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Evaluation of decay to glass samples after 1 and 2 years of exposure.

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Institute of Chemistry
Academy of Fine Arts
Wien/Austria
Weathering of Potash-Lime-Silica-Glass with Medieval Composition

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INSTITUTE OF CHEMISTRY
ACADEMY OF FINE ARTS
VIENNA/AUSTRIA
UN/ECE INTERNATIONAL CO-OPERATIVE PROGRAMME ON EFFECTS ON MATERIALS, INCLUDING HISTORIC AND CULTURAL MONUMENTS

WEATHERING OF POTASH-LIME-SILICA-GLASS WITH MEDIEVAL COMPOSITION

FINAL REPORT

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Collaborators:


<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
</tr>
<tr>
<td>BE</td>
<td>Backscattered Electrons</td>
</tr>
<tr>
<td>bind silane°</td>
<td>Product of Plusone, Pharmacia Biotech, Uppsala, Sweden</td>
</tr>
<tr>
<td>Cond.</td>
<td>Electrical Conductivity</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy Dispersive System</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy Dispersive X-Ray Analysis</td>
</tr>
<tr>
<td>NIH</td>
<td>National Institute of Health</td>
</tr>
<tr>
<td>NILU</td>
<td>Norwegian Institute for Air Research</td>
</tr>
<tr>
<td>NRA</td>
<td>Nuclear Reaction Analysis</td>
</tr>
<tr>
<td>RH</td>
<td>Relative Humidity</td>
</tr>
<tr>
<td>SE</td>
<td>Secondary Electrons</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SUN</td>
<td>Sun Hours (Duration of Sunshine)</td>
</tr>
<tr>
<td>TIF</td>
<td>Tagged Image File</td>
</tr>
<tr>
<td>TOW</td>
<td>Time of Wetness</td>
</tr>
<tr>
<td>UN/ECE</td>
<td>United Nations - Economic Commission for Europe</td>
</tr>
<tr>
<td>WDS</td>
<td>Wavelength Dispersive System</td>
</tr>
<tr>
<td>WinSTAT°</td>
<td>Statistic Software for Windows®</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction Analysis</td>
</tr>
</tbody>
</table>
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Data and Results of the Descriptive Statistics, Correlation Analysis and Multiple Linear Regression
used for the Statistical Evaluation and Correlation of the Weathering Phenomena in the Chapters 8 and 9
1. Introduction

Potash-lime-silica glass was used predominantly in the Middle Ages for stained glass windows in cathedrals, churches or other historic buildings. The alarming conditions of many of these objects has resulted in multidisciplinary cooperations among curators, restorers, conservators and scientists. These artifacts consisting of numerous pieces of glass coloured with metal oxides show accelerated deterioration, particularly on their exterior surfaces. In some cases today's air pollution threatens total destruction, although these Romanesque and Gothic objects have escaped major damages by environmental influences for centuries or, in the case of the earliest stained glass windows, even a millenium. The continuous corrosion of the exterior surface of the glass reduces its thickness and a so-called weathering crust is built up on the decomposed surface. Consequently, the transparency of the glass painting is reduced and in some cases the entire composition is barely recognisable. Depending on the chemical composition of the glass the weathering crusts formed consist mainly of gypsum (CaSO$_4$·2H$_2$O) or syngenite (K$_2$SO$_4$·CaSO$_4$·H$_2$O) as crystalline weathering products and hydrated silica as noncrystalline product [1, 2].

Analytical investigations carried out on artifacts from Great Britain, France, Italy, Spain and the German-speaking countries revealed that medieval glass was made from local raw materials. A mixture of one part sand and two parts beechwood or fern ash and chalk was common for that period. The reason for using ash instead of soda, which is typical for ancient and modern glasses, is not yet fully understood. The concentration of SiO$_2$ ranges between 46 and 61 wt% whereas the contents of K$_2$O and CaO are 4-27 % and 8 - 22 %, respectively. Additionally, also Fe, Mn and small amounts of Al, Mg, P and Na can be determined in medieval glasses, because beechwood ash contains iron and manganese in the range of 0.1 - 0.5 wt% [3, 4]. As a consequence of that chemical composition medieval glass is characterised by a low chemical stability against environmental influences. In addition, the presence of potassium instead of soda is at a serious disadvantage. It is a known fact that sodium containing glass is approximately twice as durable as glass with comparable amounts of potassium [4].

It is the purpose of this project to study the atmospheric attack on glass samples with a chemical composition similar to medieval stained glass under natural conditions. Two types of sample glasses were used in this exposure programme - one glass with high sensitivity towards atmospheric attack and one sample glass, which shows a higher chemical stability.
2. Glass - Definition, Structure and Properties

The properties and hence also the weathering behaviour of glass are a result of the special structure of this material. The definition of glass formulated by the ASTM also including metal glasses implies the general aspects of this material:

"Glass is an inorganic substance which is continuous with, and analogous to, the liquid state of that substance, but which, as the result of a reversible change in viscosity during cooling, has attained so high a degree of viscosity as to be, for all practical purposes rigid." [5]

This amorphous, meta-stable state of matter is gained by cooling a flux of the constituents in that way that the formation and crystallisation of nuclei is avoided.

Silicate glass for daily use is produced by melting a mixture of the raw materials, which can be classified in two groups:

1) Network formers (SiO₂, B₂O₃, P₂O₅, TiO₂, Al₂O₃)
These constituents in general are acidic or amphoteric oxides which are able to form a three dimensional random network. According to the theory of Zachariasen [6, 7] the structure of glass can be described by four postulates:

- An oxygen atom should not be linked to more than two network forming cations.
- The co-ordination number of oxygen around the network forming cations must be 3 or 4.
- Oxygen polyhedra should share corners and not edges or faces.
- For a three dimensional network at least three corners of each polyhedron must be shared.

2) Network modifiers (alkali and earth alkali oxides)
The network modifiers break up the network and form terminal -Si-O-M or bridging -Si-O-M-O-Si- groups. They are essential to reach the glassy state at lower cooling rates than they would be necessary with the network formers alone by widening the network and changing the Si-O angels [8]. Especially the concentration and ion radius of these glass constituents are influencing the stability and hence the weathering behaviour.
3. Corrosion of Glass

Glass corrosion is the expression for the chemical and structural destruction of glass by aqueous solutions proceeding from the surface to the bulk. It is highly dependent on the chemical composition of the glass, its surface structure and the corrosion medium.

3.1. Corrosion Mechanisms

The mechanism of glass corrosion is a continuous topic of research, but it is agreed by all parties that the process occurs in two different stages:

Stage 1: In acidic and neutral aqueous solutions the main reaction of glass corrosion is an ion exchange process between the network modifier ions of the glass and protons or hydronium ions of the corrosion medium.

\[
\text{Si-O}^- \cdot \text{M}^+ + \text{H}^+_{(sol)} \leftrightarrow \text{Si-OH} + \text{M}^+_{(sol)} \quad (1)
\]

This ion exchange leads to a decrease of the alkali and in some cases also of the alkaline earth concentration in the outermost regions of the glass and an incorporation of hydrogen into the silicate structure. A so-called „leached layer“ is formed on the glass surface.

Stage 2: Under alkaline conditions the siloxane bonds in the glass are split by hydrolysis and, as a consequence, the glass network is destroyed.

\[
\text{Si-O-Si} + \text{OH}^- \leftrightarrow \text{Si-OH} + \text{SiO}^- \quad (2)
\]

Additionally, condensation of two siloxan groups can occur re-forming a siloxane bond:

\[
\text{Si-OH} + \text{Si-OH} \leftrightarrow \text{Si-O-Si} + \text{H}_2\text{O} \quad (3)
\]

3.2. Kinetics of Glass Corrosion

In acidic and neutral aqueous solutions the glass corrosion is dominated by the ion exchange mechanism. The process known as "static leaching" is described by the equation

\[
Q = k \cdot t^n
\]

with \(0.5 < n < 1\)  
\(Q\)... amount of the leached alkali ions  
\(k\)... time constant  
t... leaching time
Corrosion and Weathering of Glass

The ratio of the volume of the corrosion medium and the affected surface of the glass has the main influence on this process. As this process continues the leaching of alkali ions leads to an increase of the pH in the corrosion medium. If the alkaline solution is not removed and the pH value increases above 9, hydrolysis is the dominant process leading to a total destruction of the silicate structure.

If the corrosion medium is renewed or the volume is high compared to the glass surface, the amount of alkali ions leached is similar to a dynamic process. The model of the "dynamic leaching" is used for the characterisation of the kinetics of the corrosion mechanism.

The solution is refreshed continuously, the leached ions are removed from the surface and ions from the bulk can diffuse to the glass surface. Under dynamic conditions the ion exchange is always the dominant process. In the literature the diffusion of the alkali ions between the reactive sites and the surface is described as the rate controlling step. This process leads to the formation of the so-called "leached layer", which mainly consists of hydrated silica [9, 10].

3.3. Weathering of Glass

In literature weathering is defined as the interaction of the environment with the glass surface [11].

