

## GLASS-SENSORS: ASSESSMENT OF COMPLEX CORROSIVE STRESSES IN CONSERVATION RESEARCH

DIETER R. FUCHS, HANNELORE RÖMICH, AND HELMUT SCHMIDT  
Fraunhofer-Institut für Silicatforschung (ISC), Neunerplatz 2,  
D-8700 Würzburg, FRG

### ABSTRACT

Glass sensors, based on K-Ca-silicate glass chips, with a low durability against corrosive stresses, offer a new method for assessing the complex environmental stress situation of monuments and pieces of art. The easy-to-handle technique is able to detect the combined impact of climatic stresses, pollution and microbiological effects as well as synergetic interactions.

The chemical composition of the sensitive glasses enables judgements within few months. This way long-term estimates can be obtained without costly long-term investigations.

The corrosion progress is determined by microscopy and IR-spectroscopy of the weathered glass sensor surfaces. The sensors are already operating in the field of stained glass window preservation. They monitor the efficiency of different kinds of external protective glazings and the remaining stresses from the in-door environment of cathedrals.

### 1. INTRODUCTION

In conservation research the evaluation of the aggressivity/corrosivity of environments has a major key function from various points of view. Basic investigation of the interaction between the materials and the environmental stress at the very spot of a site or building structure can render detailed understanding of deterioration phenomena and corrosion mechanisms. The correlation between specific stress situations and resulting decay processes also may be essential for the design of adequate protective measures as well as for the tailoring of time-lapse laboratory tests for conservation materials and techniques. The assessment of the combined corrosive efficacy induced by climatic influences, pollution-related parameters as well as synergetic effects is of high interest for judgements concerning the protective features of already applied conservation concepts.

In the field of stained glass window conservation the state-of-the-art is characterized by transferring analytical standard methods from the fields of climatology and environmental engineering into conservation research. Measurements of temperature, temperature gradients, air humidity, condensation effects, pollutant concentrations in air, precipitation, and run-off water, microbiological records - the spectra of relevant environmental parameters as well as the efforts of analyzing them can be extended at pleasure.

But up to now the knowledge about the exact conclusions between these influences and the resulting impact on the material, as well as the synergetic effects among them is still fragmentary. The parameters are changing locally and with time permanently. Scientific investigations including model calculations and simulation tests would have to set up a detailed framework first, to justify extensive - and expensive - climate and pollution control at the sites. But even when such theoretical background can be realized, the technical efforts still will be restricted to special applications and not be practicable for routine conservation, e. g. at the numberless stained glass windows.

To cope with these restrictions, alternative concepts are asked for. Studies using the original materials of the pieces of art are restricted by the heterogeneity of the assets, complexity of altered surface layers and, in most cases, being in the dark concerning the exact history of the ancient pieces. Attempts with simulation materials instead are of greater promise. Fastly corroding glass types can deliver results within shorter observation times and better comparability of different objects and situations may be obtained.

Highly sensitive model glasses are therefore discussed [1] to be used as an "integrating" measure for the combined impact of environmental stresses. To investigate the principle possibilities and basic correlations between such glass compositions and special climate and pollution situations, a small sequence of K-Ca-silicate glasses was chosen, for which already experience about the corrosion kinetics [2, 3] was given. Studying the behavior of these glasses in more detail, improving the way of preparation and using appropriate analytical methods, the aim is an easy-to-handle "glass sensor", summarizing quantifiable information of local stress by its own corrosion reaction.

## 2. EXPERIMENTAL

In order to clarify the surface effects of the sensor glasses corresponding to different chemical compositions, preparational features and environmental stress situations, various out-door as well as laboratory weathering tests were carried out. Different analytical methods were compared to decide on the most suitable ones with respect to sensitivity, reproducibility, and practicability.

### 2.1. Sensor Glasses

The glasses were molten from analysis-pure oxides and carbonates using platinum crucibles in an electric kiln at 1450 °C for about two hours. Afterwards the glass melt was poured into blocks, tempered for 30 minutes at a temperature of 30 K above  $T_g$ , and cooled to room temperature over a period of 16 hours. All batches yielded in clear glasses (Table I).

Table I. Composition of the sensor glasses (wt.%)

	SiO <sub>2</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	MgO	CaO	Al <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>
MI	48.0	3.0	25.5	3.0	15.0	1.5	4.0
M1	54.2	-	28.8	-	17.0	-	-
M1.5	55.7	-	25.8	-	18.5	-	-
M2	57.1	-	22.5	-	20.4	-	-
M2.5	58.6	-	18.9	-	22.5	-	-
MIII	60.0	-	15.0	-	25.0	-	-

The glass blocks were cut into pieces (0.7 mm thick) with a low speed saw using a diamond blade with an oil-bath cooling. These chips were polished by a fire treatment in a gas furnace (Speedburn II F) with a high heating rate. The temperature was maintained at 700 - 800 °C for 5 - 8 minutes depending on the chemical composition of the glasses. Before and after the polishing process the samples were cleaned with petroleumether (50/70) and ethanol.

