MODEL GLASS TEST SENSORS - A NEW CONCEPT TO INVESTIGATE AND CARACTERIZE EXTERNAL PROTECTIVE GLAZINGS

FUCHS D. R., PATZELT H., TUNKER G. and SCHMIDT H.
Fraunhofer-Institut für Silicatforschung (ISC), Würzburg, F.R.G.

I - Introduction

Deterioration and corrosion of our historic stained-glass windows have obviously increased within the past few decades. Therefore, measures for their protection had to be found and taken even when the reliability and long term effectiveness in some cases could not be checked out completely and systematically before applying them to the endangered works of art.

The todays usual method for protecting historic glass windows is the construction of external protective glazings. Direct climatic strains, e. g. rain water, are screened away from the original glasses and a reduction of the corrosion progress can be observed, compared with non-protected windows.

Nevertheless, the scientific knowledge of the principles of glass corrosion mechanisms confirms that such measures cannot provide a complete protection on the long run. The protective properties of the various different types of construction of double glazings must be investigated in more detail for optimisation. For reason of time, therefore new and more sensitive analytical methods are required which enable us to recognize and compare quantitatively the progress of deterioration and the efficiency of double glazings.

II - Glass corrosion and its characterization

The basic process of glass corrosion /1/ can be described by the mechanisms initiated by the attack of H_2O (Fig. 1). There is no necessity for liquid water, the water vapour of natural air humidity , too, starts and promotes the deterioration as described. It also can be approved that gaseous air pollutants, e. g. SO_2, can intensify the primary steps of ion exchange, and not only the secondary effects of building-up corrosion crusts /2/.

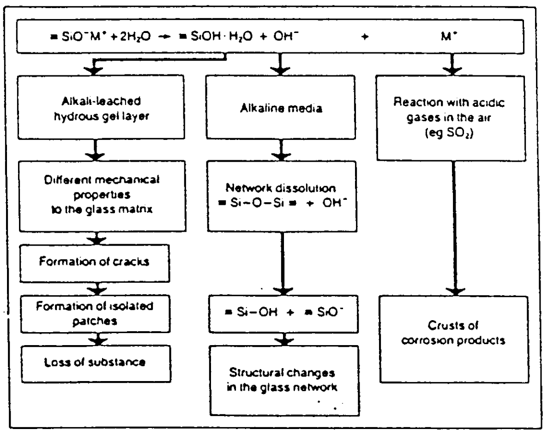

Fig. 1

Corrosion Principles of Ca-K-Silicate Glasses

It is known that the sensitivity to corrosion of historic glasses is highly affected by the chemical composition, especially by SiO_2, K_2O, and CaO content /3, 4/.

Even for small differences, e. g. between the MI and MIII model glass which are both within the typical range of medieval glasses (Fig. 2), distinct variations concerning their weathering behaviour can be observed /2/. MI-type glasses react very sensitively and show severe cracking and pitting within weeks when exposed to out-door conditions in moderately to highly polluted areas. MIII-type glasses show very slow corrosion progress and the ΔE values of out-door experiments could be correlated to the SO_2-pollution-situation of the locations even after longer periods, when the MI results already were non-representative due to material losses by cracking and pitting.

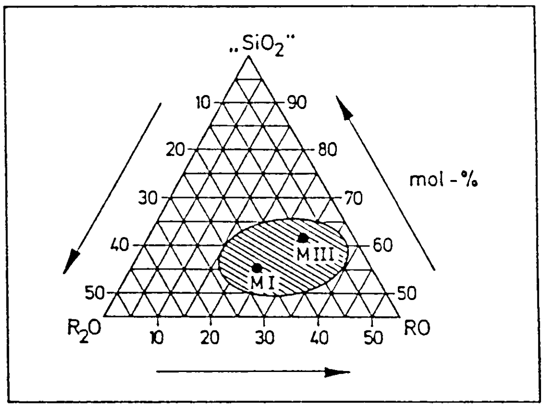

Fig. 2

Chemical composition of model glasses MI and MIII (hatched area : variation of medieval glasses /6/)

For characterizing the very first steps of corrosion, the nature of the leached, hydrous gel layer gives us the possibility to use an IR-spectroscopical method /5/. The increase of extinction (ΔE) at 3350 cm^{-1} (OH-bond) can represent the amount of ion exchange and therefore be used to quantify the earliest, still not yet visible effects (Fig. 3). Compared to usual criterions of judgement (Fig. 4) the detection limits are much lower and therefore informations can be obtained within much shorter observation times.