The mechanisms of weathering are less investigated than the corrosion processes in liquids. The three phase system of the ambient air, an adsorbed moisture film and the glass surface as well as the synergetic effects of environmental influences, such as precipitates, sun shine or the concentration of pollutant gases, make the formation of a model difficult.

Two types of weathering can occur on the glass surface depending on the moisture film:

A. Moisture is adsorbed on the glass and can evaporate. Then corrosion products remain on the surface.

B. The moisture runs off and carries away corrosion products from the surface.

The basic processes of weathering are:

- The essential step is the formation of an adsorbed water film, particularly controlled by temperature, relative humidity and dissolved products, or moisture drops on the glass surface [11].

- The alkali ions of the glass can be leached and dissolved in the water film.
Corrosion and Weathering of Glass

- Acidifying gases from the ambient atmosphere can also be dissolved in the water film adsorbed on the glass surface. In some cases an oxidation of the gas (e.g. SO₂) is described in the literature [12].

- For some compounds, especially sulphates the solubility product can be reached. In that cases precipitation and crystallisation can occur.

- The formation of the thermodynamically favourable products (especially sulphates) may run over several stages. Therefore, a cross link of the corrosion products found and the weathering mechanism of the glass can not be done.

- Further studies have shown that UV-radiation has an effect on the crystal growth of the weathering products [13].

The composition of the glass has another important influence in the formation of weathering products. El Shamy found that glasses with high concentrations of SiO₂ (>66 wt%) are more stable than glasses with SiO₂ < 66 wt%. For glasses with a SiO₂/R₂O ratio of 4,5 (R = Na, K) a formation of a dense weathering crust was observed.

The content of potassium in the glass causes additional effects on the corrosion behaviour. Glasses with K₂O < 15 mol% suffer from pitting corrosion, while higher amounts of potassium lead to the total dealkalisation in less than 72 hours and further to the formation of weathering crusts [8, 14, 15, 16].

El-Shamy [8] describes that CaO leads to an increase of the extraction of potassium and magnesium, even when the concentration of these ingredients is kept constant in the glass. Increased lime concentrations also lead to the accelerated dissolution of silica.

In sodium silicate glasses the presence of calcium, barium or strontium either in the glass or in the corroding solution lead to the formation of a protective layer on the surface, which improves the stability. The development of this diffusion barrier is stimulated by inhibitors in the corrosion solution either from the solvent or the glass itself. Oka and Tomozawa [17] describe this mechanism as the formation of silicates of Ca, Sr or Ba (not Mg).
4. The Exposure of Glass Samples within the UN/ECE Project

Within the UN/ECE project two model glasses with a chemical composition similar to medieval glass have been exposed at 23 UN/ECE test sites in Europe and North America in order to study the weathering behaviour under natural conditions. Type 1 of the two glasses (Glass M1) consists of a high amount of network modifiers and a small amount of network formers, whereas the content of network modifiers in type 2 (Glass M3) is rather low.

<table>
<thead>
<tr>
<th>Glass (wt%)</th>
<th>SiO₂</th>
<th>K₂O</th>
<th>CaO</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>P₂O₅</th>
<th>Na₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>48.00</td>
<td>25.50</td>
<td>15.00</td>
<td>3.00</td>
<td>1.50</td>
<td>4.00</td>
<td>3.00</td>
</tr>
<tr>
<td>M3</td>
<td>60.00</td>
<td>15.00</td>
<td>25.00</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Tab.1: Chemical composition of the two types of glasses used in the exposure programme.

4.1. Sample Preparation

Platelets of approximately 10 x 10 x 1.5 mm were cut from the glass bars delivered by the Fraunhofer-Gesellschaft and embedded in epoxy resin. The samples were polished with SiC-paper of mesh 600 - 4000 (grain size of 30 - 5 µm). In the last polishing step isopropanol was used instead of water in order to prevent leaching of glass components. Triplicates of the samples were mounted on glass fibre enforced plastic plates (Fig.1), covered with silicon caps, packed in polyethylene boxes conditioned with silicon gel and sent to the 23 exposition sites.
Fig.1: Glass samples prepared and mounted for the exposure.

4.2. Exposure

The 23 test sites had been selected under the aspect of a wide range of the \( \text{SO}_2 \) and \( \text{NO}_2 \) concentrations and of the relative humidity. In Fig.2 a map with the test sites is shown, where the glass samples have been exposed. The bars indicate the relative concentrations of \( \text{SO}_2 \) (left), \( \text{NO}_2 \) (middle) and the relative humidity (right).

Using the UN/ECE classification concerning the different pollutant loads the test sites can be grouped as follows [18]:

- 10 low polluted sites with both, a concentration of \( \text{SO}_2 \) and \( \text{NO}_2 < 20 \mu \text{g/m}^3 \)
- 9 moderately polluted sites with a concentration of \( \text{SO}_2 \) between 20 and \( 40 \mu \text{g/m}^3 \) or a \( \text{SO}_2 \) concentration < 20 \( \mu \text{g/m}^3 \) and a \( \text{NO}_2 \) concentration > 20 \( \mu \text{g/m}^3 \)
- 4 highly polluted sites with a concentration of \( \text{SO}_2 > 40 \mu \text{g/m}^3 \)

The environmental characteristics like traffic intensity, the surrounding and the concentrations of the pollutant gases (4 year mean values of 1987-1991) are listed in Tab.2. The complete files of the environmental data are listed and presented in the reports no. 3, 9, 10, 16, 17, 20 and 21 of NILU [19- 25].
Due to the different stabilities of the two model glasses Glass M1 was exposed for 6 months and one year, whereas Glass M3 was exposed for one and two years.

<table>
<thead>
<tr>
<th>UN/ECE Site Number</th>
<th>Characterisation</th>
<th>Test site</th>
<th>e: Environment</th>
<th>ti: Traffic Intensity</th>
<th>SO₂ [µg/m³]</th>
<th>NO₂ [µg/m³]</th>
<th>TOW [h]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>rural</td>
<td>Kaperske Hory</td>
<td>e: forest, grasspasture</td>
<td>ti: low</td>
<td>19.55</td>
<td>12.58</td>
<td>3261.25</td>
</tr>
<tr>
<td>5</td>
<td>rural</td>
<td>Ahtäri</td>
<td>e: forest, grasspasture</td>
<td>ti: low</td>
<td>3.80</td>
<td>4.98</td>
<td>3080.75</td>
</tr>
<tr>
<td>7</td>
<td>rural</td>
<td>Waldhof-Langenbergge</td>
<td>e: forest, grasspasture</td>
<td>ti: low</td>
<td>12.25</td>
<td>11.95</td>
<td>4573.00</td>
</tr>
<tr>
<td>12</td>
<td>rural</td>
<td>Garmisch-Partenkirchen</td>
<td>e: forest, grasspasture</td>
<td>ti: low</td>
<td>8.35</td>
<td>13.25</td>
<td>4592.00</td>
</tr>
<tr>
<td>14</td>
<td>rural</td>
<td>Casaccia</td>
<td>e: built-up, grass</td>
<td>ti: low</td>
<td>6.90</td>
<td>13.55</td>
<td>3466.25</td>
</tr>
<tr>
<td>23</td>
<td>rural</td>
<td>Birkenes</td>
<td>e: forest, grasspasture</td>
<td>ti: low</td>
<td>1.10</td>
<td>3.53</td>
<td>4295.25</td>
</tr>
<tr>
<td>26</td>
<td>rural</td>
<td>Aspvreten</td>
<td>e: forests, grasspasture</td>
<td>ti: low</td>
<td>2.45</td>
<td>4.55</td>
<td>3681.25</td>
</tr>
</tbody>
</table>
### The Exposure of Glass Samples

<table>
<thead>
<tr>
<th>UN/ECE Site Number Characterisation</th>
<th>Test site</th>
<th>e: Environment ti: Traffic Intensity</th>
<th>SO$_2$ [µg/m$^3$]</th>
<th>NO$_2$ [µg/m$^3$]</th>
<th>TOW [h]</th>
</tr>
</thead>
<tbody>
<tr>
<td>26 rural</td>
<td>Aspvreten</td>
<td>e: forests, grasspasture ti: low</td>
<td>2.45</td>
<td>4.55</td>
<td>3681.25</td>
</tr>
<tr>
<td>28 urban</td>
<td>Wells</td>
<td>e: built up, grasspasture ti: moderate</td>
<td>6.43</td>
<td>23.35</td>
<td>5990.75</td>
</tr>
<tr>
<td>33 rural</td>
<td>Toledo</td>
<td>e: grasspasture ti: low</td>
<td>7.85</td>
<td>14.08</td>
<td>1803.75</td>
</tr>
<tr>
<td>37 rural</td>
<td>Dorset</td>
<td>e: forest, grasspasture ti: low</td>
<td>3.30</td>
<td>1.65</td>
<td>3231.25</td>
</tr>
</tbody>
</table>

Tab.2a: Low polluted test sites (SO$_2$, NO$_2$ < 20.0 µg/m$^3$)