## 2.2. Sensor Preparation

For handling and application the sensitive model glass is integrated in a frame system as shown in Figure 1. The plastic slide frame improves the handling and mailing before and after application and stabilizes the aluminum mask which encloses the sensor system. In order to study glass corrosion effects only on one side of the model glass, the other side is protected against humidity by attaching it to a micro cover glass with a silicon glue along the edges. This chip is sealed in aluminium foil, pretreated with a special ORMOCER hot melt adhesive. The window system in the center of the sensor is necessary for characterization and spectroscopy in transmission. The sensors are stocked in a dry atmosphere to avoid corrosion before exposition.

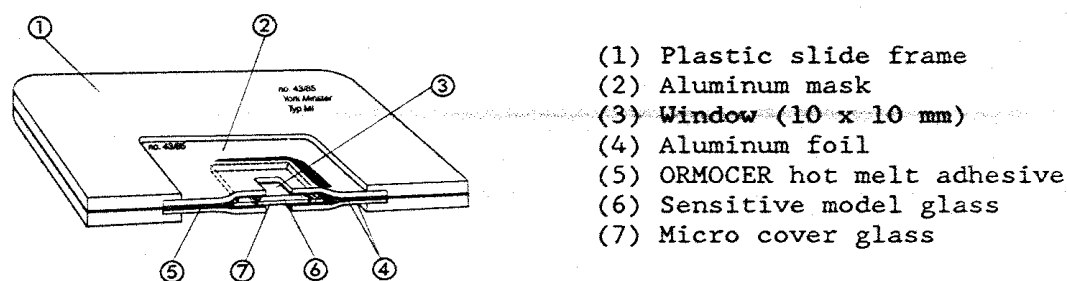


Figure 1. Construction details of a sensor.

## 2.3. Climatic Cabinet Tests

The laboratory experiments were carried out in a climatic test cabinet (Heraeus Vötsch, type VSK04/300VIS) equipped with a precision gas feeder system. The  $\text{SO}_2$  pollution level in the test chamber was set at 5 ppm, which corresponds to about 100 times the concentration in a badly polluted industrial area. Temperature and humidity were varied in cycles as shown in Figure 2.

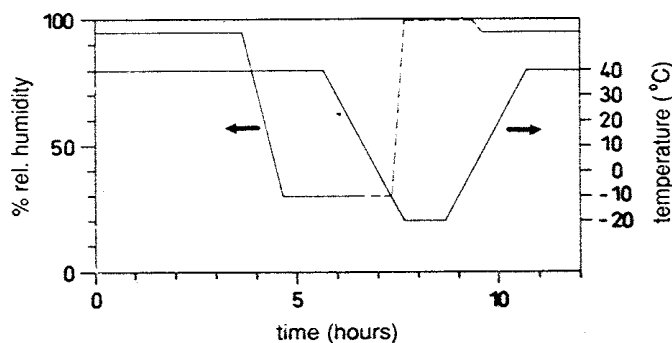


Figure 2. Temperature and relative humidity cycle of the weathering test.

#### 2.4. Combined Environmental Tests

The influence of some major pollutants on the corrosion of model glasses was studied in special gas chambers, developed by the Fraunhofer-Institut für Chemische Technologie (ICT) in Pfinztal/Germany. Starting from purified air a precision gas feed and flow system guarantees constant gas concentrations. The percentage of the noxious gases was highly increased compared to environmental conditions. In order to study the influence of SO<sub>2</sub> and its synergetic effect with other oxidizing agents the gas compositions were chosen as listed in Table II.

Table II. Gas composition in the test chambers (concentration in mg/m<sup>3</sup>).

1	2	3	4
Purified air*	Purified air* + 5 SO <sub>2</sub>	Purified air* + 5 SO <sub>2</sub> + 5 NO <sub>2</sub>	Purified air* + 5 SO <sub>2</sub> + 5 NO <sub>2</sub> + 2.5 O <sub>3</sub>

\* contains 0,03 Vol. % CO<sub>2</sub>

These four test chambers with defined pollution levels were installed out-door. The temperature as well as the relative humidity inside were regulated and corresponded to the local outside values. Half of the chamber was exposed to day light and the other half was sheltered against it.

#### 2.5. Out-Door Weathering Tests

For out-door weathering five sites in Bavaria with characteristic climatic and pollution situations were chosen as shown in Table III. The stations represent a great variety concerning their pollution level, temperature, and precipitation values. All weathering data were recorded constantly (Bayerisches Landesamt für Umweltschutz, München, and Fraunhofer-Institut für Atmosphärische Umweltforschung, Garmisch).

Table III. Out-door weathering sites

site	description	special weather conditions	air pollution	SO <sub>2</sub> (mg/m <sup>3</sup> ) monthly means	
				summer	winter
Zugspitze	mountain peak 2 900 m NN	severe alpine	very low	< 0.01	< 0.01
Wank	mountain peak 1 800 m NN	moderate alpine	very low	< 0.01	< 0.01
Alten- schneeberg	hilltop 800 m NN	in misty hill region	low	< 0.02	< 0.08
Würzburg	city area, near highway	mild	intermediate	< 0.03	< 0.10
Arzberg	residential area near lignite power plant	temperate	very high	< 0.03	> 0.10 (up to 0.30)

The sensors were exposed in special weathering devices (for construction details see Figure 3). If the front of the sensor is facing the out-door environment, the model glass surface can be affected by rain and the corrosion products may be washed off ("wet-position" weathering).

