^{2+} ions respectively. Spectral signatures of the freshly treated glass plates are dissimilar for these two treatments. Indeed, for the **ZP0.1** treatment, we distinguish a shoulder around 9665 eV in addition to the main peak around 9668 eV, while for the **ZN0.1** treatment the Zn K-edge peak appears clearly around 9665 eV accompanied by a peak of similar intensity around 9668 eV. For these two treatments, we did not get a satisfactory simulation of their spectra by linear combination of the reference compounds, although the one associated to the **ZP0.1** treatment seems to be closer to that of zinc hydroxide nitrate. These results put in evidence the specific environment of the chemisorbed Zn^{2+} ions, likely 4-fold coordinated.

For the **ZN0.1** treatment, the evolution of the XANES spectrum was more pronounced with an ageing at 80 °C (85 RH%, 1 day) as compared with an ageing at 40 °C (85 RH%, 10 days): two resolved peaks are visible, the first at around 9665 eV and the second at around 9668 eV. Interestingly, this spectral signature is close to that of the reference glass **A+Zn** (also reported in figure 6(b)). By using a linear combination of **ZN0.1** freshly treated and glass **A+Zn** reference spectra, we obtained a satisfactory spectrum simulation, with a contribution of the glass **A+Zn** of more than 80 %. This suggests that the V test at 80 °C, 85 RH%, promoted in one day the massive diffusion of Zn^{2+} ions into the glass near-surface¹³ and their coordination change to 4-fold probably by insertion into the silicate network, as depicted in figure 7. A similar evolution was observed for the XANES spectrum associated to the **ZP0.1** treatment with a V test at 80 °C, 85 RH%: the chemisorbed and physisorbed Zn^{2+} ions on glass surface progressively diffused into the near-surface and bound to the silicate network during the ageing.

Note that for the **ZP1.5** treatment, the XANES spectral signature of the freshly treated glass plate (spectrum not shown) is very similar to that of the reference compound zinc hydroxide

¹² Similar spectral signatures are referenced in the literature for ZnO , Zn_2SiO_4 , $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ and $\text{Zn}^{2+}_{\text{aq}}$ (Cismasu *et al.*, 2013)

¹³ This assumption is consistent with the evolution of the Zn in-depth profiles observed from ToF-SIMS analysis of the treated glass plates before (figure 4) and after the V test at 80 °C, 85 RH% (strong reduction of the ionic intensity at the outer surface and enlargement of the Zn profile towards a greater depth of about 50 nm – profile not shown)

nitrate, as expected. After a V test at 80 °C, 85 RH%, for 1 day, a shoulder at around 9665 eV appeared on the absorption edge, which could suggest a contribution of the Zn^{2+} ions bound to the silicate network, although no satisfactory simulation could be achieved from the reference compounds.

5. Hypotheses about the Zn(II) protection origin

The origins of the protection due to zinc salts deposit are discussed by differentiating the contributions of the Zn^{2+} ions, according to the type of speciation put in evidence in this study: as a precipitate on the surface, physisorbed on the surface, chemisorbed on the surface or bonded to the silicate network into the near-surface.

We may thus formulate 4 hypotheses:

- (i) A « buffering effect » stemming from the precipitation of Zn^{2+} ions with the OH^- ions coming from the glass alteration process,
- (ii) The neutralization of the surface charges by the zinc species chemisorbed on the surface would make it less hydrophilic,
- (iii) The zinc species chemisorbed on the surface and the one inserted in near-surface would form a passivating barrier,
- (iv) The zinc species inserted in glass near-surface would make the surface less soluble (i.e. they would stabilize the surface with respect to the dissolution products).

Concerning the hypothesis (i), zinc protection would contribute to neutralize and stabilize the glass near-surface. However, when the spraying treatment was applied on a pure vitreous silica surface the formation of zinc hydroxide nitrate was also observed despite the lack of non-bridging oxygen atoms in glass structure. Furthermore, zinc precipitates appeared less numerous on glass surface after the V tests. Thus, we assume that the contribution of the hypothesis (i) to explain the protection effect of zinc is very limited, at least in time.