<table>
<thead>
<tr>
<th>UN/ECE Site Number Characterisation</th>
<th>Test site</th>
<th>e: Environment ti: Traffic Intensity</th>
<th>SO$_2$ [µg/m$^3$]</th>
<th>NO$_2$ [µg/m$^3$]</th>
<th>TOW [h]</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 industrial</td>
<td>Helsinki</td>
<td>e: built-up ti: moderate</td>
<td>17.90</td>
<td>33.78</td>
<td>3775.75</td>
</tr>
<tr>
<td>8 urban</td>
<td>Aschaffenburg</td>
<td>e: built-up ti: high</td>
<td>17.85</td>
<td>38.88</td>
<td>3508.00</td>
</tr>
<tr>
<td>13 urban</td>
<td>Rome</td>
<td>e: built-up ti: high</td>
<td>34.30</td>
<td>68.63</td>
<td>1630.33</td>
</tr>
<tr>
<td>19 rural</td>
<td>Vredepeel</td>
<td>e: forest, grasspasture industrial farms NH$_3$ transboundary air pollution ti: moderate</td>
<td>10.88</td>
<td>32.15</td>
<td>5001.50</td>
</tr>
<tr>
<td>21 urban</td>
<td>Oslo</td>
<td>e: built-up ti: high</td>
<td>10.88</td>
<td>50.58</td>
<td>2782.50</td>
</tr>
<tr>
<td>24 urban</td>
<td>Stockholm</td>
<td>e: built-up ti: high</td>
<td>11.03</td>
<td>90.58</td>
<td>3304.75</td>
</tr>
<tr>
<td>27 urban</td>
<td>Lincoln Cathedral</td>
<td>e: built-up ti: high</td>
<td>18.25</td>
<td>46.03</td>
<td>5908.25</td>
</tr>
<tr>
<td>34 urban</td>
<td>Moscow</td>
<td>e: built-up, grasspasture ti: high</td>
<td>25.38</td>
<td>61.93</td>
<td>2562.25</td>
</tr>
<tr>
<td>36 urban</td>
<td>Lisbon</td>
<td>e: built-up, park-areas ti: high</td>
<td>9.15</td>
<td>30.33</td>
<td>2315.33</td>
</tr>
</tbody>
</table>

Tab.2b: Moderately polluted test sites (20.0 < SO$_2$ < 40.0 µg/m$^3$ or SO$_2$ < 20.0 µg/m$^3$ and NO$_2$ > 20.0 µg/m$^3$)

<table>
<thead>
<tr>
<th>UN/ECE Site Number Characterisation</th>
<th>Test site</th>
<th>e: Environment ti: Traffic Intensity</th>
<th>SO$_2$ [µg/m$^3$]</th>
<th>NO$_2$ [µg/m$^3$]</th>
<th>TOW [h]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 industrial</td>
<td>Kopisty</td>
<td>e: coal-mining ti: medium</td>
<td>83.05</td>
<td>38.10</td>
<td>2265.25</td>
</tr>
<tr>
<td>10 industrial</td>
<td>Bottrop</td>
<td>e: built-up ti: high</td>
<td>50.18</td>
<td>47.65</td>
<td>4195.00</td>
</tr>
<tr>
<td>15 urban</td>
<td>Milan</td>
<td>e: built-up ti: high</td>
<td>67.65</td>
<td>109.25</td>
<td>3245.75</td>
</tr>
<tr>
<td>39 industrial</td>
<td>Steubenville</td>
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Tab.2c: Heavily polluted test sites (SO$_2$ > 40.0 µg/m$^3$)
5. Analysis of the Weathering Phenomena

In the following section the methods used for the characterisation of the weathering phenomena will be described. Scanning Electron Microscopy (SEM) was the main technique used for the morphological identification of weathering products and the states of weathering of the glass surfaces formed during the exposure. In combination with energy dispersive x-ray microanalysis (EDS) a qualitative chemical analysis of the weathering products could be carried out. After the preparation of cross sections of the glass samples this method delivered also informations about the depths of the leached layers of glass M1, where a surface layer of several micrometers depth has been formed during the weathering process. For glass M3, which is more stable than glass M1, nuclear reaction analysis (NRA) has to be used to gain informations about the hydrogen distribution in the leached layers. The depth of these layers was less than 1 μm usually.

5.1. Scanning Electron Microscopy (SEM)

The SEM investigations of the naturally weathered glass samples were carried out with an instrument Jeol 6400 in combination with an energy dispersive x-ray microanalysis system, Link eXL. The glass samples had to be coated with a thin carbon layer prior to analysis in order to avoid any charging effects of the electrically non-conducting glass during the electron bombardment. At first the weathering phenomena on the glass samples were characterised by using the backscattered (BE) or secondary (SE) electrons (Fig.3) as well as the digital x-ray mappings (Fig.4). This simultaneous mapping of different elements enables the acquisition of element distribution images. In this case energy ranges characteristic for the interesting elements can be selected in the spectrum and the different amounts of x-rays emitted in each point of a raster over the specimen are converted into a 8 bit-grey-scale image, equivalent to 255 grey-scales. The same procedure can be done also in only one dimension, where the electron beam is scanned along a pre-defined line and changes in the elemental distribution can be visualised by profiles (line scan) [26].

The main limitation of the ED-system used has been the lack of information of light elements (e.g. C and N), which means that weathering products containing carbonates or nitrates can not be identified by chemical analysis. Especially on the surfaces of the samples of glass M1, which had been exposed in the unsheltered mode, weathering products only with Ca in the EDX were found. Also weathering products formed on the surface of glass M3 exposed in the sheltered way could not be identified in some cases.
Fig. 3: SE image (600x) of weathering products formed on a sample of glass M1 exposed for 6 months in Birkenes (Test site no. 23).

Fig. 4: Corresponding digital x-ray mappings of Na, Mg, Al, Si, P, S, Cl, K, Ca of the area shown in Fig. 3 (600x). An enrichment of Ca and S in the weathering product indicates the formation of gypsum. However, in some cases weathering products of similar shape but different chemical composition can be distinguished.
5.2. Morphological and Elemental Characterisation of the Weathering Phenomena in the SEM

5.2.1. Glass M1 after Sheltered Exposure

The main weathering product formed on the glass surfaces after six months of sheltered exposure is syngenite (K$_2$SO$_4$.CaSO$_4$.H$_2$O). That could be proved by x-ray diffraction analysis (XRD). However, the crystals seen and analysed in the SEM/EDS have different shapes and vary in their chemical composition. In general, three different shapes of the syngenite crystals could be observed:

- plate-like crystals (25 μm x 25 μm)
- needle-shaped crystals (3 μm x 20 μm)
- lanceolate crystals (15 μm x 5 μm)

The crystals formed most frequently are flat plates, which do not only occur as single grown crystals (Fig.5) but also in dense weathering crusts (Fig.6). Samples covered with weathering crusts formed by lanceolate crystals show in some cases the formation of circular arrangements (Fig.7). Syngenite crystals formed as needles are shown in Fig.8. Usually an agglomeration of such weathering products occurred on the glass surfaces after 6 months of sheltered exposure.

A comparison of the chemical composition of the various shaped crystals yielded that the ratios of Ca:S, K:S and Ca:K of similar shaped weathering products show a higher variation than the ratios of different shaped products. This may indicate that the different morphologies of the syngenite crystals are not influenced by their chemical compositions but by their "history of formation". However, after 12 months exposure almost exclusively plate-like crystals could be found on the glass surfaces.

In addition to the K-Ca sulphate long thin needles forming bundles could be determined by SEM images. These weathering products consist of Na, Mg and P and are only present in a few cases.

At some test sites also a few crystals of gypsum (CaSO$_4$.2H$_2$O) and arcanite (K$_2$SO$_4$) have been formed during the exposure. Sylvite (KCl) and halite (NaCl) could be found on the surfaces of a few samples, too, but normally Cl, which can be detected on almost each glass surface, can not be related to special corrosion products.

After 12 months exposure the same phenomena as described can be observed. As mentioned above the number of plate-like crystals has increased, whereas the amount of needle-shaped or lanceolate crystals has disappeared nearly. The size of most of the weathering products has increased during the second 6 months.

The condition of the glass surface itself varies very much on the different test sites. Some of the surfaces seem to be intact at all, whereas others are cracked and the leached layer is about
to flake off. However, comparing the glass surfaces to the samples exposed in the unsheltered mode these phenomena are neglectible.

Fig. 5: Plate-like syngenite crystals formed on glass M1 exposed sheltered for 6 months in Casaccia, test site no. 14.

Fig. 6: Plate-like syngenite crystals in the weathering crust formed after 6 months of sheltered exposure in Bottrop, test site no. 10.
Fig. 7: Lanceolate crystals formed on glass M1 after 6 months of sheltered exposure in Rome, test site no. 13.

Fig. 8: Needle-shaped syngenite crystals formed after 6 months of sheltered exposure in Aspvreten, test site no. 26.
5.2.2. Glass M1 after Unsheltered Exposure

Samples exposed under unsheltered conditions show totally different weathering phenomena than those after sheltered exposure, because most of the weathering products have been rinsed off of the sample surface. Only a few products could be found, above all products with calcium and sulphur. In most cases no elements typical for anions could be detected pointing out the presence of either carbonates, hydroxides, nitrates or organic compounds. The shapes of these products are often irregular (Fig.9).

