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QUANTIFICATION OF SALTS IN EXTRACTS FROM BRICKS („WALL OF BRICKS" AT THE WAWEL CASTLE IN CRACOW)

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Abstract: The concentration of soluble salts in the retaining wall of the Wawel Castle was estimated. This wall bears the pressure of a steep, earthen slope of medieval fortifications. The analyses have shown that the samples contain mainly sulphate, nitrate, chloride, calcium, sodium and potassium. The concentration of the ions increases distinctly from the inner side of the wall toward the outer, exposed part. Due to the specific position of the wall and in contrast to most other buildings, water penetrates the retaining wall from the side abutting the scarp, while capillary suction from the foundations is of minor importance.

Key words: soluble salts, bricks, Wawel Castle, Cracow.

Introduction

Bricks as a construction material began to be widely used in Poland in the 14th century (Gothic). Like any other stones they also undergo similar processes of deterioration. Durability of brick walls depends, among others, on the composition of clay raw materials, firing conditions, and also on the composition of mortar. Bricks were used in construction of the retaining wall between the foothill and the Herbowa Gate of the Wawel Castle in Cracow (Fig. 1). Different parts of the wall were erected in various periods. Its outer part comes from the 1920s, the core from the mid-19th century, and the foundations from the Renaissance, resulting in different states of preservation of the bricks (Kozłowski & Stępień 1997). The wall is situated on the northern side of the castle hill and bears the pressure of a steep, earthen slope of medieval fortifications. Besides its architectural value, its other asset is in a number of stone tablets commemorating sponsors who rendered financial assistance toward restoration of the castle after World War I (Fig. 2). The wall was strongly damaged, and salt efflorescences can be seen at its surface. As the wall was poorly preserved, displaying numerous cracks and loosenings, it had to be renovated. During renovation and conservation of the wall, the author took brick samples to estimate the concentration of soluble salts.

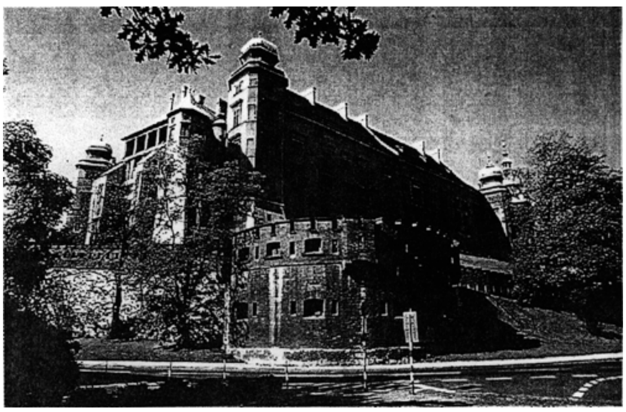

Fig. 1. View of the Wawel Castle in Cracow.

Fig. 2. „Wall of bricks" at the Wawel Castle with stone tablets commemorating contributors who rendered financial assistance toward restoration. (Photo P. Stępień).

Sampling and methods

Considering the specific localization of the wall, which tightly abuts an earthen scarp from one side, the samples were taken through the wall in three horizontal profiles, at different heights above the ground level. The profiles A, B, C were situated 5 m, 2.5 m and 0.5 m above the level of the pavement, respectively. In every profile three samples were taken from the inner side of the wall (abutting the earthen scarp), central part and outer side of the wall.

In the laboratory, salts were extracted from the crushed samples of bricks (ca. 2 g) in redistilled water (pH = 7.2, cond. = 2 μS/cm). The solutions were then filtered, using Porafil membrane filters (CA type, 0.45 μm), and the conductivity and pH of the filtrates measured. The contents of chloride, sulphate, nitrate, phosphate and fluoride anions were analysed using liquid ion chromatography (LIC), and those of sodium, potassium, calcium and magnesium cations using atomic absorption spectroscopy (AAS).

Results

According to the chemical analyses, the degree of contamination varies in the analysed profiles (Table 1). Sulphate, nitrate, chloride, calcium, sodium and potassium have been found to be the main ions. Concentrations of fluoride and phosphate ions were much lower and sometimes even below the detection limit. Magnesium was very low as at the pH observed this element forms the insoluble hydroxide.

PROFILE A

The samples situated at the highest part of the wall show intermediate conductivities and contain sulphate, nitrate, chloride, sodium, potassium and calcium. The pH values vary from 9.51 (inner wall) to 8.82 (outer wall) (Table 1). The concentrations of ions grow from the inner side of the wall towards the outer side (Fig. 3).