Regarding the hypothesis (iii), zinc protection would slow down but would not stop the penetration of molecular water into the silicate network, as we systematically observed the growing of the hydrated layer during the alteration despite the treatment. This hypothesis could explain why calcium is not extracted from the glass during alteration. Indeed, the divalent Ca^{2+} and Zn^{2+} ions may take the same diffusion paths into the network.

Concerning the hypothesis (iv), zinc protection would contribute to stabilize the surface and the near-surface. Indeed, it is known that the introduction of ZnO in silicate glasses increases their critical pH of dissolution, which would explain the greater chemical durability in immersion conditions of silicate glasses containing ZnO (Paul, 1977).

From all previous considerations, it appears that the most efficient Zn(II) species for glass protection would be the ones chemisorbed on the surface and those inserted in glass structure into the near-surface. As demonstrated earlier, these species form with a thermal activation. Moreover, the thermal activation would promote the progressive release of Zn^{2+} ions by the zinc precipitates spread out on the surface. Then, at high temperature (80°C and to a lesser extent 40°C) the duration of the protective action probably increases. It may explain that no benefit of the spraying treatment was observed at ambient temperature, after 2 years of experiments. Thus, a moderate heating step during the treatment seems necessary.

6. Effects of the spraying treatment on a pre-altered surface

In this research concerning the protection of ancient glass objects in museum, it is obviously crucial to evaluate the effects of the zinc treatment on altered surfaces. To this purpose, experiments including a pre-ageing step before treatment and ageing were initiated on glass replicas. The choice of the experimental conditions for the pre-ageing step was not at all trivial, as we aimed

at reproducing in a short time the surface of glass objects that aged naturally during centuries. To be close to the ambient conditions in museum, these accelerated ageing tests were conducted with our lowest ageing temperature (40 °C), at 85 RH%. The duration of the pre-ageing step was chosen to develop altered layers thick enough to study the progression of Zn²⁺ ions in depth, but no more than 1 µm thick, to avoid the flaking of the altered layer in the region near the interface (Alloteau *et al.*, 2018).

After a **ZP1.5** treatment on these pre-altered surfaces, Zn(II) was present mainly as precipitates on surface, the nature of which appeared different from that on non-altered surfaces and could not be clarified. From ToF-SIMS analysis, whether before or after the final ageing step, the progression of Zn²⁺ ions into the altered layer was limited to some tens of nm (profiles not shown). Furthermore, the spraying treatment of the pre-altered samples did not show any positive effect on the reduction of the atmospheric alteration kinetics at 40 °C, 85 RH%.

Thus, the efficiency of the zinc salts spraying treatment seems strongly influenced by the glass surface state prior to the treatment. We emphasize that these preliminary results concerning pre-altered glass surface cannot be used alone to predict the relevance of a zinc salts treatment for ancient glass objects, considering the probable differences between these artificially altered layers and the surfaces of ancient glass objects in terms of morphology, composition and structure (Alloteau, 2017).

7. Conclusion

In this study, the protective action of a zinc salts spraying treatment against glass atmospheric alteration has been evaluated for a chemically unstable glass replica (Na,K-rich silicate) representative of glass compositions from the Middle-Age. This treatment, which potentially meets the conservation requirements of Cultural Heritage artifacts, showed a remarkable efficiency in accelerated ageing tests (80 °C or 40 °C, 85 RH%), when applied at low concentration ([Zn²⁺] ~ 1.5 µg/cm²) on a non-altered surface. This efficiency was more pronounced at 80 °C than at 40 °C, 85 RH%, but could not be demonstrated at ambient temperature. We propose that temperature effects are related to the predominant role of chemisorbed Zn(II) species on the glass surface and into the glass near-surface, of which formation is thermally activated, in the protective action. Furthermore, the temperature would promote the progressive release of Zn²⁺ ions from zinc precipitates spread out on the surface, which could explain the increase of the protective action duration with the concentration of deposited Zn²⁺ ions.

