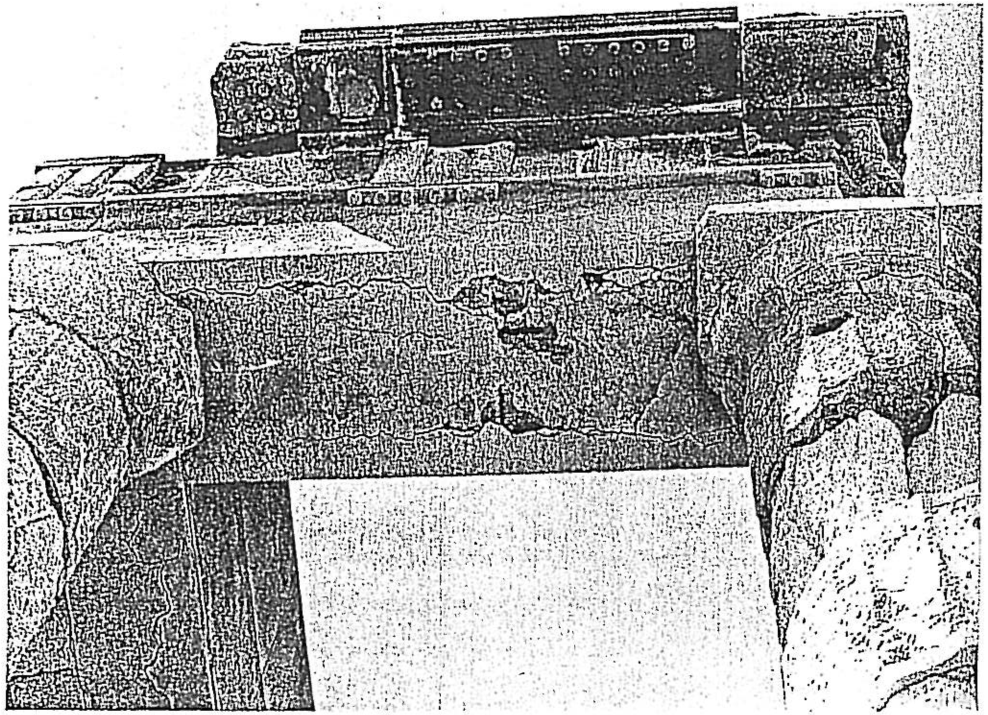

Fig.7: All the fore-mentioned techniques and their disastrous effects can be seen: cracking of drums caused by the reinforced concrete core, corrosion of steel rods in the artificial architrave, deterioration of the biocalcarenite due to soluble sulfates of the cement.

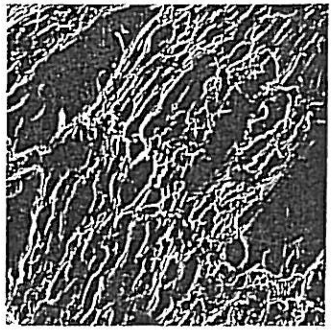

Fig.8: S.E.I., 1200x Fig.9: S.E.I., 720x Fig.10:S.E.I., 160x
Fig.8: Crystals of gypsum in pores of cement paste.
Fig.9: Microstructure of the stone when in contact with concrete: debris of disaggregated stone due to the action of salts (fractured surface).
Fig.10: Actual state of the microstructured of the cement paste from concrete core of a column of the hellenistic stoa.

PRESERVATION OF STAINED GLASS WINDOWS: NEW MATERIALS AND TECHNIQUES

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Summary

A progress report is given for the NATO-CCMS-study on stained glass conservation. New materials for protection of the bulk glass and for fixation of paint layers are presented. The discussion includes model glass investigations, leading to a better understanding of the corrosion mechanisms as well as new techniques for assessing the efficiency of external protective glazings.

1. INTRODUCTION

The progressive weathering of our historic glass windows as caused by climatic influences and the effects of pollutants is seriously threatening the survival of these valuable cultural assets (1, 2). Material research must not only concentrate on the investigation of basic corrosion phenomena and mechanisms, but head for new and long lasting techniques and materials. Time-compressing laboratory tests and pilot studies in-situ must characterize the efficiency of routine and innovative measures.

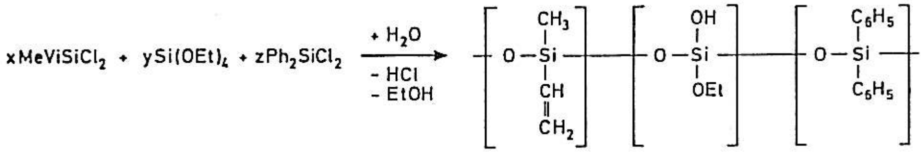
Funded by the Minister for the Environment of the Fed. Rep. of Germany and supported by the NATO-Committee on the Challenges of Modern Society, in 1983 the ISC established an international development project with new attempts in this field of material research. The major objectives are:

- Long-lasting protective coatings as additional or alternative conservation techniques
- Addition of new glass-substance to the stressed and loosened surface layers
- Characterization tests on the effects of protective measures.

