STONE AS SENSOR MATERIALS FOR MONITORING ENVIRONMENTAL INFLUENCES

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1.0 Introduction

The need for protection and conservation of objects, such as buildings, technical constructions, historical monuments etc., has resulted in an increasing demand for in-situ monitoring of environmental influences. In particular the assessment of weathering processes in their early stages is of importance. Sensor materials may take over that task at low costs. So far metals and glasses have been successfully applied (VDI-Richtlinie 3955). A different, very effective approach is offered by the use of stone materials. Because of their chemical-physical properties they are specially apt for monitoring objects constructed of porous materials and. In addition, out of a variety of stones a specific material can be selected for specific applications.

Field exposure experiments provide a method to find out which stone may serve as sensor material. In contrast to weathering simulation experiments in the laboratory, the frame of experimental conditions is compatible with the constraints given at application. An important requirement is, however, that the material properties and the environmental (meteorological and air pollution) parameters as well have been carefully characterized (Brüggerhoff and Mirwald, 1992).

2. Materials, sites, experimental set up and methods

For the field exposure experiments various, very homogenously composod stone materials were seleceted being characterized by different key properties. i) Baumberg Calcareous Sandstone (BCS) is a cretaceous biomicritic sediment in Westfalia (Germany) consisting of 46-66 vol.% calcite, 18-35 vol.% quartz, 9-14 vol.% clay minerals and of 1.5 vol.% glauconite. Petrophysical basic values are: porosity 19 vol.%, pore median 0.28 mm, specific surface 10 m^2/g, water take up coefficient 2.25 $kg/m^2h^{0.5}$.

ii) Obernkirchener Sandstone (OKS) of Lower Saxonia (Germany) is in pore and hygric properties similar to BCS. Therefore, it has been selected as a sort of reference material in this study. This slightly quartzitic silt-sandstone (quartz 87 vol.%, clay minerals 13 vol.%) guaran-tees a very low weatherability, in particular a high resistivity against $S0_2$-pollution impact.

iii) Kelheim Limestone (KL) of Northern Bavaria is a jurassic relatively pure limestone mainly built up of debris of reef organisms (pelmicrosparite): calcite (97 vol.%) and small amount of clay minerals (3 vol.%). Characteristic petrophysical values are: porosity: 6 vol.%, pore median: 0.46 mm, specific surface: 1 m^2/g, water uptake coefficient: 2.65 $Kg/m^2h^{0,5}$.

iiii) The alpine marble from Laas (LM) of South Tirol (Italy) is medium to coarse grained, of granoblastic hypidiomorphous texture and consists of 99 vol.% calcite. In small amounts dolomite, mica, quartz, tremolite and accessories may be present. Compared to the sedimentary materials the marble exhibits as a metamorphic rock considerably different petrophysical properties: porosity < 1 vol.%, specific surface at 0.3 m^2/g.With respect to its weathering behavior it is less reactive on chemical attacks but proved to be specially sensitive on frost/thaw impact.

Six exposure sites Duisburg, Eifel, München, Kempten (all Germany), Innsbruck and Obergurgl/Ötztal (both Tirol/Austria) have been selected for this study ((Mirwald and Brüggerhoff (1995), Mirwald et al., (1998)). The sites in Diusburg and Eifel are representative for industrial and low immission locations in North Western Germany, those of Munich and Kempten for urban and rural middle European climate conditions.While the site in Innsbruck stands for variable urban alpine climate and immission situations, the site at Obergurgl/Ötz-Valley, represents high alpine, but low pollution conditions. With respect to their metereological and air pollution properties all sites are relatively well characterised.

Our field exposure experiments base on the concept of the "dry and wet exposure technique" using stone slabs (50x50x5 mm) which were mounted on Mank's carrousels (VDI 3955) and freely exposed or shelteredly installed on racks. While the exposure experiments in Germany were performed up to 5 years, those in Austria were limited to 22 months.

Out of a variety of different methods which were considered to provide useful sensor criteria we choose the changes in sample mass and change in ultrasonic velocity as parameters. In context with the monitoring of mass change of the exposed samples, we obtained, in addition, very informative data from chemical analyses of the salt components $S0_4^{2-}$, $N0_3^-$, Cl^- and F^-.

3.0 Results and Discussion

Ideally, monitoring of objects by sensor materials should be carried out under dry conditions. However, "wet" exposure data provide important additional information, since under real conditions the influence of rain and/or undrained water can not be excluded.