Consequently, according to all the results obtained in this study, a conservation treatment based on zinc salts could be relevant at low concentration but only by performing a moderate heating of the glass surface during the deposit. However, the influence of the glass surface state appeared critical regarding the treatment benefit. For instance, on a surface pre-altered at 40 °C, 85 RH%, the diffusion of Zn²⁺ ions through the altered layer was very limited in depth. The Zn²⁺ ions did not reach the interface with the pristine glass possibly explaining the result that the treatment was not efficient on such a surface. Nevertheless, it is important to emphasize that the artificially altered surfaces were not strictly identical to the ones of slowly altered ancient glasses. A satisfactory reproduction of natural alteration is a very tricky and limiting issue for the study of a conservation solution and efforts should be extended to better simulate the behavior of ancient glass surfaces. Indeed, it is a pre-requisite to develop a zinc deposit protocol, designed to promote the formation of the zinc chemisorbed species at the interface with the pristine glass.

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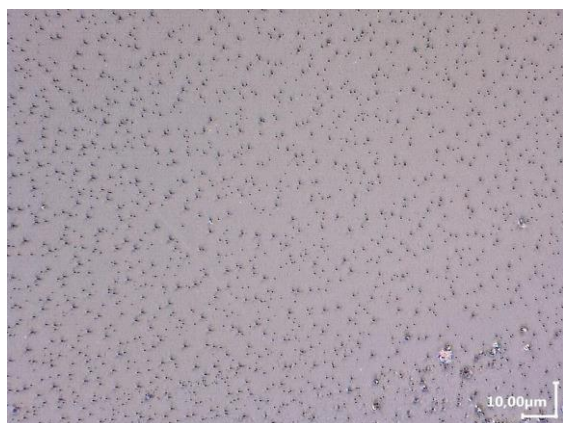
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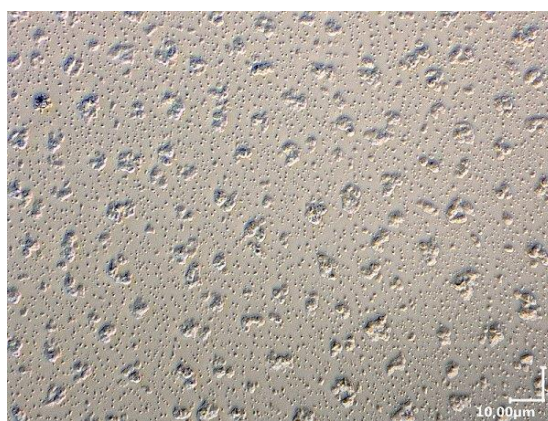
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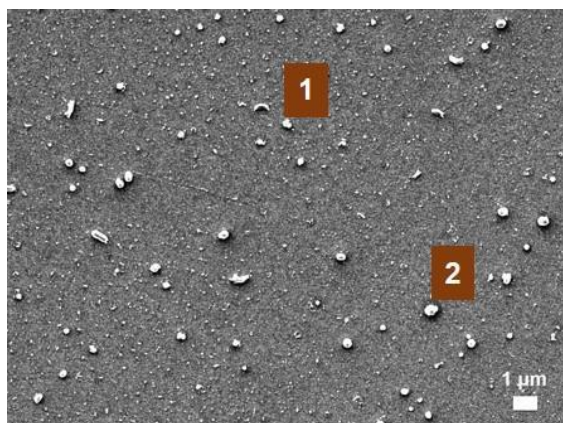
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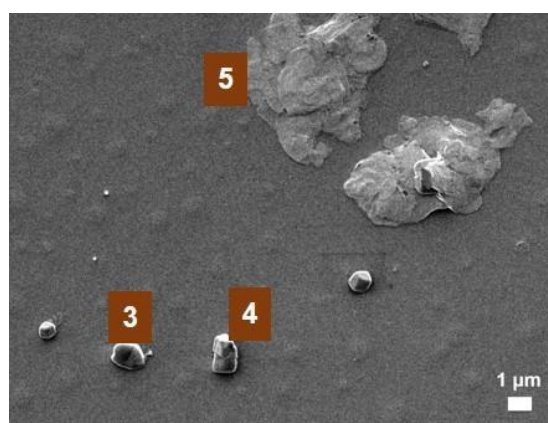
(a)