For model glasses, e. g type MI (Fig. 5), changes of the thickness of the gel layer in the range of 0.2 up to about 4.0 µm could be analysed /2/ with an estimated accuracy of ± 0.1 µm.

According to these experiences quantification of corrosion is possible long before any alterations can be observed microscopically.

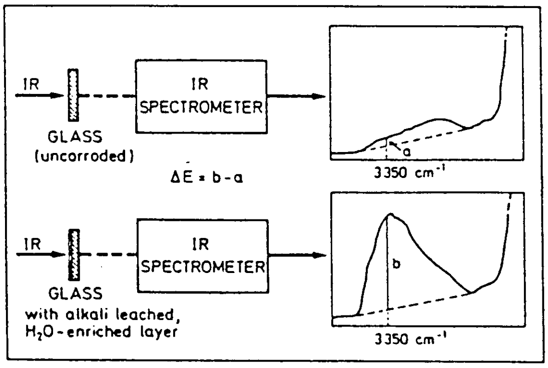

Fig. 3

IR-Method for characterizing the leaching process
(ΔE = 0.1 equivalent about 1 μm)

weathering periods	effects	analytical methods
after centuries	▪ crusting ▪ cracking ▪ pitting ▪ loss of glass and paint material	visible
within decades	▪ milkiness by layers of corrosion products and cracking of the surface	magnifier microscope
within years	▪ growth of micro-cristallites ▪ microcracking of the leached surface layer	
within weeks and months	▪ leaching of the glass surface, building up a hydrous gel layer	IR-analysis of model glass sensors

Fig. 4

Ranges of observation methods

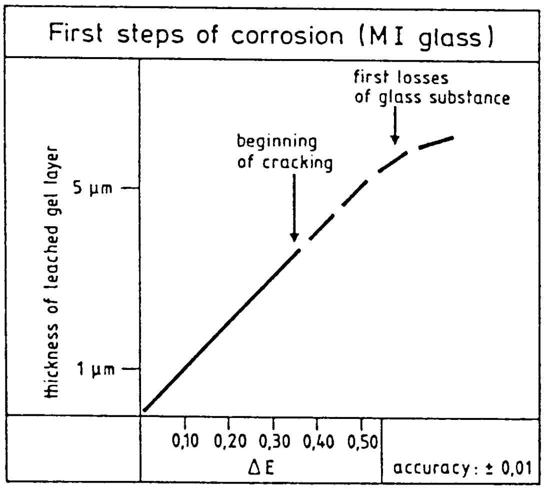

Fig. 5

Correlation of IR-Data and leaching depth

Unfortunately, this method cannot be applied to historic original glasses due to different factors :

- for IR measurements parts of the panel are to be removed and releaded twice which means high work costs
- low transparency of stained glass
- scattering effects due to natural surface roughness of weathered historic glasses
- no possibility to compare the individual results because of the differences of the glasses concerning chemical composition, physical history and surface conditions.

Due to these restrictions a different concept had to be developed which was possible by using different model glasses and special preparation features.

Based on the knowledge of the weathering behaviour of model glasses and the IR characterization of gel layers a method can be proposed to monitor the effect of external protective glazing on the protection of stained glasses in a practical and easy way.

III - Model glass test sensors

If small model glass samples, prepared according to the best application of the IR method, easy handling and high reproducitability /2/, are characterized by IR spectroscopy and then exposed at the surface of historic glass windows to the local weathering conditions, they can act as reliable indicators of the corrosive stress at the specific chosen place. The ΔE value, measured after a well defined (and compared to up to now usual observation times very short) period, e. g. six months, directly characterizes the in-situ-situation concerning glass corrosion.

By using not only one single glass type, but a representative spectra of chemical variations, this can lead to a sensor system by which informations for a wide range of applications can be obtained :

- arranged behind (e. g. on top of the original glass) and in front of a double glazing (Fig. 6) the protective efficiency of the specific protective measure can be judged directly by comparing the ΔE results after a chosen time of exposure
- spread over the full area of a historic glass window with double glazing protection, a set of such sensors can supply informations about differing conditions at different spots of the structure
- comparison of the results achieved with these sensors at different construction types of glazings can help to choose those with the best protective properties
- installation at different spots at one specific historic building may allow to discriminate different small-scale situations, e. g. microclimatic conditions due to architectonical reasons or influence of rain water attack, and may help on deciding the proper protective measures.

