DETERIORATION OF BUILDING CERAMICS BY ENVIRONMENTAL FACTORS - A CASE STUDY ON ZSOLNAY CERAMICS FROM THE MUSEUM OF APPLIED ARTS (BUDAPEST)

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1. Introduction

Nowadays much more attention is being paid to the influence of mankind on our environment than previously. The expansion of urban conglomerations and the developing industry has resulted in an increased amount of aggressive pollutants [1]; therefore in the 21st century one of the major roles of society is to conserve its historical and cultural heritage. Pollutants from transport, heating and industry deposit on the built environment, causing its deterioration. Deterioration of natural building materials, like stone (e.g. freshwater and coarse limestone), is subject of numerous studies [e.g. 2], however few studies are designed to research the effect of air pollutants (e.g. sulfur dioxide, nitrogen oxides, soot, dust) on man-made silicate-based materials (ceramic, glaze, glass, etc.). In Budapest there are many examples of historic buildings covered with glazed ceramics (e.g. the Museum of Applied Arts, Parliament, the Geological Institute and Matthias Church).

It is widely accepted that, as Tournié and Ricciardi state, "the high melting temperatures of ceramics and glasses implies that diffusion coefficients of most of the elements are too low at ambient temperature to be significant at human lifespan and these materials are often considered to be corrosion resistant" [3]. However, the air pollutants derived from different sources can damage ceramics and glasses easily if these silicate-based materials are exposed for a long time to the harmful factors. The most important reactions are dissolution of ceramic, glass and glaze, material transport to the contacting meteoric water or moisture, formation of new phases on the surface of the weathered object (so-called "hydrated silica" layer) and appearance of cracks/microcracks on the surface [3].

Our purpose is to reveal the effects of air pollutants on building ceramics (glazed ceramic roof tiles and decorative items) that originating from the Museum of Applied Arts, Budapest. In order to determine the deterioration mechanisms, we have examined the phase composition and the microfabrics of the ceramic body and the glaze, and studied the depositions accumulated on the surface of the ceramics.

2. Environmental factors

Building materials (natural and man-made) are continuously exposed to environmental factors, which often cause the premature aging of the material in consequence of physical,

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chemical and biological degradation processes. Besides the principal gaseous pollutants such as SO_2, NO_x and CO_2, the effect of aerosols and the presence of various forms of water (e.g. meteoric water, moisture) are also important factors in deterioration. Gases easily form different acids with the contacting water (sulphuric acid, nitric acid or carbonic acid) which can corrode the building materials. Aerosol particles, dust and soot also play a significant role in the deterioration. The study of these pollutants is of paramount importance to understand the chemical mechanism of the so-called black crust appearing on the surface of the building materials. Sulphate (usually gypsum) is generally the dominant component of the black crust, and diverse particulate matters are always observed [4].

The presence of many bacteria (like the sulfur oxidizing *Acidithiobacillus thiooxidans, Acidithiobacillus caldus*) and fungi (like *Penicilium Sp.*, *Fusarium Sp.*) on the weathered surface is also frequent. These living organisms promote formation of cracks and ion dissolution from the material (Ca^{2+}, K^{+}, Mg^{2+}), thus facilitating the process of weathering [5]. In addition to the above-mentioned degradation processes, air movement and solar radiation also play a role in the weakening of the building materials, causing shorter life span and decrease of permanence.

3. Samples and methods

The Museum of Applied Arts is located in the centre of Budapest, next to one of the roads with the heaviest traffic, Üllői Street (Fig. 1). Due to its location, the building is intensively exposed to air pollution and anthropogenic effects.

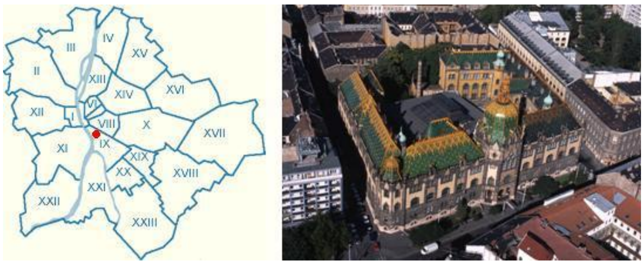

Figure 1. Schematic map of Budapest (on the left), where the red dot shows the location of the Museum of Applied Arts. Yellow and green glazed roof tiles and pyrogranite decorative items are clearly seen on the top of the investigated building (on the right)

The sampled ceramics are pyrogranite decorative objects, unglazed and glazed roof tiles. The role of the glaze layer is to decorate and protect the ceramic body. The ceramics were manufactured by one of the leading ceramic factories in Hungary, Zsolnay Porcelain Manufacturer. Since the construction of the Museum in 1896 the ceramic tiles and pyrogranite elements suffered numerous environmental and human influences therefore, the objects were damaged and from time to time had to be replaced. During sampling we collected ceramics of different ages (i.e. from different renovation periods) and with diverse glazes covered by a thick black deposition layer (Fig. 2).