(b)



(c)



(d)

Fig. 1: Surface states of glass plates **A** some hours after a spraying treatment, for different amounts of deposited Zn^{2+} ions. (**ZP0.1** ($[\text{Zn}^{2+}] \sim 0.1 \mu\text{g}/\text{cm}^2$) (a,b), **ZP1.5** ($[\text{Zn}^{2+}] \sim 1.5 \mu\text{g}/\text{cm}^2$) (c,d)). Optical images (a,c), SEM images (b,d). 1,3: NaNO_3 , 2,4: KNO_3 , 5: $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$.

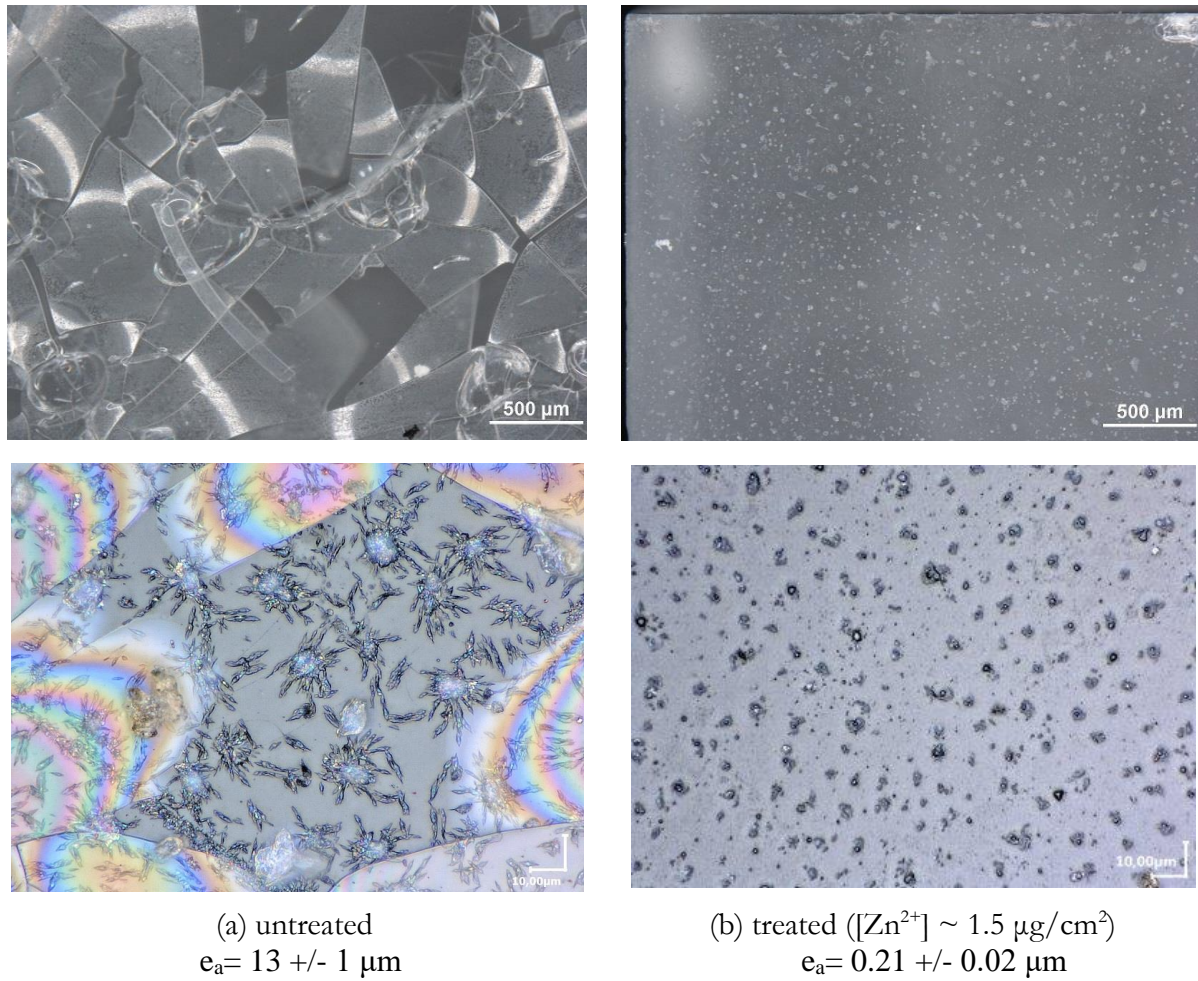