PROFILE B

The samples situated 2.5 m above the pavement level show low conductivities in the inner and central parts of the wall but high conductivities in the outer part of the wall. The pH value is the lowest in the sample from the outer part. The dominant ions are sulphate, potassium, calcium and sodium. The concentrations of nitrate and chloride are lower. The concentrations of ions increase distinctly from the inner side of the wall (i.e. that abutting the scarp) toward the outer, exposed part (Table 1, Fig. 4).

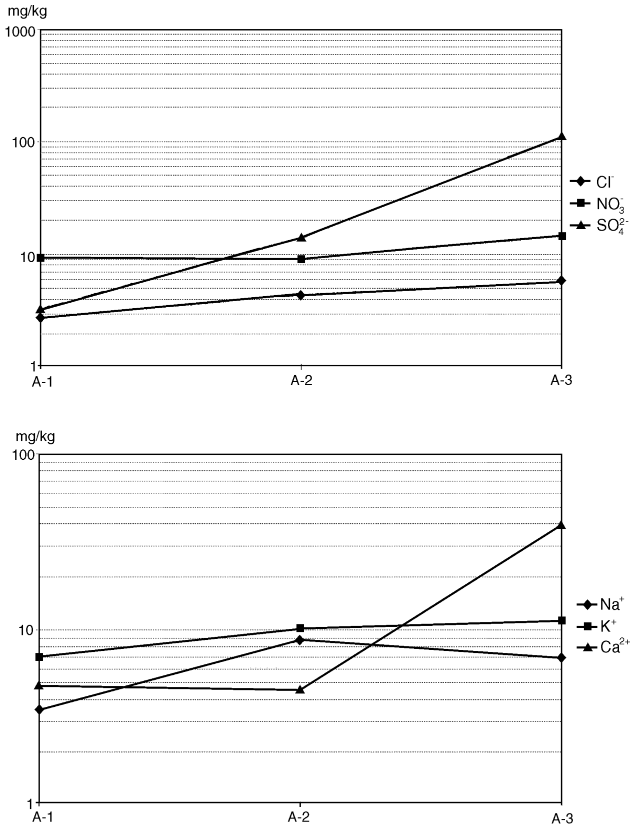

Fig. 3. Concentration of ions in the „wall of bricks" at the Wawel Castle in Cracow. **A** — horizontal profile situated 5 m above the level of the pavement, 1 — inner side of the wall (abutting the earthen scarp), 2 — central part of the wall, 3 — outer side of the wall.

PROFILE C

Extracts from the samples close to the pavement exhibit low (in the inner part) to intermediate (in the central and outer part) conductivity. The pH value decreases from the inner (9.62) to the outer (8.90) parts of the wall (Table 1). The analyses have shown that all the samples contain mainly nitrate, sulphate, chloride, also potassium, sodium and calcium ions. There is a distinct horizontal variation in concentrations

Table 1: Chemical analyses of water extracts from the "wall of bricks" at the Wawel Castle (mg/kg leached surface — the nine last columns).

Profile	Sample locality	Cond. μS/cm	pH	F^-	Cl^-	NO_3^-	SO_4^{2-}	PO_4^{3-}	Na^+	K^+	Ca^{2+}	Mg^{2+}
A	A1	75	9.51	0.5	2.8	9.5	3.3	0.2	3.5	7.0	4.8	0.11
	A2	142	9.65	0.2	4.3	9.0	13.8	0.4	8.7	10.1	4.5	0.09
	A3	242	8.82	1.9	5.6	14.0	107.0	0.2	6.8	11.1	38.7	0.82
B	B1	66	9.30	0.2	1.7	2.2	6.0	0.3	3.9	5.4	4.9	0.06
	B2	81	9.20	0.2	2.3	5.9	8.2	0.4	2.8	6.0	6.3	0.09
	B3	1262	8.34	1.5	16.5	130.0	485.5	b.d.	77.4	100.5	90.5	0.51
C	C1	91	9.62	0.3	1.1	1.7	2.5	0.4	5.9	7.1	7.1	0.02
	C2	384	9.08	0.2	3.8	9.0	27.1	0.3	4.1	7.0	14.5	0.52
	C3	307	8.90	0.3	21.4	91.2	75.5	0.1	46.5	40.7	16.5	0.72