Figure 2. A green glazed tile from the roof of the the Museum of Applied Arts (on the left) and the studied samples of pyrogranite elements (on the right)

The mineralogical composition and texture of the ceramics was studied with a Nikon SMZ 800 stereomicroscope and Nikon E600 polarizing microscope. The phase composition of the ceramic body and the depositions accumulated on the objects was determined by X-ray diffraction analysis (XRD) with a Philips PW 1730 diffractometer. The surface of the glazed and unglazed (back) sides of some selected ceramics was studied with an Amray 1830 I/T6 scanning electron microscope (SEM). The SEM technique was also used to observe the microstructure of the ceramic body and the glaze, their interface and the alterations of the glaze, as well as the depositions on both sides of the objects. For this analysis, cross-section preparations were used.

4. Results and Discussion

Based on phase composition and microstructure, the studied ceramics can be divided into three groups (Table I).

Table I. Phase composition and textural characteristics of the studied ceramics

Types	Phase composition	Characteristic of ceramic body/glaze
Group 1	quartz>mullite> cristobalite, K-feldspar	ceramic body: matrix: white; grains: size max. 1 mm, white; structure: compact, few pores glaze: contains inclusions, 170-200 μm thick, lead glaze ceramic-glaze interface: sharp
Group 2	quartz> cristobalite, mullite	ceramic body: matrix: white; grains: size max. 1.5 mm, yellow; structure: porous glaze: few inclusions, 250 μm thick, lead glaze and unglazed items ceramic-glaze interface: sharp
Group 3	quartz, mullite> cristobalite, K-feldspar, plagioclase, +/-calcite	ceramic body: matrix: red, grains: size max. 0.5 mm, white; structure: porous glaze: some inclusions, 270-280 μm thick, lead glaze ceramic-glaze interface: glaze impregnated the upper 150 μm part of the ceramic body

The tiles, depending on their exposure, are covered by a grey-black deposition (contamination) layer, which firmly adheres to the surface. The deposition layer contains dust, soot and aerosols in variable quantity. Different types of spherules often appear on it, occurring on the glazed and the unglazed back sides of the tiles (Fig. 3). Fe-rich, silicate spherules and spherules with complex composition, containing Si, Ca, K, Al and S, can be distinguished, which are natural or artificial in origin. We also observed artifical carbonaceous forms. The artificial spherules probably originated from fossil fuel (coal and oil) combustion [6], thus they are generated by industry and other human activities (e.g. heating).

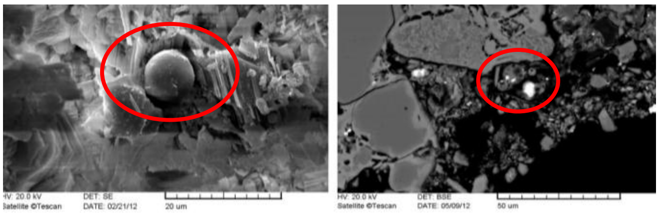

Figure 3. Scanning electron microscope pictures of natural and artificial spherules. 20 µm wide natural spherule with complex composition (Si, Fe, Ca, Al rich) in compact gypsum crust on the glazed side of a ceramic tile (on the left) (SE image) and a bright Fe-rich and several dark, carbonaceous artificial, 5-15 µm sized (in diameters) spherules in the dust layer on the unglazed (back) side of a ceramic tile (on the right) (BSE image)

Gypsum accumulates on the surface of tiles, occurring as a constituent of the deposition layer. It can be observed in different forms on the glazed and unglazed (back) sides of the ceramic tiles, depending on their exposure. On the glazed side less gypsum is present in laminar form, whereas on the unglazed, back side, where the gypsum crystals were protected from the environmental influences, dense, compact and laminar crystals also appear (Fig. 4).

Gypsum generally originates from dust, which settles down and recrystallizes on the surface of tiles [2]. Another source of gypsum can be construction waste, since gypsum-containing binder is used to fix the tiles [7], or it can form by the reaction of sulphur-dioxide and carbonate.