Fig. 2: Optical images of the surface of glass A plates several days after a V test (80 °C, 85 RH%, 3 days), (a) untreated, (b) treated (ZP1.5) prior to the V test. e_a : altered layer thickness.

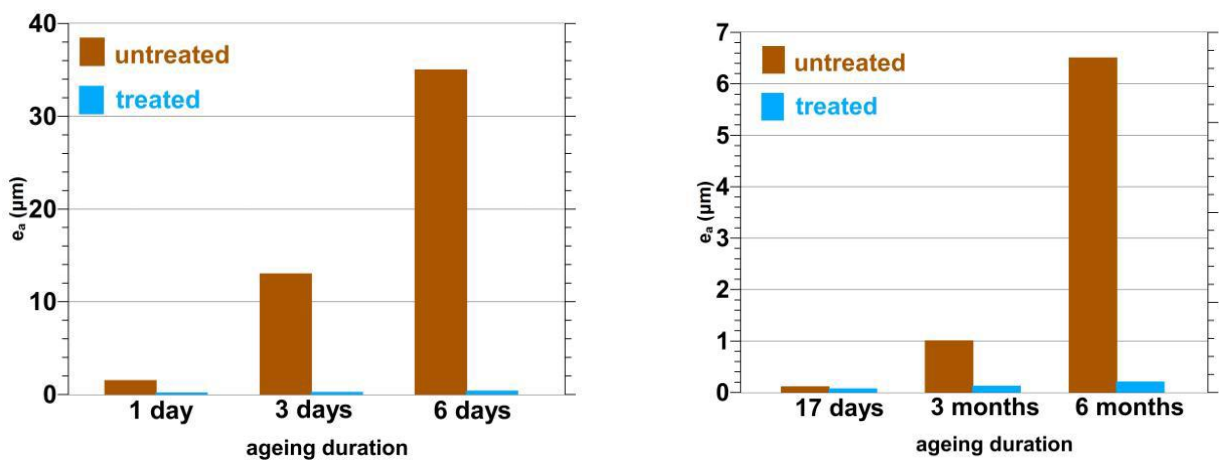


Fig. 3: Comparison of the altered layer thickness with or without the ZP1.5 treatment, as a function of the ageing duration, after V tests at 80 °C or at 40 °C (85 RH%). The corresponding numerical values are reported in Table 1.