The sensor can also be placed vice versa so that the model glass faces the sample holder. These "dry-position" samples are corroding under different weathering conditions. They are sheltered against rain, but still get stressed by condensation effects and air humidity.

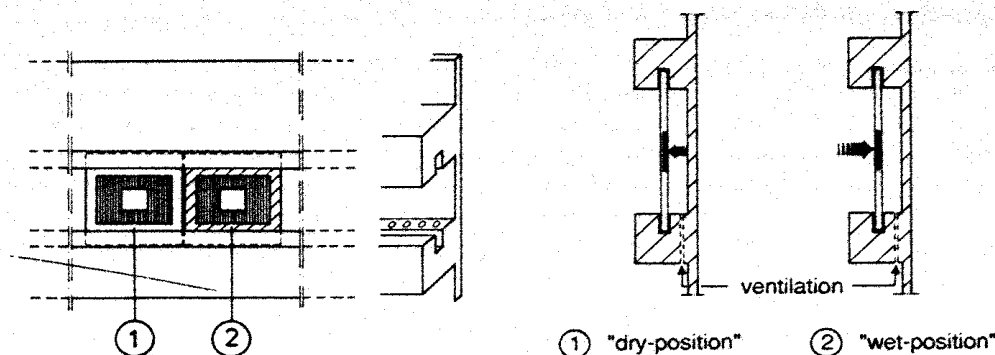


Figure 3. Sketch of a sample-holder for out-door weathering.

## 2.6. Pilot Studies at Monuments

Pilot studies at external protective glazings were carried out in York, Gouda and Nürnberg using the arrangement as shown in Figure 4.

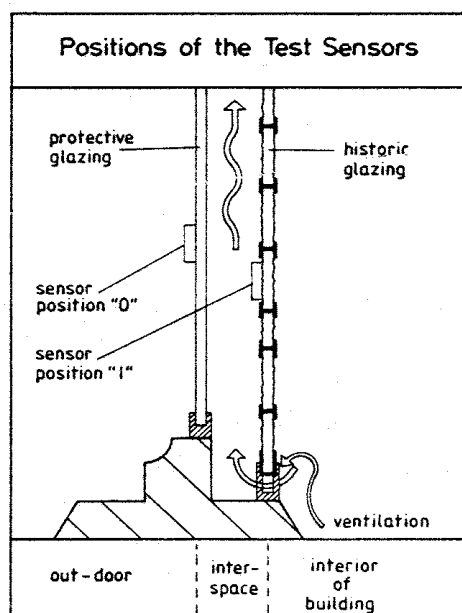


Figure 4: Sensor positions.

Sensors were placed on the outer surfaces of the original glass window and the double glazing. For each position a set consisting of two types of sensors (MI and MIII glasses) were used. After removing the slide frame, the sensors were attached in their weathering position assuring durable fixation and good temperature exchange between the sensor and the glazing surface. The samples were investigated by IR-analysis and microscopy in the laboratory after a weathering time of twelve months at the site.

## 3. ANALYTICAL METHODS

**Infrared Analysis:** All IR-analysis were carried out using a Perkin Elmer 253 spectrophotometer. For the characterisation of the corrosion process of model glasses the most important part of the IR absorption spectra ranges between  $4000$  and  $2000 \text{ cm}^{-1}$ . The difference in the intensity ( $\Delta E$ ) of the OH-absorption bands at  $3300 \text{ cm}^{-1}$  of a sample before and after exposition indicates the degree of corrosion of the glass.

**Scanning Electron Microscopy/Energy Dispersive X-Ray Analysis:** Micrographs of corroded model glass surfaces were taken on a Scanning Electron Microscope (SEM) Cambridge S600. The glass samples were pretreated by gold sputtering. Leaching effects were determined by element mapping of a cross section using Energy Dispersive X-ray analysis (EDX) on a Kevex System 7000.

**X-Ray Photoelectron Spectroscopy:** X-ray photoelectron spectroscopy (XPS) was applied to determine concentration depth profiles of relevant elements (e.g. K, Ca, Si) in the model glass samples. The measurements were carried out on a LHS 10 Leybold spectrometer with Mg-K $\alpha$  radiation under vacuum. An argon ion beam with a discharge potential of 4.5 kV was used for etching very thin layers from the sample. The analysis was carried out alternately with this sputtering. The etching time was calibrated with float glass samples (25 nm/1000 s).

**Analysis of Secondary Corrosion Products:** Corrosion products on selected sensors were analysed qualitatively and quantitatively. After scratching away the crust from the glass surfaces its mineralogical composition was determined by X-ray powder diffraction on a vertical goniometer (Philips PW 1050, Cu-K $\alpha$ ). For other samples the amount of corrosion products was determined by weight loss after rinsing with water.