The "dry" data of KL which are only available from the sites in Germany give a principle idea how the pollutant component $S0_2$ reacts on fairly pure limestone of intermediate porosity. Characterically, the mass change of the samples and the corresponding sulfate content depend linearly on the $S0_2$-presentation of each site. (This quantity is defined as the product of three variables: the monthly average concentration of $S0_2$ (g/m^3), the monthly average wind speed (m/s) and the duration of exposure (sec)). A striking finding is that the increases in mass of the "dry" samples are some 20% smaller than the mass of sulfate content analyzed!

The BCS-data display a similar behavior in principle. However, the rough quantitative comparison between KL and BCS (after two years of exposure) shows that the mass gain of BCS is by a factor 2-5 larger than that of KL. The related sulfate contents are even higher than the mass changes, about twice as high. This indicates a more complex weathering behavior compared to the KL which is mainly due to the micritic composition of BCS and its related high porosity. Probably also biogenic impact plays an considerable role in the weathering process during the summer seasons.

Data on OKS show also a linear relation between mass increase and $S0_2$-presentation. Despite the inert quartzitic composition OKS exhibits significant sulfate contents. The sulfate content determined from all sites are of similar order of magnitude and their correlation to the local $S0_2$-immision situation is mostly not good. This suggests, that the occurrence of "gypsum" is not the result of an in-situ formation but rather is a part of the particulate matter which is deposited on the samples.

Data of Laas Marble (LM) are only available from the Austrian sites so far. The data reflect to a lesser extent specific reaction on immission impacts, however, there is a pronounced sensisivity on frost-thaw events which are characteristic for the alpine clima region.

The "wet" data obtained on the carbonatic materials exhibit all mass losses which seem primarily related to dissolution of calcite and of sulfate deposits. In contrast, OKS shows almost no mass losses. Analyses of $S0_4^{2-}$, NO_3^-, Cl^- and F^- on all materials yielded data scattering which suggests that rain leaching is an important factor at wet exposure, nevertheless, the dominant parameter seems rather the pollution situation.

Ultrasonic measurements were performed on the samples from the Austrian exposure sites ouly. While the two sedimentary materials exhibited slight increases in their ultrasonic velocities (usv) (starting materials: 3200-3900 (m/s), after 1.5 years of exposure: 34004100 (m/s)) under all circumstances, the marble samples always showed a significant decrease (starting materials: 6500-7000 (m/s), after 1.5 year of exposure: 50004000 (m/s)). The negative or positive changes in usv is mainly attributed to intergranular loosening or cementation effects respectively. The marble data exhibit in a presentation of log usv versus log l/t an almost linear behavior what enables to estimate when the critical velocity at some 2500+ 500 (m/s) (Köhler, 1993) will be approached which preceeds physical desintegration.

4.0 Conclusion

The exposure data show that all four materials respond to environmental impacts, on air pollution as well on metereological factors (humidity/rain, frost-thaw) within half a year already. With respect to the impact of air pollution different response behavior of the different materials is noticeable. This leads to the concept of partial weathering processes where each one contributes in a different way to the weathering process as a whole. A number of such partial processes may be specified:

i) formation of autigenic sulfate (gypsum) in a carbonate bearing material by $S0_2$ pollution impact as encountered in KL, BCS and LM,

ii) deposition of particulate matter, "dust" (cf. Neumann, 1994), where among others also exogenic sulfate (gypsum?) plays an important role as this is demonstrated by the OKS-data,

iii) mechanically induced grain loosening and grain losses due to various factors, such as H_20 leaching (see „wet" data) as well as hygric swelling and shrinkage, salt-solution/salt-cristallisation processes, thermal dilatation and frost/thaw impact effects (see, for example LM).

Under the aspects of monitoring specific environmental loads the biomicritic BCS proves to be very sensitive on any kind of air pollution immission, while the quartzitic OKS which exhibits chemical inertness may serve as a collector of particulate matter.

The metamorphic LM again owns a particular sensisivity on frost-thaw events.

This concept of stone sensor materials is also applicable to other stone materials, provided a good homogeneity of the material is given and the mineralogical and petrophysical properties are sufficiently characterized for allowing a qualitative or even rough quantitative interpretation of weathering phenomena.

With respect to the practical application of these sensors, the small slab sized form of the samples allows to install them even in particularly small or esthetically sensible locations of an object, e.g. on monuments. Furthermore, a grid of monitoring sensors distributed over an object yields a detailed insight in the specific microsituation of environmental influences and their intensity at the structure. Monitoring of environmental load and damages are an essential part of maintenance concepts, however, often omitted because of high costs. With this kind of stone sensors a fast responding and low cost tool is available.

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