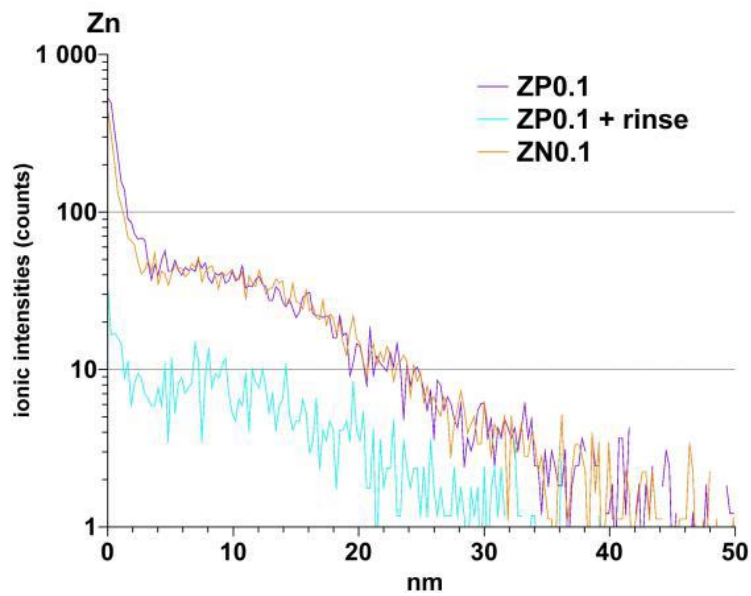


Fig. 4: Zn in-depth profiles obtained by ToF-SIMS analysis from glass surfaces (0 nm corresponds to the glass surface) for ZP0.1 (with or without rinse) or ZN0.1 treatments, obtained from freshly treated glass A plate

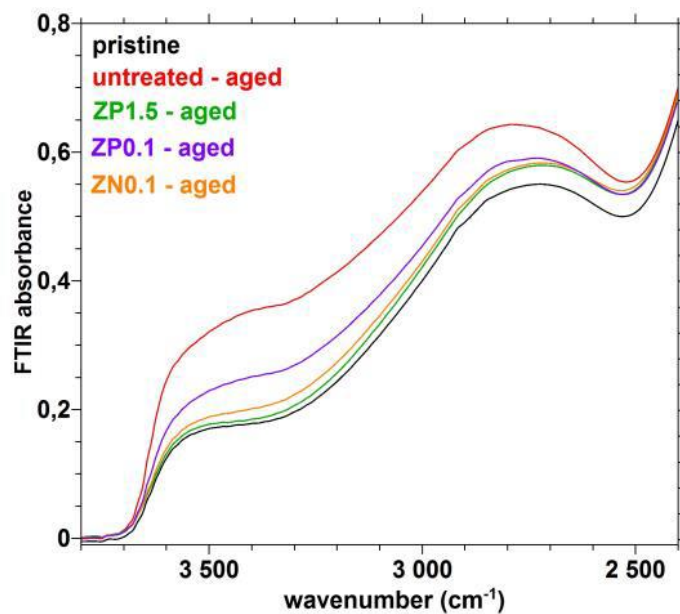
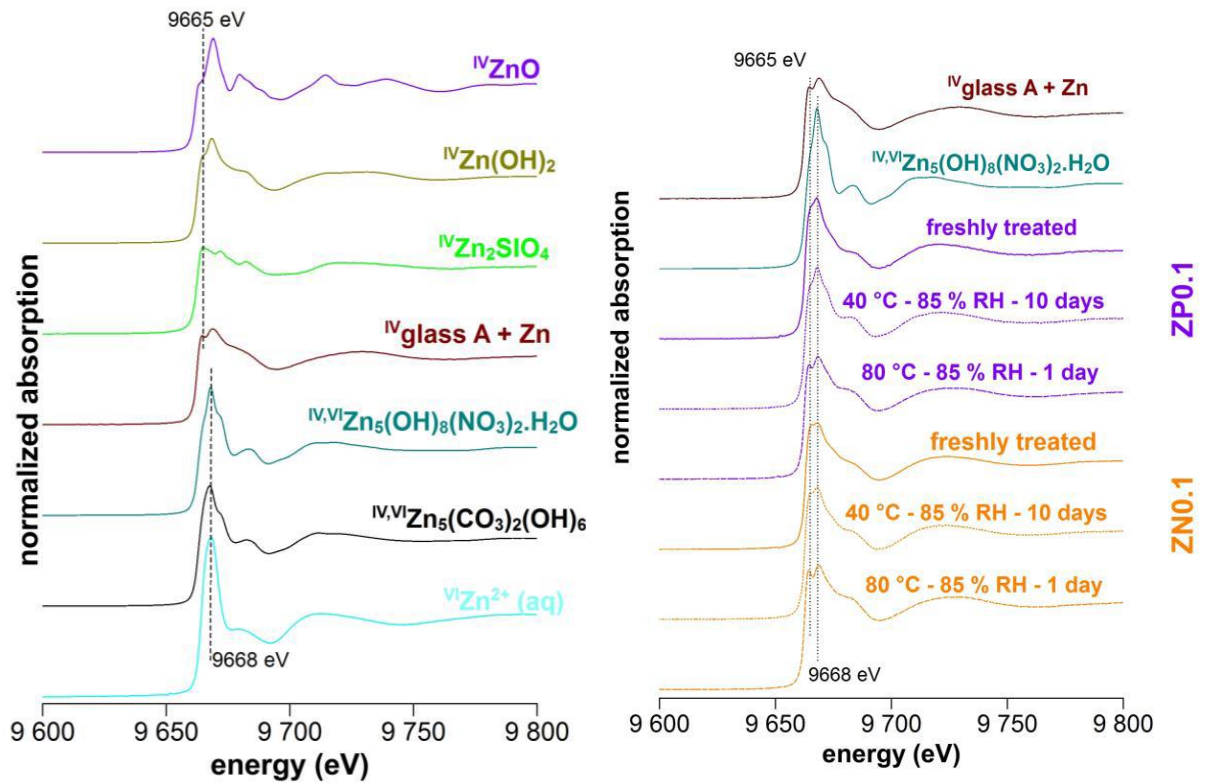