#### 4. RESULTS AND DISCUSSION

The results reported here can be divided into two sections: basic characterization of the weathering behavior of different sensor glasses, and first pilot studies using glass sensors of type MI and MIII glasses for evaluation of the stress situations at three specific stained glass windows equipped with different types of external protective glazings.

##### 4.1. Basic Investigations

For the discussion about the comparability of glass sensor results with the situation of historic stained glasses, one has to consider that even among the original pieces of stained glass the spectra of chemical compositions, surface conditions, and corrosion phenomena are very wide.

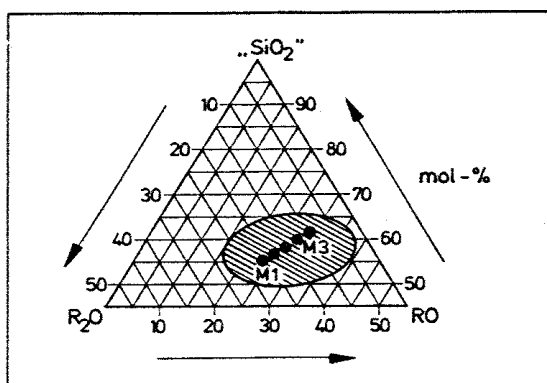
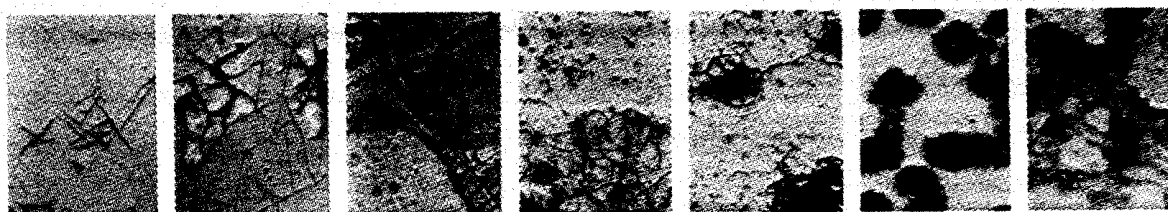


Figure 5. Chemical composition of the sensor glasses.  
Hatched area: variation of medieval glasses [4]

Investigations and experiences from one historic sample cannot directly be transferred to another one. The same is valid for the model glasses (Figure 5). The major demands for glass sensors are: comparable (qualitatively similar) corrosion mechanisms and sensitivity for the same environmental stresses, but with quantitatively "accelerated" corrosion progress (Figure 6).



..... microcracking ..... secondary surface ..... pitting .....

Figure 6. Micrographs of MI glass: development of surface deterioration within a total out-door weathering period of one year (site Arzberg). Width of each micrograph: 300  $\mu\text{m}$ ; type of weathering situation: "wet position", see 2.5.

The phenomenological states, documented by Figure 6, are totally comparable with the corrosion features known from medieval original glasses, but the progress for the sensor glass reaches deterioration levels within months which for historic glasses are known to be reached after centuries. The first steps, visible in the microscopic surveys, are governed by microcracking of the glass surface. Details are given by SEM/EDX results (Figure 7).