Only on few glass surfaces crystallised weathering products could be found. EDX analysis indicate that KCl (Fig.10) and gypsum crystals (CaSO₄.2H₂O) have been formed. More severe weathering phenomena can be observed at the glass surfaces of the samples. The leached layers are cracked and flaked off to a high extent causing a channel-like structure into the glass (Fig.11). In some cases BE images show a depletion of elements with higher atomic numbers around the cracks and element distributions reveal the presence of weathering products containing K in some domains. After 12 months additionally Ca can be detected in some micro cracks and sometimes the „intact“ glass can be observed after detaching of pieces of the leached layer (Fig.12).

Fig.9: Typical weathering product containing Ca and formed on the glass samples M1 under unsheltered exposure in Toledo, test site no. 33.
Fig. 10: KCl crystals laying on the severely cracked leached layer of a sample of glass M1 exposed unsheltered in Birkenes, test site no. 23.

Fig. 11: A detached piece of the leached layer is still laying next to its former place. A channel-like structure can be observed. (Garmisch-Partenkirchen, test site no. 12).
5.2.3. Glass M3 after Sheltered Exposure

Contrary to the surfaces of glass M1, which are predominantly covered with syngenite crystals, the main weathering product found on glass M3 is gypsum (CaSO₄·2 H₂O). Single crystals as well as agglomerations of this calcium sulfate could be observed on the glass surfaces, as shown in Fig.13. That weathering product is almost present as regular hexagonal crystals (Fig.14). The size of these weathering products is increasing during the second year of exposure. After one year of sheltered weathering the crystals are of an average dimension of approx. 5 x 5 to 15 x 15 μm², after the two year exposure their typical dimension is 30 x 30 μm². In a few cases also crystals with a size of 100 x 100 μm² could be found. Additionally, arcanite (K₂SO₄) forming either needles (1 x 20 μm²) or cubes is present on the sample surfaces, sometimes forming agglomerates with gypsum (Fig.15, 16). After two years of exposure only weathering products in the form of a cube or prism and no needle-shaped crystals could be observed. These products are consisting of Ca and S and are surrounded by products of K, S and Cl, obviously an early stage of the formation of the arcanite crystals.

After one year as well as after two years exposure the glass itself shows a smooth and apparently unweathered surface [27, 28].
Fig. 13: The surface of a glass sample M3 exposed sheltered in Ähtäri, test site no. 5, for two years is covered with agglomerations and single crystals of gypsum.

Fig. 14: Gypsum crystals formed on the surface of glass M3 during 24 months sheltered exposure in Moscow, test site no. 34.
Fig. 15: Arcanite needles surrounding gypsum plates after 12 months of sheltered exposure in Aspvreten, test site no. 26.

Fig. 16: Digital x-ray mapping of Si, P, S, Cl, K, Ca showing the different distribution of these elements in the corresponding SE image (Fig. 15). The gypsum crystals are surrounded by a weathering product containing K, S and Cl.
5.2.4. Glass M3 after Unsheltered Exposure

After 12 months exposure no cracks can be observed on the surfaces of glass M3 and also no weathering products have remained on the samples. In some cases air-born particles and globular networks probably of organic origin containing Na, Mg, P, S and Cl could be found on the glass samples. The weathering phenomena do not change drastically after two years exposure. However, pitting corrosion has started and some pieces of the leached layer have already flaked off at the test sites 6, 8, 10, 13, 33 and 39 [27, 28].
5.3. Quantification of the Weathering Phenomena

Three different methods were used to quantify the weathering phenomena. Samples exposed under sheltered conditions were characterised by their degree of covering by the weathering products, which was evaluated by means of the SEM images and an image analysis software (NIH image Rel. 1.59). In the case of unsheltered exposure the depths of the leached layers were used for the characterisation. For this purpose cross sections were prepared of the samples of glass M1 and analysed in the SEM. Glass M3 could not be analysed in this way due to the rather thin surface layer formed during weathering. Hydrogen depth profiles gained by nuclear reaction analysis (NRA) were used therefore.

5.3.1. Evaluation of the Degree of Covering

Digital images of the sample surfaces coated with carbon were acquired at magnifications of 60x and 200x using the backscattered electron signal in the case of glass M1 and the secondary electron signal in case of glass M3. A maximum contrast between the weathering products formed and the glass surface of the specimens could be achieved. The digital images were converted into the TIF 6.0 format and processed with the image processing and analysis software of NIH (Rel. 1.59).

In a first step the images (Fig.17) were scaled in μm, obvious errors in the images like patterns of detached corrosion products were corrected (Fig.18) and the legend, which had been blanked in automatically by the SEM software, was replaced by characteristic surface domains.

![Fig.17: Original BE image](image1)
![Fig.18: Correction of errors](image2)
![Fig.19: Binary image](image3)

Afterwards the distinction between the surface covered with weathering products and the uncovered glass surface was done with a thresholding tool of the software. After a conversion of the image into a binary file (Fig.19) the sizes of the crystals and of the agglomerations could be calculated by the software and were listed in a text file. That could be evaluated by
Analysis of the Weathering Phenomena

the commercial data processing software Excel, version 7.0. The ratio of the area covered by products to the total area of the image was used for further calculations.

\[ CS = \frac{A_c}{A_t} \cdot 100\% \]

CS... covered surface [%]
A_c... area covered with weathering products [μm²]
A_t... total area of the image [μm²]

It has to be mentioned that only the covering of the area was calculated instead of the covering with masses based on the simplifying assumption that the heights and densities of the corrosion products are constant. A measurement of the heights of the weathering products in the SEM was not possible because of inhomogeneous coverings.

5.3.2. Evaluation of the Depths of the Leached Layers by the Analysis of Cross Sections in the SEM

The exposed glass samples were treated with „bind silane” to enhance the adhesion between the sample surface and the resin used for embedding the samples for preparing cross sections. Subsequently, the samples were cut perpendicular to the glass surface and polished with SiC paper (500 - 4000 mesh). In the last polishing step isopropanol was used instead of water in order to prevent further leaching of glass components. Afterwards the samples were coated with carbon and examined in the SEM. The leached layer could be visualised by taking backscattered electron images due to its lower content of potassium and calcium compared to the bulk glass. Additionally, the relative concentrations of Si, K and Ca could be analysed with digital linescans perpendicular to the leached layer. The BE images and intensity profiles of the various elements were saved as TIF-files therefore and evaluated by the image processing and analysis software of NIH. The distance between the transition points of the elemental intensity plateau in the resin and in the bulk glass was measured (Fig.20).
At least three measurements were carried out over the cross section in order to avoid errors caused by inhomogeneous depths of the leached layers in the sample. These values were finally averaged excluding outliers caused by cracked and detached parts of the leached layer. The evaluation of the depth profiles of calcium and potassium resulted in different depths of the leached layers. The leaching of potassium ions proceeded into deeper regions of the glass than the leaching of calcium. Since the depths of the leached layers measured in the backscattered electron images were equivalent to those from the potassium profiles these values were used for further calculations.

The leached layers of glass M1 exposed for 12 months in the unsheltered mode reached depths of up to 22 µm, whereas most of the samples of glass M3 showed layers significantly smaller than 1 µm in spite of the longer exposure period of one and two years. Since the accuracy of these measurements would have been too low the depths of the leached layers had to be analysed by nuclear reaction analysis (NRA).
5.3.3. Evaluation of the Depths of the Leached Layers by NRA

Nuclear Reaction Analysis is based on the nuclear reaction $^1\text{H}(^{15}\text{N}, \alpha \gamma)^{12}\text{C}$, which takes place at a resonance energy of 6.385 MeV.

\[ ^{15}\text{N} + ^1\text{H} \xrightarrow{\gamma} ^4\text{He} + ^{12}\text{C} \]

$^{15}\text{N}^{++}$ ions are accelerated onto a sample surface with an energy higher than the resonance energy. By the emission of $\alpha$-rays an excited $^{12}\text{C}$ nucleus is formed, which reaches the energy ground level by emitting $\gamma$-rays. An increase of the energy of the primary ions leads to a deeper intrinsing depth of the ions and as a result of scattering effects the volume where the resonance energy is reached is moved into deeper regions of the sample (Fig.21).

Nuclear reaction analysis provides the hydrogen depth distribution from the outermost region of the sample surface to approximately 2.5 $\mu$m. The change of the hydrogen content from the surface to the bulk glass can be used for measuring the depth of the leached layer (Fig.22) [29, 30].
Analysis of the Weathering Phenomena

Nuclear Reaction Analysis of Glass M1

Fig. 22: Hydrogen depth profile of a glass sample M1, exposed in the sheltered mode in Birkenes, test site no. 23, for 6 months. The high H concentration in the leached layer drops to almost 0% in the bulk glass.
6. Results

In Tab.3 the results obtained by the analysis of the exposed glass samples are summarised. The weathering phenomena observed in the SEM as well as the various data are listed in Annex 1 of this report. In Tab.3 the following abbreviations were used:

Test Site (column 1) - number of test site used for the glass exposure (see also Tab.2).