2. ORGANIC-INORGANIC POLYMERS (ORMOCERes): NEW PROTECTIVE COATINGS

In the past the conservation of glass with coatings based on organic polymers did not yield satisfactory results in terms of long-term efficiency and stability. The development of new coating materials based on organic-inorganic polymers, tailored for perfect adhesion to corroded glass surfaces, offered improved protection (3).

The base-material of the lacquer is synthesized by a hydrolysis and condensation reaction:



$$x\,\mathrm{MeViSiCl_2} + y\,\mathrm{Si(OEt)_4} + z\,\mathrm{Ph_2SiCl_2} \xrightarrow[-\mathrm{HCl},\ -\mathrm{EtOH}]{+\mathrm{H_2O}} \left[-\mathrm{O-Si(CH_3)(CH{=}CH_2)}-\right]\left[-\mathrm{O-Si(OH)(OEt)}-\right]\left[-\mathrm{O-Si(C_6H_5)_2}-\right]$$

Best results were achieved by a composite coating with additional inorganic particles (Fig. 1). After years of laboratory tests using model glasses first and original glasses in the later phase of the project (4) in outdoor and high-stress climate chamber tests (Fig. 2), now first pilot applications at cathedrals in several countries were possible, e.g. at York Minster and the Kölner Dom.

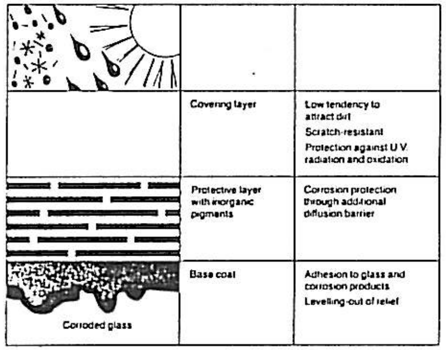


Fig. 1 Composite coating: properties of the different layers

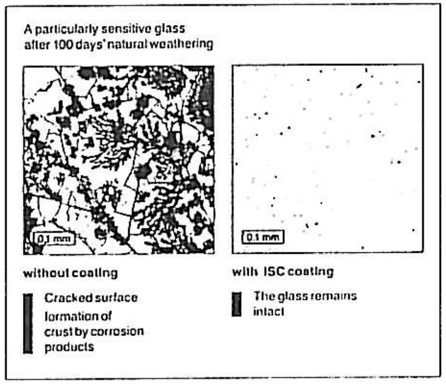
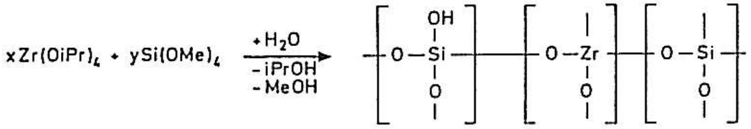


Fig. 2 Microscopic result of tests using sensitive model glass

3. INORGANIC GELS: FIXATION OF ENDANGERED PAINT LAYERS

Conventional materials for the consolidation of unstable paint (Schwarzlot, enamels) are organic polymers (e.g. epoxy resins) with inadequate ageing properties. New attempts concentrate on inorganic gels based on sol-gel-techniques:



$$x\,\mathrm{Zr(OiPr)_4} + y\,\mathrm{Si(OMe)_4} \xrightarrow[-\mathrm{iPrOH},\ -\mathrm{MeOH}]{+\mathrm{H_2O}} \left[-\mathrm{O-Si(OH)(O-)}-\right]\left[-\mathrm{O-Zr(-)(O-)}-\right]\left[-\mathrm{O-Si(-)(O-)}-\right]$$

The -Si-O-Zr- network is built up by a hydrolysis and condensation process which adds new glass material to the porous and endangered surface layers, (Fig. 3) thus preparing the object (by irreversible solidification) before applying the necessary (reversible) protective coating.

SEM-micrographs of a treated sample show thin layers covering the porous paint, giving adhesion to the glass.

Tests including ultrasonic treatment confirm the consolidation effect, but further development work (under research now) must optimize the reactive properties as well as application details.

Fig. 3 SEM-documentation of the fixed paint layers (35 000 x)

4. BASIC STUDIES ON CORROSION MECHANISMS OF MODEL GLASSES

The primary steps of glass corrosion can be described by an ion exchange reaction:

$$\equiv\mathrm{SiO^-\,M^+} + 2\,\mathrm{H_2O} \longrightarrow \equiv\mathrm{SiOH\cdot H_2O} + \mathrm{OH^-} + \mathrm{M^+}$$

The complex corrosion process is governed by the chemical composition of the glass (Fig. 5), the attack of water and pollution effects, e.g. by SO_2 (Fig. 6). For the basic understanding of the mechanisms and tailoring of time-lapse weathering tests (for testing new materials), systematic investigations using unprotected model glasses (Fig. 4) are running.