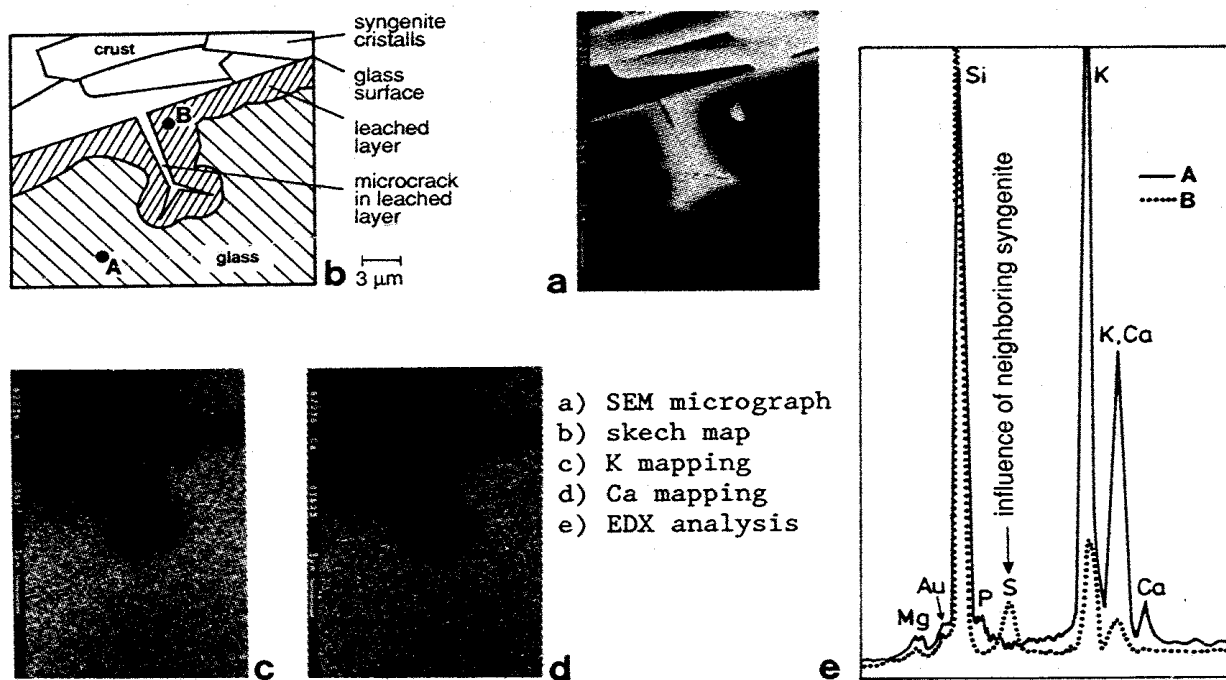


Figure 7. Cross section of corroded sensor glass surface

The element mapping and EDX analysis results make evident that for the sensor glass the same ion exchange reaction is relevant which is well-known for glass-water-interaction [5]. Especially for K-Ca-silicate glasses this reaction is favored to a very high degree. K and Ca are replaced by  $\text{H}_3\text{O}^+$  and additional water molecules in the glass network, reacting in a "secondary" step with  $\text{SO}_2$  and moisture to build up a corrosion crust of syngenite and/or gypsum (depending on the K/Ca ratio of the glass and on the climatic conditions).

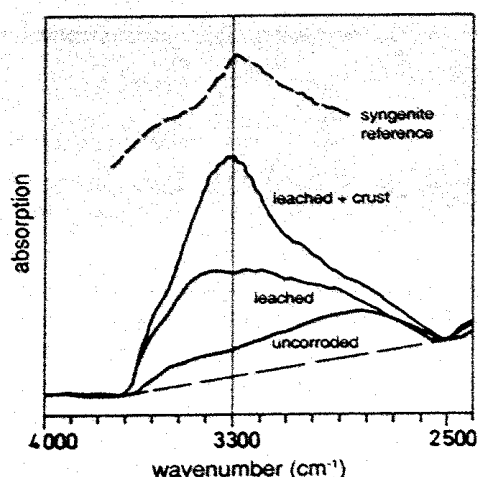


Figure 8. IR analysis of corroded glass samples.

This IR method was checked by gravimetric determination of the mass of corrosion products (Figure 9) and by cross section SEM control for selected samples.

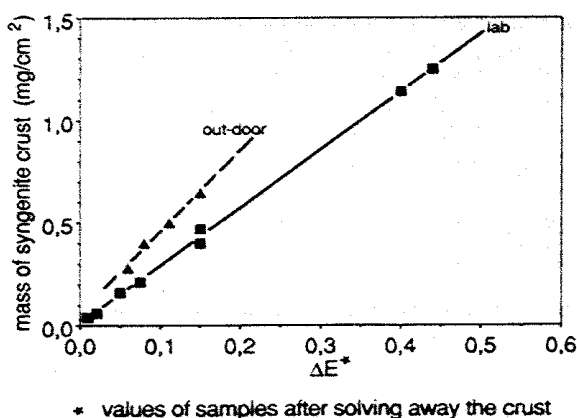


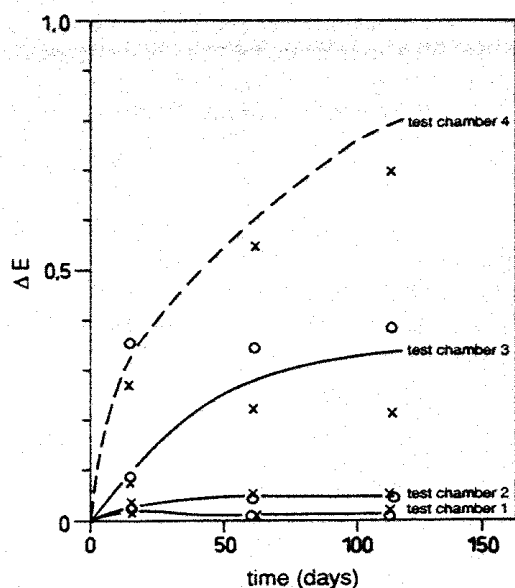
Figure 9. Correlation of IR and gravimetric results for MI sensor glass

For the interpretation of sensor glass results under natural out-door stress situations it is important to get information about their behavior when exposed to defined simulated stress parameters. For MI and MIII glasses various data from out-door tests [3] as well as from climatic cabinet tests [6, 7] were already published. It could be shown that MI is highly sensitive to  $\text{SO}_2$ , whereas MIII reacts rather slowly even under severely polluted environments. In out-door weathering tests MIII never reached the "secondary surface" or "pitting" corrosion levels displayed in Figure 6. The fast deterioration reported on for MI glass causes problems in the interpretation of the IR data of samples weathered in high polluted atmospheres (too low, when already gel layers have peeled off). In these cases the "slow" MIII glass is favored. It can still be applied, when MI already has exceeded the range of reliable IR measurements. Some MIII data for the combined environmental tests (see 2.4.) are given in Figure 10.