LL6M1U (column 2) - thickness of the leached layer of glass M1 after 6 months of unsheltered exposure. The thickness was determined in a cross section of the specimen by SEM.

CS6M1S (column 3) - covered surface (degree of glass surface covered by weathering products) after 6 months of sheltered exposure of glass M1.

LL12M1U (column 4) - thickness of the leached layer of glass M1 after 12 months of unsheltered exposure. The thickness was determined in a cross section of the specimen by SEM.

CS12M1S (column 5) - covered surface (degree of glass surface covered by weathering products) after 12 months of sheltered exposure of glass M1.

HD12M3U (column 6) - thickness of the leached layer (determined by hydrogen depth distribution by NRA) of glass M3 after 12 months of unsheltered exposure.

HD12M3S (column 7) - thickness of the leached layer (determined by hydrogen depth distribution by NRA) of glass M3 after 12 months of sheltered exposure.

CS12M3S (column 8) - covered surface (degree of glass surface covered by weathering products) after 12 months of sheltered exposure of glass M3.

HD24M3U (column 9) - thickness of the leached layer (determined by hydrogen depth distribution by NRA) of glass M3 after 24 months of unsheltered exposure.

HD24M3S (column 10) - thickness of the leached layer (determined by hydrogen depth distribution by NRA) of glass M3 after 24 months of sheltered exposure.

CS24M3S (column 11) - covered surface (degree of glass surface covered by weathering products) after 24 months of sheltered exposure of glass M3.
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7. Environmental Parameters used for the Statistical Analysis

The environmental data, which were used for the statistical evaluation were measured at the various test sites, collected and evaluated by NILU. Since there was a lack of environmental data of the year 1995, data of the year 1994 were used for the statistical evaluation. They describe the climatic situation in a better way than calculated values. Nevertheless, they are describing the beginning of the weathering at all test sites in the same way, which would not be guaranteed by calculated values.

Since O$_3$ was not measured at each test site calculated values have been used in these cases, which were gained by the empirical equation

\[ O_{3\text{calc}} = 58.2 - 0.6\text{NO}_2 \]

In Tab.4 and Tab.5 the environmental data of the exposure periods of one and two years, respectively, are summarised, which have been used for the statistical evaluation.
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Tab. 5: Environmental data X/93 - X/94 evaluated by NILU, which were used for the statistical evaluations of the measured weathering phenomena after one and two years of exposure.
8. Statistical Evaluation and Correlation of the Weathering Phenomena with the Environmental Data

"WinSTAT 3.1 for Windows" software was used for the statistical evaluation of the weathering phenomena summarised in Tab.3. The Kolmogorov Smirnov test for normal distribution as well as the cumulative plots performed with the data revealed that the probability of normal distribution of the weathering data was rather low in most cases. Therefore, the logarithmic values were calculated, which showed better fits in the normal distribution. In a next step a Pearson correlation was performed with the environmental data summarised in Tab.4 and 5. Additionally, the measured values were correlated with cross terms calculated from the original environmental data, which should also show synergetic effects of different environmental parameters. SO$_2$×NO$_x$ and SO$_2$×O$_3$ were used to determine possible influences on the oxidation mechanism, SO$_2$×RH and NO$_x$×RH, SO$_2$×TOW and NO$_x$×TOW for the characterisation of possible influences of humidity on the weathering process. In the case of the unsheltered exposure also the term mm×H was used which describes the H concentration per area. These terms and the following statistical calculations are listed in annex 1.

After the correlation analysis the redundancy of the parameters was tested with principal component analysis. It is obvious that cross terms containing environmental parameters which were correlated with the environmental data could be excluded with a high probability (e.g. the concentration of SO$_2$) from further calculations. Therefore, the following analysis with multiple linear regression was mainly performed with only one of the cross terms containing a parameter of humidity and pollutant concentrations (in most cases SO$_2$×RH or NO$_x$×RH). Also attempts using multiple linear regression with all of these terms proved the higher significance of the cross terms including the relative humidity and pollutant concentrations compared to the cross terms containing the time of wetness.

Since some data of test sites were skipped by the statistical software due to missing environmental data these analyses were repeated with all data available, if a parameter with missing data was too insignificant to remain in the linear regression. Nevertheless, these calculations are listed in annex 1 in order to compare the quality of the regression with the same number of values.
9. Discussion of the Results

9.1. Unsheltered Exposure of Glass M1 (6 Months)

The dose-response function found depends on the SO$_2$ concentration and the cross term mmxH (Fig.23). The depths of the leached layers increase by:

\[
\ln(\text{LL6M1U}) = -0.13717 + 0.56722 \ln(\text{SO}_2) + 10.2395 \text{ mmxH}
\]

\[\begin{align*}
N &= 18 \\
R &= 0.88938 \\
R^2 &= 0.791
\end{align*}\]

The equation is based on a data set of 18 test sites only due to missing of data of the pH of the test sites no. 37 and 39, missing of precipitation (mm values of test site no. 14) and missing of the environmental data of the test sites no. 27 and 28. Most of the data used are in the 95% confidence interval of the regression line except the results of the sample exposed at test site no. 3. A following regression analysis of the residues with the residual environmental parameters was not successful at all.

The dominating factor for the weathering of glass M1 is the SO$_2$ concentration in the ambient atmosphere (Fig.24). As will be shown with the data of the samples exposed in the sheltered mode the statistical influence of the humidity is negligible for glass M1 compared to the concentration of the acidifying gases. RH included in the regression analysis as an additional variable does not increase the correlation coefficient to a reasonable extent ($R^2 = 0.79$, N =18). The relative humidity also does not alter the deviation of the value of test site no. 3. It seems to be a fact that even under environmental conditions with low humidity water is sufficiently adsorbed on the glass surfaces for the procedure of the weathering process. The influence of the pH and of the amount of precipitation on the leaching of glass constituents is evident (Fig.23 and 24).
Discussion of the Results (Glass M1)

\[ \text{ln}(LL6U)_{\text{calc}} = -0.137 + 0.567 \ln(SO_2) + 10.240 \text{ mmyxH} \]

Fig. 23: Plot of the dose-response function for glass M1 exposed under unsheltered conditions considering SO$_2$ and mmyxH ($R^2 = 0.791, N = 18$).

\[ \text{ln}(LL6U)_{\text{calc}} = 7.767 \times 10^{-2} + 0.465 \ln(SO_2) \]

Fig. 24: Plot of the linear regression of the depths of the leached layers of glass M1 after 6 months unsheltered exposure considering the SO$_2$ concentration in the ambient atmosphere only ($R^2 = 0.43, N = 21$).
9.2. Sheltered Exposure of Glass M1 (6 Months)

The dose-response function found depends on the $\text{SO}_2$ and the $\text{NO}_2$ concentration in combination with the relative humidity (Fig.25). The degree of the glass surface covered with weathering products (covered surface) increases by:

$$\ln(\text{CS6M1S}) = 2.11019 + 0.42948 \ln(\text{SO}_2) + 1.66670 \times 10^{-4} \text{NO}_2 \times \text{RH}$$

$$N = 20$$
$$R = 0.721$$
$$R^2 = 0.519$$

The equation is based on the evaluation of the data of 20 test sites only due to missing of the $\text{NO}_2$ data of test site no. 37 and missing of the environmental data of the test sites no. 27 and 28. Compared with the data of unsheltered exposure the results are more scattered due to weathering products already spalled off. Especially for samples with a high degree of covered surfaces the weathering crust is already detaching and the surface analysis gets more difficult and more incorrect due to the growth of the thickness of the weathering crust. Nevertheless, the function shows a reasonable result since the formation of the weathering products depends on the amount of ions leached out of the glass. This process depends on the pH of the leachate on the sample surface, which is influenced by moisture and the absorbed pollutants. Similar to the unsheltered exposure the $\text{SO}_2$ concentration has the main influence (Fig.26) and does not depend on the relative humidity statistically. The cross term $\text{NO}_2 \times \text{RH}$ yields to a slightly better fit than using the $\text{NO}_2$ term only.
Discussion of the Results (Glass M1)

Fig.25: Plot of the dose-response function for glass M1 exposed under sheltered conditions considering the SO$_2$ concentration and the cross term NO$_x$RH ($R^2 = 0.519$, $N = 20$).

\[
\ln(\text{CS6M1S})_{\text{calc}} = 2.11 + 0.429 \ln(\text{SO}_2) + 1.667 \cdot 10^{-4} \text{NO}_x\text{RH}
\]

Fig.26: Plot of the linear regression of the covered surfaces of glass M1 after 6 months unsheltered exposure considering the SO$_2$ concentration in the ambient atmosphere only ($R^2 = 0.43$, $N = 21$).

\[
\ln(\text{CS6})_{\text{calc}} = 2.139 + 0.553 \ln(\text{SO}_2)
\]
9.3. Unsheltered Exposure of Glass M1 (12 Months)

The dose-response function found depends on the $\text{SO}_2$ concentration and the cross term mmxH (Fig.27). The depths of the leached layers increase by:

$$\ln(\text{LL.12M1U}) = -2.75562 + 0.43647 \ln(\text{SO}_2) + 1.58549 \times 10^{-01}\text{mmxH} + 4.63359 \times 10^{-02}\text{RH}$$