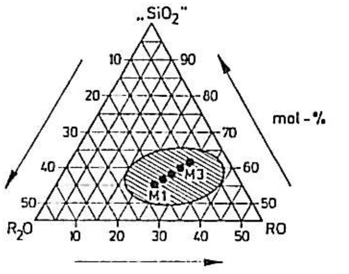


Fig. 4 ● Range of model glasses
▨ variation of medieval glasses

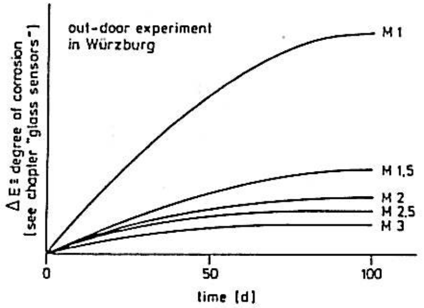


Fig. 5 Influence of glass chemistry on the corrosion progress

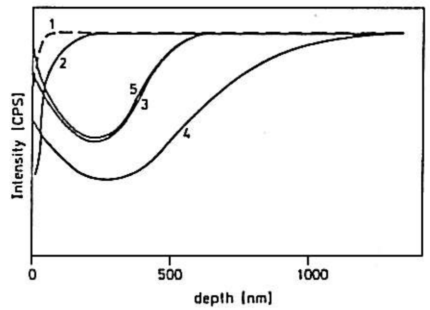


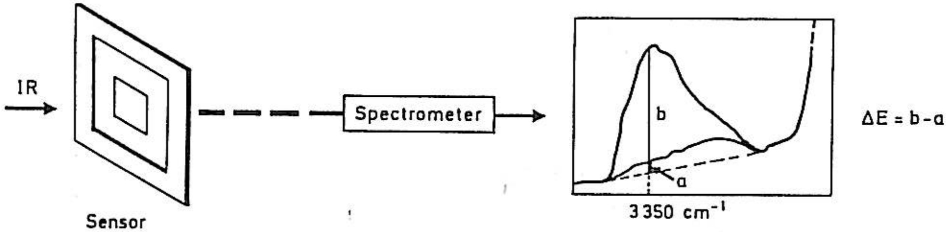
Fig. 6 XPS-profiles, monitoring the effect of SO_2 on Ca-leaching (glass M1)

1 = blank
2 = 1.5 h climate chamber
3 = 1.5 h climate chamber + 5 ppm SO_2
4 = 3 h climate chamber + 5 ppm SO_2
5 = 50 d out-door, appr 0.05 ppm SO_2

The quantitative results of the IR-analysis are confirmed by XPS-investigations. The leaching profiles for K, Ca, and Si in the submicron range detect the first primary steps of corrosion. As in this stage of development, no secondary effects (crusting) are included, the results demonstrate the direct impact of acidic gaseous pollutants to the glass corrosion: increasing the SO_2-level (100x) in a climate chamber accelerates the leaching rate of MI-model glass.

5. GLASS SENSORS: ANALYSING THE EFFICIENCY OF PROTECTIVE GLAZINGS

Special glass sensors, featuring high sensitivity model glass surfaces, can act as reliable indicators of complex corrosive stresses (5). Quantitative judgements are possible using IR-spectroscopy:



If the uncorroded state of the glass (a) is characterized by measurement of the OH-bond, and the sensor is exposed to a specific environment for a definite time (e.g. 1 year), the sensor surface will show certain deterioration effects corresponding to the local corrosive stresses. A second IR-measurement afterwards (b) will give a quantitative result (ΔE), correlating with the complex environmental situation. Applied in front and behind protective glazings (Fig. 7), sets of such sensors can help to judge the real protective effect of the various types of these constructive measures.

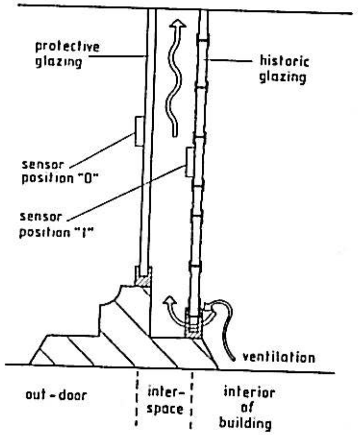


Fig. 7 Cross-section of external protective glazing settings. Sets of sensors are fixed on those places, where the remaining environmental stresses are to be determined. Comparison of the ΔE-data of these sensors after one year exposure gives information about the efficiency of the specific construction measure.

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