For the evaluation of the major corrosion effects therefore two layers should be taken into account: the leached "gel" layer of the glass and the crystalline crust of corrosion products (K-Ca-sulfate-hydrates). For the combined characterization of these layers (both containing OH groups), the IR analysis proved to be suitable [3]. The difference of absorption at  $3300 \text{ cm}^{-1}$  ( $\Delta E$ ) allows to assess the corrosive progress without large efforts and with high accuracy (Figure 8).

The differences between the out-door and climatic cabinet (lab) tests can be explained by incorporation of dust, soot, and other deposits into the surface crusts in out-door environments which are not present under "clean" laboratory conditions.





The interpretation of the IR data show that  $\text{SO}_2$  alone, even together with humidity and in highly increased concentrations, does not increase the corrosion rate of MIII glass. When oxidizing gases like  $\text{NO}_2$  and  $\text{O}_3$  are added, the leaching increases tremendously. This accelerating effect is intensified by sun light (chamber 4) leading to material losses by peeling after about two months.

Figure 10. IR data for MIII glass, test chambers like Table II  
o with natural day light  
x sheltered against radiation

New perspectives and applications might be possible, if by tailoring of the chemical composition not only accelerated weathering but also selective interaction with specific stress parameters could be achieved. To prove the IR data, for MIII therefore as an additional analytical method XPS (element concentration depth profiles) was used. The Ca leaching depths are given in Figures 11 and 12.

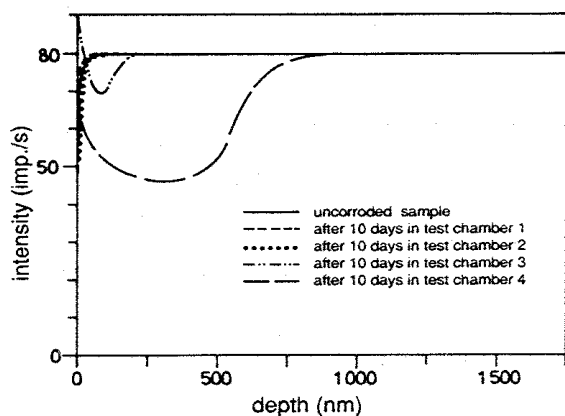


Figure 11. Ca depth profile for MIII after 10 days weathering in different atmospheres

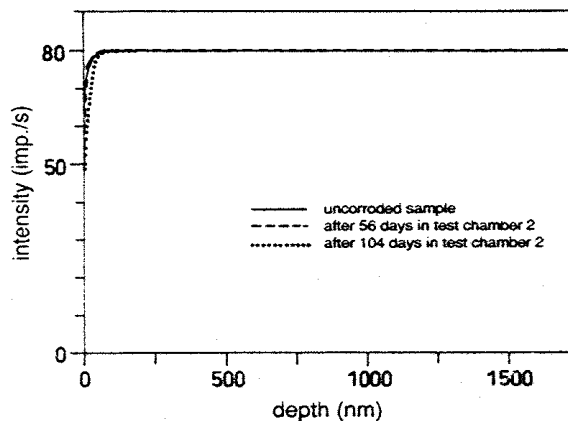


Figure 12. Ca depth profile for MIII after long term weathering in test chamber 2

The XPS results are in accordance with the IR data. Primary the  $\text{NO}_2$  and  $\text{O}_3$  contents of the test atmosphere are controlling the weathering rate of MIII. Increased  $\text{SO}_2$  alone, even with high air humidity, does not affect the leaching depth considerably.

Under "natural" conditions such inert behavior of MIII is not given, as oxidizing gases are always present. In out-door experiments MIII therefore does not reveal its principle differences compared to what is reported [8] about MI, but fits into the sequence of the investigated glasses (Figure 13).

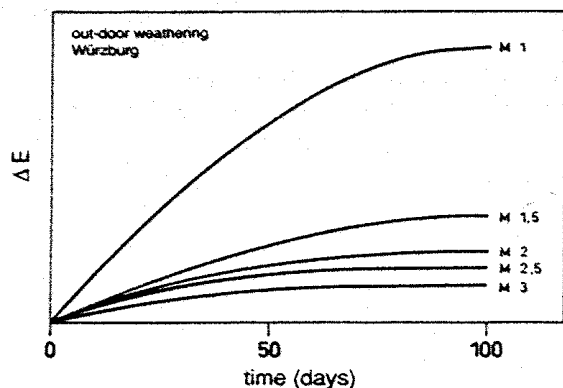


Figure 13. Influence of glass composition on the corrosion progress.

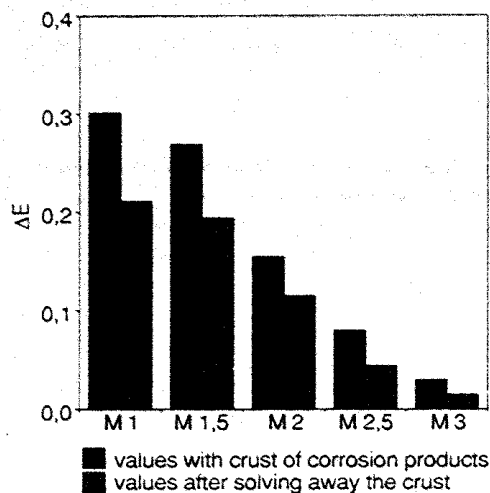


Figure 14. IR data for different sensor glasses after 3 hrs climatic cabinet test.