N = 18
R = 0.803
$R^2 = 0.644$

This equation is based on the data of 18 test sites due to missing of the pH of the precipitation at the test sites no. 37 and 39, missing of mm precipitation of test site no. 14 and missing of the environmental data of the test sites no. 27 and 28. The most outlaying result is the depth of the leached layer at test site no. 15. This could be caused by the extreme high NO$_2$ concentration in the ambient atmosphere at this test site. Including any terms containing NO$_2$ in the regression analysis results in negative coefficients for NO$_2$ and a regression analysis of the residues with the residual environmental parameters was not successful either. Compared with the dose-response function of the exposure for 6 months an additional influence of the relative humidity (Fig.28), which is even higher than the influence of the cross term mmxH, is remarkable. This may indicate that the weathering process of glass M1 is not slowed down or even stopped during periods without precipitation. The dominance of the $\text{SO}_2$ concentration instead of the content of $\text{SO}_4^{2-}$ ions in the precipitation might be a hint for this fact, too.
Discussion of the Results (Glass M1)

Fig. 27: Plot of the dose-response function for glass M1 exposed under unsheltered conditions for 12 months showing the influence of SO$_2$, RH and mmxH ($R^2 = 0.644$, $N = 18$).

Fig. 28: Plot of the multiple linear regression considering the SO$_2$ concentration and RH ($R^2 = 0.32$, $N = 21$).
9.4. Sheltered Exposure of Glass M1 (12 Months)

The dose-response function found depends on the SO$_2$ and the NO$_3$ concentration in combination with the relative humidity (Fig.29). The degree of the glass surface covered with weathering products (covered surface) increases by:

\[
\ln(\text{CS6M1S}) = 0.4575 + 0.23090 \ln(\text{SO}_2) + 3.94312 \times 10^{-4} \text{NO}_3 \times \text{RH} + 2.37361 \times 10^{-3} \text{RH}
\]

N = 20
R = 0.675
R$^2$ = 0.456

The equation is based on the data of 20 test sites only due to missing of the data for NO$_2$ of test site no. 37 and missing the environmental data of the test sites no. 27 and 28.

As already discussed in chap.9.2, the detaching of weathering products formed on the glass surface and the increase of the thickness of the weathering crust lead to relative high deviations from the regression line. Nevertheless, none of the test sites was excluded.

Similar to the glass samples exposed unsheltered for 12 months an increase of the influence of the relative humidity compared to the 6 months exposure can be observed. Especially the influence of the term NO$_3 \times$ RH has become most significant (Fig.31). It must be assumed that the weathering process is blocked by the high amount of weathering products covering the glass surfaces and the fact that the depths of the leached layers have increased to approximately 10 $\mu$m.
Discussion of the Results (Glass M1)

\[ \ln(CS12S)_{\text{calc}} = 0.458 + 0.0237 \text{RH} + 0.231 \ln(SO_2) + 3.943 \times 10^{-4} NO_2 \times \text{RH} \]

Fig. 29: Plot of the dose-response function for glass M1 exposed for one year under sheltered conditions considering the relative humidity, the SO\(_2\) and NO\(_2\) concentration in the ambient atmosphere (R\(^2\) = 0.456, N = 20).

\[ \ln(CS12S)_{\text{calc}} = 2.312 + 0.2044 \ln(SO_2) + 3.643 \times 10^{-4} NO_2 \times \text{RH} \]

Fig. 30: Plot of the multiple linear regression considering SO\(_2\) and NO\(_2\)\times\text{RH} (R^2 = 0.43, N = 20).
Fig. 31: Plot of the linear regression considering the term NO₂xRH only  
($R^2 = 0.40, N = 20$).
9.5. Unsheltered Exposure of Glass M3 (12 Months)

The function found and describing the increase of the depths of the leached layers depends on
the SO$_2$ concentration, the cross term NO$_2$xRH and the amount of precipitation (Fig.32). The
depths of the leached layers increase by:

$$\ln(\text{HD12M3U}) = 6.29753 - 0.21473 \ln(\text{SO}_2) - 6.68545 \times 10^{-4} \text{NO}_2\times\text{RH} + 1.98794 \text{ mm}$$

N = 19
R = 0.808
R$^2$ = 0.653

The equation is based on the data of 18 test sites only due to missing of the NO$_2$ concentration
of test site no. 37, missing of the precipitation (mm) of test site no. 14 and missing of the
environmental data of the test sites no. 27 and 28.

Fig.32: Plot of the multiple linear regression considering SO$_2$, NO$_2$XRH and mm (R$^2$ = 0.64, N = 20).
Discussion of the Results (Glass M3)

The dose-response function for the unsheltered glass samples (Fig.32) outlines clearly the dependence of the thickness of the leached layer formed on the glass surface on the SO$_2$ concentration in the ambient atmosphere but also on the NO$_2$ content, which is different to glass M1. Similar to glass M1 exposed for 6 months the relative humidity does not show any influence at all. In some cases the multiple linear regression of the weathering phenomena with RH yields to lower regression coefficients than the statistical evaluation of the results considering the SO$_2$ and NO$_2$ content only. The term mmxH yielded also a lower correlation coefficient than considering only the amount of precipitation. As can be seen in Fig.34, the SO$_2$ concentration has the dominant influence on the weathering process of glass M3 during the unsheltered exposure.

However, a negative coefficient must be observed for SO$_2$ as well as for NO$_2$ and cross terms of these acidifying gases. That can not be explained by the actual models of glass corrosion and will be discussed in chap. 10.

The SEM analyses of the specimens reveal that in general no weathering products can be observed on the surfaces of the glass samples after unsheltered exposure with the exception of air born particles. Most of the glass samples do not show any destruction such as cracks of the leached layer, either.

\[
\ln(\text{HD12M3U})_{\text{calc}} = 6.430 - 0.225 \ln(\text{SO}_2) - 4.536 \cdot 10^{-5} \cdot \text{NO2xRH}
\]

Fig.33: The multiple linear regression shows a negative dependence of the increase of the depth of the leached layer with SO$_2$ and NO$_2$xRH ($R^2 = 0.61$, $N = 20$).
Fig. 34: SO$_2$ has the main influence on the increase of the depth of the leached layer. However, the linear regression resulted in a negative coefficient, which cannot be explained by the actual models of glass weathering ($R^2 = 0.59$, $N = 21$).
9.6. Sheltered Exposure of Glass M3 (12 Months)

The only significant dependence of the increase of the depths of the leached layers formed on the glass surfaces during weathering under natural conditions is the cross term NO$_2$ x RH (Fig.35). The depths of the leached layers increase by:

\[
\ln(\text{HD12M3S}) = 5.3977 + 1.46051 \times 10^4 \text{NO}_2 \times \text{RH}
\]

\[
N = 20
\]
\[
R = 0.459
\]
\[
R^2 = 0.210
\]

This dose-response function is based on a data set of 20 test sites only due to missing of the NO$_2$ concentration of test site no. 37 and missing of the environmental data of the test sites no. 27 and 28.

Fig.35: Plot of the dose-response function for glass M3 exposed for 1 year under sheltered conditions considering the term NO$_2$ x RH ($R^2 = 0.21, N = 20$).
Discussion of the Results (Glass M3)

The scattering of the results can be explained by the contribution of the volume of the weathering products to the measured depths, since the analysis was performed without removing the weathering products from the sample surfaces. A correlation between the depths of the leached layers determined by NRA and the degree of surface covered with weathering products is shown in Fig.36.

![Graph showing correlation between HD12M3S and CS12M3S](image)

Fig.36: The plot leached layer versus covered surfaces shows a correlation at most of the test sites. Extreme outliers are only test site no. 6, 13, 15, 28 and 34.

Excluding the test sites no. 6, 13, 15, 28 and 34, where obviously no coincidence with the linear correlation in Fig.36 occurs, results in the equation:

\[
\ln(\text{HD24M3S}_{\text{con}}) = 5.16851 + 2.57987 \times 10^{-4} \text{NO}_2 \times \text{RH}
\]

N = 15
R = 0.715
R² = 0.511
Discussion of the Results (Glass M3)

\[ \ln(\text{HD12M3S}_{\text{corr2}})_{\text{calc}} = 5.169 + 2.580 \times 10^{-4} \cdot \text{NO}_2 \times \text{RH} \]

Fig. 37: Plot of the dose-response function of glass M3 exposed under sheltered conditions \( (R^2 = 0.51, N = 15) \).
9.7. Unsheltered Exposure of Glass M3 (24 Months)

The dose-response function found depends on the $SO_2$ concentration, the cross term $NO_2$ x RH and the amount of precipitation (Fig.38). The depths of the leached layers increase by:

\[
\ln(\text{HD24M3U}) = 6.12262 - 0.14797 \ln(\text{SO}_2) - 9.39594 \times 10^{-4} \text{NO}_2 \times \text{RH} + 3.33119 \times 10^{-4} \text{mm}
\]

\[
N = 18 \\
R = 0.841 \\
R^2 = 0.708
\]

The equation is based on a data set of 18 test sites due to missing of the $NO_2$ concentration of test site no. 37, missing of precipitation (mm) of the test sites no. 14 and 37 and missing of the environmental data of the test sites no. 27 and 28.