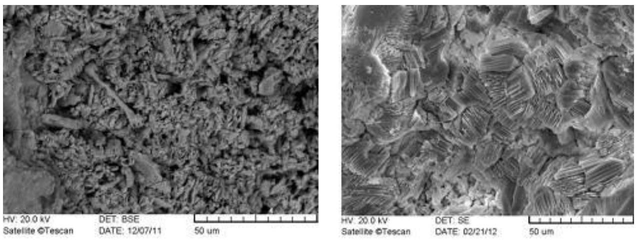

Figure 4. Dense, compact gypsum layer (on the left, BSE image) and laminar gypsum layer (on the right, SE image) on the unglazed, back side of the ceramics

We have also found traces of biological activity, which are probably residues of former microorganisms (bacteria, lichen and/or fungi) (Fig. 5). These residues appear near to the cracks on the surface. In some dark deposition layer calcium oxalate (weddelite) was identified, which could have been generated by the reaction of a calcium-bearing phase and oxalic acid produced by bacteria/fungi/lichen [8]. Such organic mineral could also originate from biomineralization of microorganisms [9].

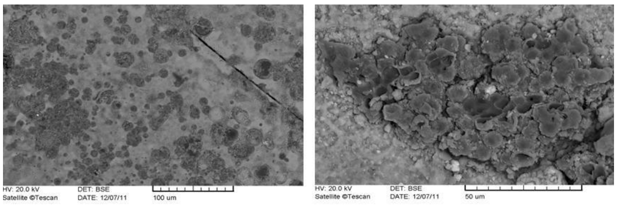

Figure 5. Residues of former organisms (bacteria/fungi/lichen) appear in "bubble-like" (on the left) and other forms (on the right) on the glazed side of the ceramics (BSE images)

The most conspicuous result of the deterioration is the appearance of a very thin weathered surface layer of glaze on some tiles of the ceramic group 2. The deposition on the weathered glaze layer shows a higher lead content than the weathered glaze itself; however both layers have lower lead content than the unweathered glaze (Fig. 6).

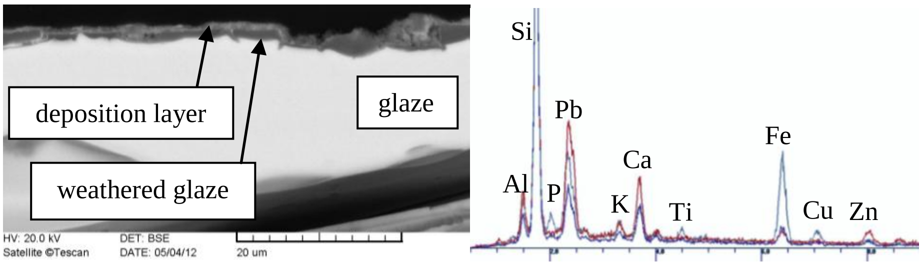

Figure 6. Cross-section of a glazed ceramic tile: the upper light grey deposition layer and the dark grey weathered glaze beneath covering the unaltered glaze (on the left). In the bottom-right corner of the BSE image a 10 µm wide crack is located in the glaze. X-ray spectra show the chemical composition of the deposition layer (grey), the weathered glaze (blue) and the unaltered glaze (red) (on the right)

One possible interpretation of the phenomenon is that lead, as one of the major components of the glaze, was dissolved, basically leached from the surface layer of the glaze by rainfall and migrated to the upper deposition layer, as Schreiner et al. observed on some corroded medieval window glass [10]. Behind this the weathered glaze is also fragmented in several places, not only on the surface but also in the glaze. Formation of cracks thus facilitates the weathering process moving toward the interior glaze (Fig. 7).

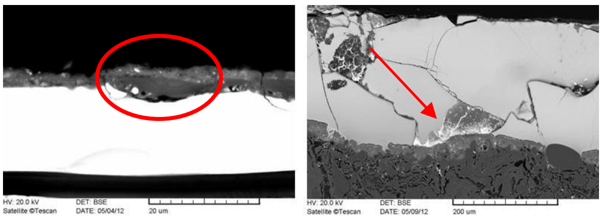

Figure 7. The weathered surface layer of glaze is fragmented (on the left) and the weathered glaze with bright precipitations rich in lead occurs along the cracks and at the ceramic-glaze interface (on the right) (BSE images)

5. Conclusion

Our purpose was to study the deterioration of Zsolnay building ceramics, mainly glazed roof tiles of the Museum of Applied Arts, Budapest. We distinguished three groups among the studied ceramics. A grey-black deposition layer was observed on the tiles, which frequently contains natural and artificial spherules. Gypsum in diverse quantity and appearance occurs on the ceramics. We identified residues of former biological activity (bacteria/lichen/fungi), confirmed also by the presence of calcium oxalate (weddelite). We demonstrated that in some tiles the glaze had started to weather. If this phenomenon continues for a long period, it will result in the deterioration of the whole glaze.

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