The relation between "dry-position" and "wet position" weathering (see 2.5.) is important for the comparison of sensor results from out-door and sheltered (e. g. behind protective glazings) situations. The main difference is the loss of the secondary corrosion crust, if rain can dissolve and wash off the crystallites. In "dry" positions the syngenite/gypsum crust normally is preserved and adds its part to the IR absorption. This contribution by the crust may be assessed by comparing the  $\Delta E$  values before and after solving away the corrosion products. For laboratory conditions an example is given in Figure 14. Results from out-door tests point out that about one third of the total  $\Delta E$  is given by the corrosion layer, two third by the leached layer.

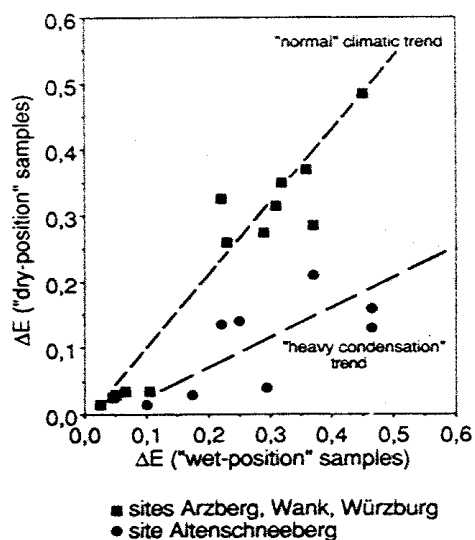


Figure 15. Correlation between "wet" and "dry" weathering positions.

Additionally to this analytical fact, correlation between "wet" and "dry" results are complicated by the changes in the corrosive stresses. If MI sensors are exposed in both positions at different sites and for different periods, no fixed correlation can be stated (Figure 15).

Normally, both  $\Delta E$  values are within the same range. The contribution of the crust for the "dry" position is approximately as high as the contribution by increased leaching for the "wet" position, induced by higher stress level without sheltering. At sites with extremely heavy condensation and rain, the "wet" corrosion progress exceeds the crust's contribution at the "dry" position.

The analytical results of more than 2000 laboratory and out-door experiments, for which only few examples are presented here, show that in principle a set of two sensor glasses (one "fast" corroding, one "slow", and long term reliable) may be used as indicators and integrating controls for complex corrosive stresses.

#### 4.2. Pilot Studies at Stained Glass Windows

At three historic windows with different types of external protective glazings glass sensor studies were carried out as explained in 2.6. The  $\Delta E$  results are given in Figure 16.

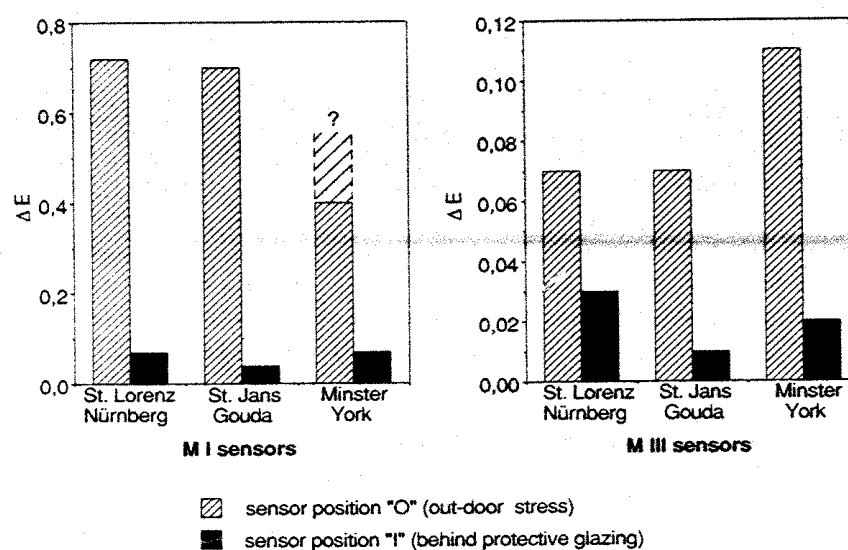


Figure 16. Pilot study results for MI and MIII sensors (sensor positions see Figure 4).

The  $\Delta E$  values for St. Lorenz and St. Jans show that the out-door stress at both sites was similar. The protective efficiency of the St. Jans external glazing is higher which is indicated by MI as well as MIII. At York, the MI sensor at the out-door position already showed material losses (peeling) which was evident in the microscopic check easily. Therefore, the MI result at position "I" cannot directly be compared with the data of the other sites. This gap of information is clarified by the MIII sensors. The out-door stress level is found to be higher for York Minster than at the other sites. The "protected" situation may therefore be assessed as better shielded than at the Nürnberg window. Fitting all this information together, the St. Lorenz glazing system was least efficient among the objects under test, the St. Jans conservation performance was best. This is conform with assessments based on microclimatological surveys [9] which helped to optimize the St. Jans glazing system.

