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Chemical durability of glaze on Zsolnay architectural ceramics (Budapest, Hungary) in acid solutions

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Zsolnay glazed architectural ceramics are among the most famous Hungarian ceramics, however, there is no profound knowledge about the deterioration of these building materials. The present study aims to reveal the influence of acidic solutions in the deterioration of Zsolnay ceramics. The studied ceramics are glazed roof tiles, which originate from two buildings in Budapest: one is located in the densely built-up city centre with high traffic rate and another one is in a city quarter with moderate traffic and more open space. The roof tiles represent the construction and the renovation periods of the buildings. The ceramics were mainly covered by lead glazes in the construction period and mainly alkali glazes in the renovation periods. The glaze of the tiles were coloured with iron (for yellow glaze) or chromium/copper/iron (for green glazes) in the case of the building located in the city centre, whereas cobalt was used as colorant and tin oxide as opacifier for the blue glaze of the ceramics of the other building.

Six tiles were selected from each building. Sulphuric acid (H2SO4) solutions of pH2 and pH4 were used to measure the durability of the glazes up to 14 days at room temperature. The surfaces of the glazed ceramics after the treatment were measured by X-ray diffraction, Raman spectroscopy and SEM-EDS techniques to determine the precipitated phases on the surface of the glaze. Electron microprobe analysis was used to quantitatively characterise phases found and to determine the chemical composition of the treated glaze. The recovered sulphuric acid solutions were measured with ICP-OES technique in order to quantify the extent of the ion exchange between the glaze and the solutions.

There is a significant difference in the dissolution rates in the treatments with sulphuric acid solutions of pH2 and pH4, respectively. The solution of pH2 induced greater ion exchange (approx. 7-10 times) from the glaze compared to the solution of pH4. Alkali and alkali earth metals and lead indicate the most intensive dissolution. Greater amount of ion-exchange was observed for the lead glaze covering the ceramics from the construction periods of both buildings. Sulphate phases (e.g. anglesite, gypsum, anhydrite) newly appeared on corroded glaze parts and pits are clearly seen on the surface of the ceramics originated especially from the first renovation period of the building located in the city centre.