

8 Abstract

Research on structural damage of buildings has shown that increasing emissions of certain air pollutants have considerably accelerated the weathering process of historically significant buildings made of natural stone. Only cost-intensive maintenance and restoration measures can preserve our historical and cultural heritage from further deterioration caused by the on-going weathering process.

The factors and processes involved in the continuous weathering of natural stone are varied. The individual damaging mechanisms can be attributed to physical, chemical, or to some degree, biological processes as well. The combined action of these processes through a period of several centuries has led to complex damage symptoms. Since the latter half of the 19th century, anthropogenic emissions have increased substantially. The resulting deposition of acidically coreacting components results in a significant acceleration of chemical processes; a prime example for this process is the Cologne Cathedral. The central requirement of historical monument conservation is to preserve the original substance of the buildings to the greatest possible extent. The original natural stone is substituted by other materials only if its stability is insufficient. New protective materials for stone may offer long-term protection by reducing the speed of deterioration of the stone and partially compensating for the loss of stability of the natural stone.

An important part of developing and testing new protective systems is the continued development of testing procedures which facilitate the evaluation of the effectiveness of those protective materials under realistic conditions. Later damage on buildings which could result from the use of such hydrophobing agent can be avoided by implementing quality controls with regard to the long-term effectiveness of new protective materials for stone. At the same time, the effectiveness and durability of these protective materials on natural stone will be tested under realistic conditions.

One of the goals of this thesis is the continued development and practical application of a method of damage-free testing of sandstone, which had been treated with protective materials. A practical way of testing the effectiveness of hydrophobing agent is the calculation of the deposition of sulfur dioxide by the determination of sulfate in the specimens after exposure, which makes it possible to quantify the degree to which harmful emissions from the air and rain are absorbed.

This new method was used for the first time within the scope of an R&D project sponsored by the German Federal Ministry of Education and Research entitled “New solutions for the restoration and conservation of natural stone surfaces in historical monuments.” The test material came from the western gable of the tower of the neogothic St. Luke’s Church in Zwickau-Planitz, which was built in 1875. In this building, Cotta sandstone was used as facing for the brickwork. The protective materials used were polyurethane-based polymers. Protective material 219 (SM 219), which is hydrophobic, is an oligodimethylsiloxane-modified polyurethane. For protective material 288 (SM 288), which is hydrophilic and consolidating, no precise data were available for reasons of patent protection.

For the study of long-term weathering, two test facilities belonging to the project partners were utilized, where physical, chemical, and biological weathering factors could be selectively simulated. The samples were examined before, during, and after the simulation experiments. The method, which had been developed for cumulative measurement of depositions of sulfur dioxide on stone surfaces, was used for this test. After the simulation experiments had been completed, parts of the stone test specimens were sawed apart parallel to the surface and ground up. After elution of the stone meal with water and after the eluate was centrifuged and filtered, the cations and anions were determined, using ionic chromatography analysis and ICP-OES.

The salt content of the stone specimens showed a high degree of dispersion. The ion content in the specimens showed differences not only in the overall concentration but also in how it was dispersed throughout the stone. Application of the protective material resulted in lower overall concentrations. The distribution pattern of the ions in the deep layers, however, remained similar. After a 52-week simulation experiment in the Versuchsanlage zur Entwicklung naturnaher Umweltsimulationskonzepte (VENUS – Testing Facility for the Development of Nature-Based Environmental Simulation Concepts), test specimens, which had been impregnated with the SM 219 protective material, showed no changes in the distribution pattern. Even ions, which form easily soluble salts (Na, Cl⁻, NO₃⁻), were found in the top layers of the stone. Test specimens, which had been treated with SM 288 and put through the simulation at the VENUS facility, showed significant changes in the depth profile of the distribution of the salts. The content of sodium, chloride, and nitrate were considerably lower than in the blank value specimens. The gypsum content had shifted to the deeper layers of the test specimen.

After a 50-week long simulation experiment in the biological-chemical simulation (BCS) facility, the distribution of salts in the test specimens showed a higher degree of gypsum enrichment in the top layers of the stone in those specimens, which had remained untreated. While the test specimens, which had been impregnated with SM 219, showed changes of the nitrate and chloride concentrations only in that area, which had remained untreated, the high gypsum concentrations on the surface of the stone of the specimens impregnated with SM 288 indicate a reaction of the stone with the pollution gases in the atmosphere.

The depth profile of the salt distribution after both simulation experiments showed a high concentration of gypsum on the surface of the stone in those specimens, which had remained untreated; this is a result of new formation of gypsum, which had occurred in the BCS chamber. A higher concentration of nitrates in the top layers of the stone resulted from conversion of ammonia ions by nitric bacteria. Upon completion of the simulation experiments, the ion concentrations in the test specimens impregnated with SM 219 had scarcely changed at all. In the specimens impregnated with SM 288, large amounts of gypsum were generated.

The SO₂ deposition values of the untreated specimens showed considerable dispersion. After impregnation of the specimens with SM 219, the values decrease significantly, and this proves the effectiveness of the protective material. These tests showed that the protective material does not react with sulfur dioxide; thus the pollution gas has no additional coreactant except the stone itself. A change in the deposition speed therefore indicates a change in the effect of the protective material itself. Before the simulation experiments, the protective effect of SM 288 is comparable with that of SM 219. A UV treatment, which was performed after the impregnation, did not show clear results.

According to the simulation at the VENUS facility, the test specimens impregnated with SM 219 showed only an insignificant change in the deposition speed. The set of specimens where SM 288 was used showed a substantial increase of the deposition values, indicating that the protective material was causing damage. After the experiment in the biological-chemical simulation chamber, both the untreated specimens and the test specimens impregnated with a protective material showed a more or less reduced deposition speed. As kryo-SEM tests have shown, this is caused by new formation of gypsum on the surface. The biofilms, which were formed during the operation of the experiment, also reduced the deposition speed. This was shown in an additional experiment using untreated stone lamina. Use of a confocal laser microscope system permitted the examination of the

biofilm. In this experiment, it was possible to achieve complete coverage of the stone surface. A biofilm decreases the absorption of SO₂ by 50 to 70 percent, depending on the type of stone.

In addition to the simulation facilities mentioned previously, another experimental chamber was set up for the simulation of salt weathering. Large amounts of sodium chloride were applied to freshly broken stone specimens. With the help of the experimental setup, it was possible to show that this causes irreversible damage to the stone. Using this chamber and the associated deposition measurements, it was possible to carry out a test of the durability of the protective materials (in this case only SM 219) with regard to damage to the stone through salt crystallization for the first time. Although during this experiment there was substantial elongation in the stone, no significant changes in the deposition values were noticeable. In order to make a final judgement, it will be necessary to conduct additional experiments using all the varieties of natural stone and all protective materials, which are available.