To compare constructive conservation techniques with other attempts to seal the endangered historic glass windows, e. g. protective coatings based on ORMOCERes [3, 7], additional sensors were placed at the same positions as reported above. Their sensitive glass surfaces were coated with the lacquers and at the end of the one-year test period the sensors were analyzed after solving away the coating (using toluene). For St. Lorenz the microscopic and IR results are given in Figure 17.

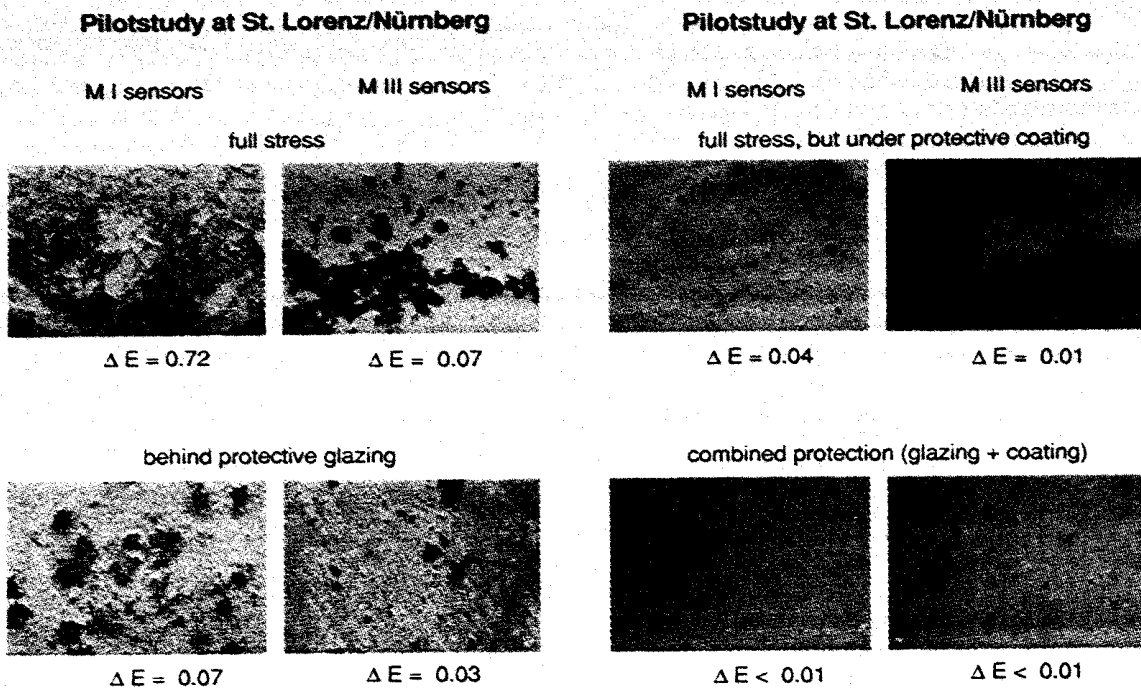


Figure 17. Comparison of glass sensor results from St. Lorenz, including sensors coated with ORMOCER (width of micrographs: 500  $\mu\text{m}$ ).

The micrographs as well as the  $\Delta E$  values prove that within the test period of one year the better conservation effect was reached by using the coating compared to the glazing. Combined protection offered the highest performance. It is also evident that deposition of dust and soot in the interspace behind the protective glazing, introduced by the ventilation system of the double glazing, may give an important contribution to the corrosion progress.

It should be stated here that these first pilot studies were heading for testing the principle suitability of the sensor method in practice. The results should not be taken as totally concluded judgements for the three specific windows, as for this purpose more comparative data and statistical information are required.

## 5. CONCLUSION AND PERSPECTIVES

The basic investigations concerning the correlation between different environmental stress situations and different types of glass sensors up to now were confined to very few parameters. Broader spectra of glass compositions and more diversified stress combinations are required, if improved understanding of the interaction and tailored design of glass compositions for specific applications shall be obtained.

But even the fragmentary results reached now already allow suitable new techniques for assessing the stress situation and conservation efficiency for historic stained glass windows and external protective glazings. The glass sensor method, based on MI and MIII glass, has been adapted in conservation practice. At more than 30 prominent cathedrals and churches in six European countries glass sensors at the moment are applied for monitoring out-door and in-door stress levels as well as the protective effect of various conservation measures.

The principle results of the basic research have pointed out that chemical glass design, suitable preparation features, and appropriate analytical methods offer a highly sensitive, easy to handle and integrating technique which may not be restricted to stained glass only. In the fields of monument conservation and environmental research and engineering, integrating methods for assessing complex stress situations are demanded in many respects. As the glass sensors are sensitive against air humidity, rain, pollution, and various minor influences - spectra of importance for many materials and assets - new applications may be discussed in future.

## 6. ACKNOWLEDGEMENT

The project was partially funded by the Bundesministerium für Umwelt, Naturschutz und Reaktorsicherheit, Bonn, and by the Umweltbundesamt, Berlin. The authors also wish to thank F. Jörg (ICT), Th. Freund, C. Cronauer, and M. Buck for the valuable assistance in these studies, and W. Röhm for preparing the figures.

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