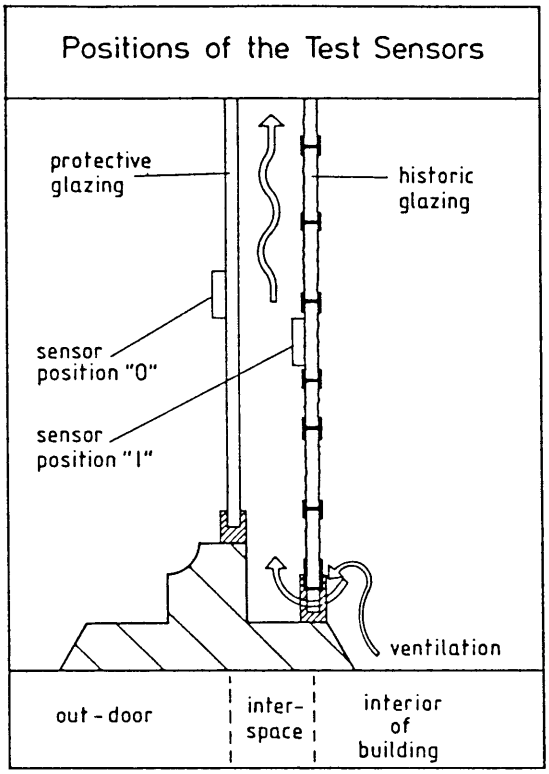

Fig. 6

Example for application

The application of such test sensors is easy and causes nearly no local efforts and inconveniences :

- the main work is done in the laboratory (preparation and IR measurements), not at the historic building, where only two times something is to be done : installing and removing of the sensors after the test period
- the sensors are small (less than 10 cm long and 5 cm broad, 1 mm thick) and light-weight, so they can be fixed to the windows without esthetic disturbance of the work of art
- there are no problems by instruments, cables or other items brought into or onto the historic object. Only the small sensors have to be transported which easily can be done by mail. Therefore, such investigations can be arranged without high running costs.

Compiling all these features of the model glass test sensors and the IR method used, one can state that with this new concept additional informations on the properties of double glazings or other protective measures may be achieved. The method can be used with rather low efforts and may supply results within periods less than one year.

IV - Pilot studies

To investigate the suitability of such sensors, pilot studies for one year had been carried out /2/ with model glasses MI and MIII at three different locations : St. Lorenz/Nürnberg, St. Janskirche/Gouda, and York Minster. The results are given in Table 1. The comparison of the both positions "O" and "J" (see Fig. 6) shows that a reduction of corrosion by the double glazings was given. But it also points out that still, even within the short period of time, the remaining corrosive stress resulted a non-neglectable progress of leaching which will produce further deterioration on the long run.

ΔE-Values for the Model Glass M I

	Position "0" Back-side of Protective Glazing (out-door conditions)	Position "I" Back-side of Historic Glazing ("protected" interspace)
St. Lorenz Nürnberg	0,72	0,07
St. Jans Gouda	0,70	0,04
Minster York	0,40	0,07

ΔE-Values for the Model Glass M III

	Position "0" Back-side of Protective Glazing (out-door conditions)	Position "I" Back-side of Historic Glazing ("protected" interspace)
St. Lorenz Nürnberg	0,07	0,03
St. Jans Gouda	0,07	0,01
Minster York	0,11	0,02

Fig. 7

Results of pilot studies

V - Bibliography

/1/ SCHOLZE H., HELMREICH H., and BAKARDJIEV J. : Untersuchungen über das Verhalten von Kalk-Natrongläsern in verdünnten Säuren. Glastech. Ber. 48 (1975), 237 - 247.

/2/ FUCHS D., PATZELT H., and TUNKER G. Immissionsschutz für historische Glasfenster - Internationale Untersuchungen neuer Methoden. Forschunds-bericht UFOPLAN-Nr. 106 08 005/02, 1987.

/3/ NEWTON R. G. : The deterioration and conservation of painted glass : A critical bibliography - Corpus Vitrearum Medii Aevi, Great Britain - Occasional Papers II, Oxford University Press, New York, 1982.

/4/ SCHEREINER M. and SCHOLZE H. : Korrosionsmechanismen an historischen Glasfenstern (Literaturstudie). Forchungsbericht UFOPLAN-Nr. 106 08 104, 1985.

/5/ TUNKER G., PATZELT H., SCHMIDT H., and SCHOLZE H. : Neue Wege zur Erhaltung historischer Glasfenster. Glastech. Ber. 59 (1986), Nr. 9, 272 - 278.

/6/ ILIFFE C. J. and NEWTON R. G. : Using triangular diagrams to understand the behaviour of medieval glass. Verres Réfract. 30 (1976) 30 - 34.