![Graph showing the dose-response function for glass M3](image)

**Fig.38**: Plot of the dose-response function for glass M3 exposed under unsheltered conditions considering the $SO_2$ concentration, mm precipitation and the cross term $NO_2$ x RH ($R^2 = 0.71, N = 18$).
Discussion of the Results (Glass M3)

Similar to the samples exposed for 12 months in the unsheltered mode negative coefficients for the acidifying gases SO$_3$ and NO$_x$ can be observed. The influence of the cross term NO$_3$RH is even higher for the thickness of the leached layer formed after 24 months exposure than for the glass specimens after 12 months (Fig.39, 40). Also the amount of precipitation highly contributes to the correlation. After excluding this parameter the $R^2$ decreases from 0.63 to 0.55 (Fig.39, 40).

![Graph](image)

\[ \ln(\text{HD24U})_{\text{calc}} = 6.129 - 0.216 \ln(\text{SO}_2) + 2.657 \times 10^{-4} \text{ mm} \]

Fig.39: The multiple linear regression yields to a negative coefficient for SO$_2$ but a positive one for the amount of precipitation ($R^2 = 0.63$, $N = 18$).
Fig. 40: Plot of the dose-response function for glass M3. SO₂ has the main influence on the weathering of glass M3 exposed unsheltered for 24 months ($R^2 = 0.55$, $N = 20$).
Discussion of the Results (Glass M3)

9.8. Sheltered Exposure of Glass M3 (24 Months)

The dose-response function found depends on the SO$_2$ concentration and the cross term NO$_2$xRH (Fig. 41). The depths of the leached layers increase by:

\[
\ln(\text{HD24M3S}) = 5.2429 + 1.1351 \times 10^{-4} \text{NO}_2\text{xRH} + 0.24069 \ln(\text{SO}_2)
\]

\[N = 20\]
\[R = 0.595\]
\[R^2 = 0.355\]

The equation is based on a data set of 20 test sites only due to missing of the NO$_2$ concentration of test site no. 37 and missing of the environmental data of the test sites no. 27 and 28. The highest statistical significance has the influence of SO$_2$ (Fig. 43).

![Graph showing the dose-response function for Glass M3 after 24 months sheltered exposure](image)

**Fig. 41:** Dose-response function of glass M3 after 24 months sheltered exposure ($R^2 = 0.35$, $N = 20$).

A plot of the covered surface versus the depths of the leached layers (Fig. 42) shows a correspondence between the growth of the leached layer and the weathering products formed. Only test site no. 24 is an extreme outlier with a covered surface of 36.5%.
Discussion of the Results (Glass M3)

Fig. 42: The amount of weathering products formed after 2 years of exposure is proportional to the depth of the leached layer.

Fig. 43: Dependence of the increase of the depths of the leached layers on the SO$_2$ concentration ($R^2 = 0.28$, N = 21).
Discussion of the Results (Time Dependence)

9.9. Time Dependence of Glass Weathering

It has to be mentioned and kept in mind for the whole chapter that calculations of the time dependence of glass weathering with only two data sets of two exposure periods will not deliver reliable results. In spite of this fact the calculations were performed to show possible trends, which will have to be proved by additional exposures.

The change in the amount of the weathering phenomena ($Y$) was calculated by statistical regression analysis including the factor time ($t$) in equations of the following kinds:

\[
\begin{align*}
Y &= A + B \cdot t \\
Y &= A \cdot t^B \\
Y &= A \cdot e^{B\cdot t} \\
Y &= A + B \cdot \ln(t) \\
Y &= A + B/t \\
Y &= 1/(A + B \cdot t) \\
Y &= t/(A + B \cdot t)
\end{align*}
\]

with $Y = CS(t)$, $LL(t)$, $HD(t)$

CS... Degree of glass surface covered with weathering products
LL... Thickness of the leached layer (determined by SEM)
HD... Thickness of the leached layer (determined by NRA)

Since the glass samples have been exposed only for two periods each of these functions resulted in a $R^2$ of 1. Therefore no decision which of these equations describes the time dependence of the change of the weathering phenomena best could be done. Including the principal state of the weathering process at $t = 0$ months with $CS(0) = 0.01 \%$, $LL(0) = 0.01 \mu$m or $HD(0) = 0.01$ nm resulted in more differentiated $R^2$. The values of 0.01 units instead of zero are necessary, because zero values would have resulted in unsolvable equations in most cases. Besides the values are negligible compared to the weathering phenomena after the end of the exposure periods. With this assumption in any case the exponential equation $Y(t) = A \cdot t^B$ ($t$ in months) resulted in the best fit with the highest $R^2$, similarly to the equations for the time dependence of metal corrosion [4].

After the calculation of the $A$ and $B$ values these factors were set in relation to the original environmental data for glass M1 and the one year data for glass M3 by multiple regression analysis. A comparison of the $R^2$ of glass M1 calculated with both, the original values and the one year data, pointed out that the differences in the statistical significances are negligible.
9.9.1. Unsheltered Glass M1

The A values of glass M1 are statistically dependent on the ln(SO₂) and the mmxH terms. With a sample number of 16 a R² of 0.44426 was gained by the equation:

\[
A = 0.0111563 + 6.05177 \cdot 10^{-4} \cdot \ln(SO₂) + 0.027791 \cdot mmxH \\
R^2 = 0.44, N = 16
\]

B is also depending on the ln(SO₂), but also on the relative humidity RH.

\[
B = 1.28514 + 0.16535 \cdot \ln(SO₂) + 0.0132219 \cdot RH \\
R^2 = 0.41, N = 21
\]

The equation of the time dependence of glass M1 exposed unsheltered using these equations for the A and B values finally resulted with LL(t) = A \cdot t^B in a R²= 0.37 (N = 36) unless if the one year or the original environmental data were used.

In a second method t was included in the data set for multiple regression analysis as an additional parameter instead of the A and B values, resulting in a better R² of 0.58 with a sample number of N= 35.

\[
LL(t) = -19.0811 + 0.54887 \cdot t + 0.15438 \cdot RH + 3.11064 \cdot \ln(SO₂) + 75.0261 \cdot mmxH
\]

In this equation t is the less significant term compared to ln(SO₂) and mmxH. It also must be mentioned again, that in this case only two periods could be considered resulting in an inestimable but probably high error.

9.9.2. Sheltered Glass M1

Factor A is not depending on any environmental parameter, factor B shows a dependence on ln(SO₂) and NO₂xRH.

\[
B = 3.00433 + 0.10351 \cdot \ln(SO₂) + 1.41713 \cdot 10^{-4} \cdot NO₂xRH \\
R^2=0.48, N = 20
\]

With the median A value A* = 0.015136 the equation of the time dependence CS(t) = A* \cdot t^B is resulting in a R² of only 0.10, wherefore in spite of the mentioned limitations by the lack of more exposure periods the two time values were included in the matrix as a separate parameter. But also in this case no significant dependence of the amount of surface covered (CS) on time could be recognised. The only significant parameter is NO₂xRH, with a R²= 0.41.
9.9.3. Unsheltered Glass M3

Factor A only depends significantly on ln(SO₂).

\[ A = 0.0137911 - 1.64357 \cdot 10^{-4} \cdot \ln(\text{SO}_2) \]

\[ R^2 = 0.48, \quad N = 18 \]

Factor B can be expressed by

\[ B = 3.64096 + 9.84186 \cdot 10^{-5} \cdot \text{mm} - 0.0584839 \cdot \ln(\text{SO}_2) - 2.68161 \cdot 10^{-5} \cdot \text{NO}_2 \times \text{RH} \]

\[ R^2 = 0.70, \quad N = 18 \]

By the equation \( HD = A \cdot t^B \) the time dependence of the weathering of glass M3 exposed unsheltered can be described with a \( R^2 = 0.11 \) (\( N = 37 \)).

9.9.4. Sheltered Glass M3

In contrast to the equations calculated for the two exposure periods negative coefficients of the SO₂ concentration and the RH were calculated for the regression equation for factor A, resulting in a theoretical decrease of the depth of the leached layer with time, which is not the fact in reality.

\[ A = 0.012903 + 7.3844 \cdot 10^{-5} \cdot T - 2.8307 \cdot 10^{-4} \cdot \ln(\text{SO}_2) \]

\[ R^2 = 0.49, \quad N = 20 \]

\[ B = 3.3415 + 2.26424 \cdot 10^{-3} \cdot \text{NO}_2 + 0.0678683 \cdot \ln(\text{SO}_2) \]

\[ R^2 = 0.34, \quad N = 20 \]

With \( HD(t) = A \cdot t^B \) the weathering progress is described with a \( R^2 = 0.23 \) (\( N=40 \)).
Conclusion

10. Conclusion

In Tab.6 the parameters, which are significantly influencing the weathering of the two model glasses, are listed together with the correlation coefficients ($R^2$) of the dose-response functions calculated with these parameters of a data set of $N$ test sites.