Fig. 5: Transmission FTIR spectra obtained on pristine and aged glass plates A (untreated or treated before the V test). V test at 80 °C, 85 RH%, 1 day. Fig. 5: Transmission FTIR spectra obtained on pristine and aged glass plates A (untreated or treated before the V test). V test at 80 °C, 85 RH%, 1 day.



(a) references

(b) references and treated glass plates

Fig. 6: Zn K-edge XANES spectra of Zn-bearing reference samples (a glass, an aqueous solution and 5 crystalline phases) and of treated glass plates A (ZP0.1 and ZN0.1), shortly after the treatment or after a V test (40 °C, 85 RH%, 10 days or 80 °C, 85 RH%, 1 day). All spectra are normalized to the same area.

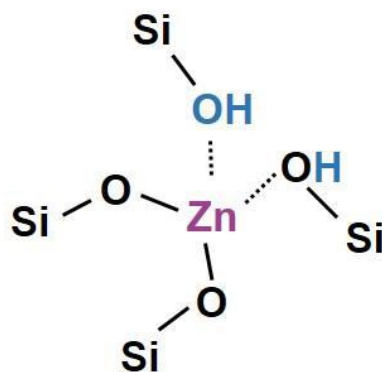


Fig. 7: Possible structural configuration of Zn^{2+} ions bonded to the silicate network into the glass near-surface after a V test (80 °C or 40 °C, 85 RH%). This configuration is inspired from the local environment of Zn^{2+} ions in silicate glasses described in the Ref. (*Le Grand et al., 2000*).

		80 °C		
		1 day	3 days	6 days
untreated		$1.5 \pm 0.5 \mu\text{m}$	$13 \pm 1 \mu\text{m}$	$35 \pm 3 \mu\text{m}$
treated (ZP1.5)		$0.15 \pm 0.02 \mu\text{m}^*$	$0.21 \pm 0.02 \mu\text{m}^*$	$0.35 \pm 0.1 \mu\text{m}$
		40 °C		
		17 days	3 months	6 months
untreated		$0.11 \pm 0.01 \mu\text{m}^*$	$1 \pm 0.2 \mu\text{m}$	$2.5 \pm 0.2 \mu\text{m}$
treated (ZP1.5)		$0.07 \pm 0.01 \mu\text{m}^*$	$0.12 \pm 0.02 \mu\text{m}^*$	$0.2 \pm 0.02 \mu\text{m}$

Table 1: Altered layer thickness (e_a) of glass A developed with V tests of various ageing durations at 80 °C or 40 °C (85 RH%), as determined by SEM observations or (*) from ToF-SIMS profiles.

pH	untreated	treated (ZN0.1)
10.3	-23.8 mV	-3.9 mV
7.9	-9.9 mV	-1.3 mV
7	-8.2 mV	-2.3 mV
5	-6.8 mV	-4.8 mV

Table 2: Zeta potentials measured from solutions of treated (ZN0.1) or untreated glass powders, for different pH values