<table>
<thead>
<tr>
<th>Glass, Exposure Conditions</th>
<th>Parameters</th>
<th>$R^2$</th>
<th>$N$</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1 unsheltered 6 months</td>
<td>+ SO$_2$</td>
<td>+ mmxH</td>
<td>0.79</td>
</tr>
<tr>
<td></td>
<td>+ SO$_2$</td>
<td></td>
<td>0.43</td>
</tr>
<tr>
<td>M1 sheltered 6 months</td>
<td>+ SO$_2$</td>
<td>+ NO$_2$xRH</td>
<td>0.52</td>
</tr>
<tr>
<td></td>
<td>+ SO$_2$</td>
<td></td>
<td>0.43</td>
</tr>
<tr>
<td>M1 unsheltered 12 months</td>
<td>+ SO$_2$</td>
<td>+ RH</td>
<td>+ mmxH</td>
</tr>
<tr>
<td></td>
<td>+ SO$_2$</td>
<td></td>
<td>0.32</td>
</tr>
<tr>
<td>M1 sheltered 12 months</td>
<td>+ SO$_2$</td>
<td>+ NO$_2$xRH + RH</td>
<td>0.46</td>
</tr>
<tr>
<td></td>
<td>+ SO$_2$</td>
<td></td>
<td>0.43</td>
</tr>
<tr>
<td></td>
<td>+ SO$_2$</td>
<td></td>
<td>0.40</td>
</tr>
<tr>
<td>M3 unsheltered 12 months</td>
<td>- SO$_2$</td>
<td>- NO$_2$xRH + mm</td>
<td>0.64</td>
</tr>
<tr>
<td></td>
<td>- SO$_2$</td>
<td>- NO$_2$xRH</td>
<td>0.61</td>
</tr>
<tr>
<td></td>
<td>- SO$_2$</td>
<td></td>
<td>0.59</td>
</tr>
<tr>
<td>M3 sheltered 12 months</td>
<td></td>
<td>+ NO$_2$xRH</td>
<td>0.21</td>
</tr>
<tr>
<td>5 test sites excluded, see chap. 9.6.</td>
<td>+ NO$_2$xRH</td>
<td>0.51</td>
<td>15</td>
</tr>
<tr>
<td>M3 unsheltered 24 months</td>
<td>- SO$_2$</td>
<td>- NO$_2$xRH + mm</td>
<td>0.71</td>
</tr>
<tr>
<td></td>
<td>- SO$_2$</td>
<td></td>
<td>0.63</td>
</tr>
<tr>
<td></td>
<td>- SO$_2$</td>
<td></td>
<td>0.55</td>
</tr>
<tr>
<td>M3 sheltered 24 months</td>
<td>+ SO$_2$</td>
<td>+ NO$_2$xRH</td>
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</tr>
<tr>
<td></td>
<td>+ SO$_2$</td>
<td></td>
<td>0.28</td>
</tr>
</tbody>
</table>

Tab.6: Parameters influencing the weathering of glass M1 and M3. The correlation shows that with increasing SO$_2$ and NO$_2$ contents in the ambient atmosphere the weathering process is accelerated except for glass M3 unsheltered for 12 and 24 months, where a negative coefficient was observed.
10.1. Glass M1

Glass M1 shows a high sensibility towards the SO$_2$ concentration in the ambient atmosphere. Even in the unsheltered exposure mode its influence is higher than that of the concentration of SO$_4^{2-}$ ions in the precipitation.

After 6 months of sheltered exposure additionally an influence of the NO$_2$ concentration can be observed. In the first stages of weathering a moisture film with an adequate thickness seems to be present on the glass surfaces even under conditions with low relative humidity (RH) because the relative humidity does not show significant influences on the weathering process after 6 months of sheltered exposure. After 12 months of sheltered exposure an additional influence of the relative humidity can be determined.

Under unsheltered conditions the H$^+$ concentration per area (mmxH) has an important influence. The correlation coefficient obtained for the 6 months as well as for the 12 months exposure with and without the cross term mmxH have a remarkable difference. Additionally, the relative humidity influences the correlation for 12 months exposure. This fact can be caused by the higher demand of humidity for the weathering of the glass with a leached layer of several micrometers thickness.

10.2. Glass M3

The weathering of glass M3 is also predominantly caused by the concentration of the acidifying gases SO$_2$ and NO$_2$ in the atmosphere. Under sheltered conditions this is the only parameter responsible for the weathering process. NO$_2$xRH shows the main influence after one year exposure, whereas the increase of the depths of the leached layers after two years of sheltered exposure can be mainly correlated with the SO$_2$ concentration in the ambient atmosphere.

Under unsheltered conditions a significant dependence of the weathering process on the concentrations of the acidifying gases can be observed, too. However, the terms of SO$_2$ as well as for NO$_2$xRH are negative which means that less weathering occurs at higher contents of the pollutants. This fact can not be explained with the actual models of glass weathering. One possible explanation of this result determined can be leaching and consequently network dissolution of the leached layer. Under these circumstances a degraded surface should be observed in the SEM. However, the SEM images show a smooth and rather unweathered glass surface.

Another explanation of the negative influence of SO$_2$ and NO$_2$xRH could be the formation of a protective layer on the surface of glass M3, which has a high content of calcium. It is a known fact in the literature that CSH phases (xCaO$_y$SiO$_2$H$_2$O; 2<x<6, 1<y<6, 1<z<10.5 ) can be formed [32, 33] which influence the diffusion coefficients of Na as well as K. In many cases a reduced leaching rate of these ions could be detected.
Conclusion

Further weathering experiments and surface analytical investigations will be necessary to study and explain that weathering phenomenon.

10.3. Time Dependence of Glass Weathering

Generally, with only two data sets no reliable equations for the time dependence of glass weathering can be calculated. Including the initial state of the glass samples at \( t = 0 \) increases the probability of finding correct functions but a secure information about the long-term behaviour can only be gained by additional exposure periods.

In Tab.7 the environmental parameters forming the terms A and B of the equations \( Y(t) = A \cdot t^b \) are listed. \( Y \) represents the different weathering phenomena CS(t), LL(t) and HD(t). The correspondence of the calculated values with the analysed values are documented by the \( R^2 \).

<table>
<thead>
<tr>
<th>Glass, Exposure Conditions</th>
<th>Parameters</th>
<th>( R^2 )</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1 unsheltered</td>
<td>A + SO₂</td>
<td>+ mmxH</td>
<td>0.44</td>
</tr>
<tr>
<td></td>
<td>B + SO₂</td>
<td>+ RH</td>
<td>0.41</td>
</tr>
<tr>
<td></td>
<td><strong>Time dependence:</strong> LL(t) = A \cdot t^b</td>
<td><strong>0.37</strong></td>
<td><strong>36</strong></td>
</tr>
<tr>
<td>M1 sheltered</td>
<td>A no statistical significant environmental influence</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>B + SO₂</td>
<td>+ NO₂xRH</td>
<td>0.41</td>
</tr>
<tr>
<td></td>
<td><strong>Time dependence:</strong> CS(t) = A^* \cdot t^b</td>
<td><strong>0.10</strong></td>
<td><strong>40</strong></td>
</tr>
<tr>
<td></td>
<td>(A^*...median value)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M3 unsheltered</td>
<td>A - SO₂</td>
<td></td>
<td>0.48</td>
</tr>
<tr>
<td></td>
<td>B - SO₂</td>
<td>- NO₂xRH</td>
<td>0.70</td>
</tr>
<tr>
<td></td>
<td><strong>Time dependence:</strong> HD(t) = A \cdot t^b</td>
<td><strong>0.11</strong></td>
<td><strong>37</strong></td>
</tr>
<tr>
<td>M3 sheltered</td>
<td>A - SO₂</td>
<td>+ T</td>
<td>0.49</td>
</tr>
<tr>
<td></td>
<td>B + SO₂</td>
<td>+ NO₂</td>
<td>0.34</td>
</tr>
<tr>
<td></td>
<td><strong>Time dependence:</strong> HD(t) = A \cdot t^b</td>
<td><strong>0.23</strong></td>
<td><strong>40</strong></td>
</tr>
</tbody>
</table>

Tab.7: Parameters influencing the A and B values of the equations \( Y(t) = A \cdot t^b \) of the time dependence for the state of the weathering phenomena analysed.
Conclusion

The predominant influence of the \( \text{SO}_2 \) concentration became obvious also in the evaluation of the time dependence of the weathering of glass M1 similar to the dose-response equations for the single exposure periods. The velocity of the increase of the depths of the leached layers and the amount of the sample surfaces covered corresponds with the increasing values of the environmental parameters \( \ln(\text{SO}_2) \), mmxH, RH and \( \text{NO}_2 \times \text{RH} \).

An increase of the thickness of the leached layer with time can be predicted for glass M3, too. The different influence of the pollutant gas concentrations on glasses exposed unsheltered or sheltered can be read from the exponential term B. However, further weathering experiments and surface analytical investigations are necessary to study and explain the weathering phenomenon and get the time dependence of glass M1 and M3 more clearly.
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