b.d. value below the detection limit

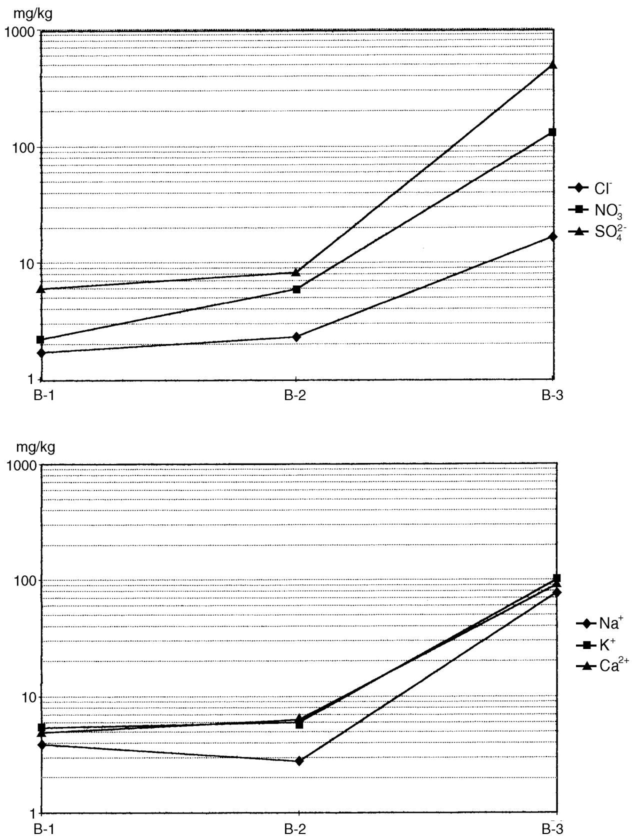

Fig. 4. Concentration of ions in the „wall of bricks" at the Wawel Castle in Cracow. **B** — horizontal profile situated 2.5 m above the level of the pavement, 1 — inner side of the wall (abutting the earthen scarp), 2 — central part of the wall, 3 — outer side of the wall.

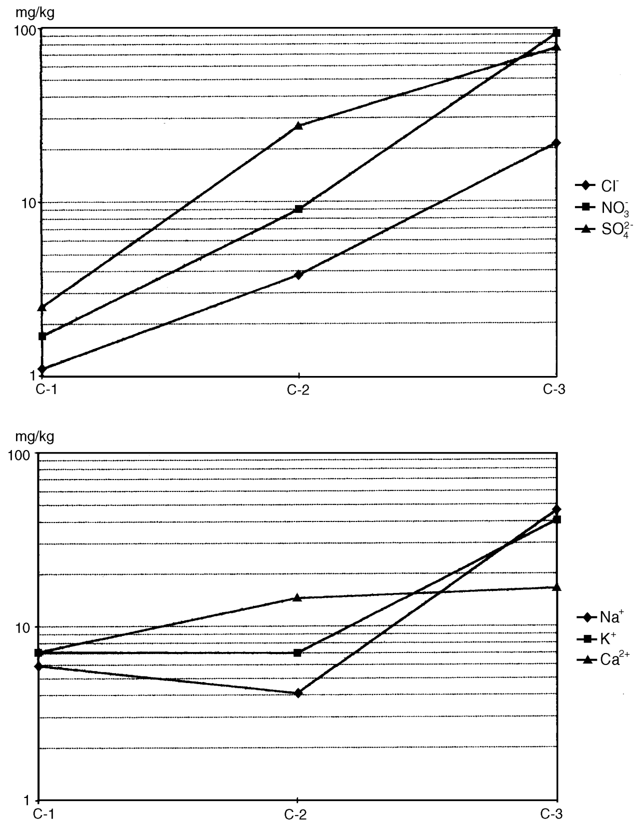

Fig. 5. Concentration of ions in the „wall of bricks" at the Wawel Castle in Cracow. **C** — horizontal profile situated 0.5 m above the level of the pavement, 1 — inner side of the wall (abutting the earthen scarp), 2 — central part of the wall, 3 — outer side of the wall.

of ions (Fig. 5). The highest level has been found in the outer part of the wall.

Conclusions

The analyses have shown that conductivities of the samples examined vary from low — below 100 μS/cm — to high — above 1200 μS/cm. The pH value varies from ca. 9.65 to 8.34. The highest conductivities and lowest pH have been found in the samples from the outer part of the wall, especially those situated 2.5 m above the level of the pavement.

The samples contain sulphate, nitrate, chloride, calcium, sodium and potassium ions with the dominance of SO_4^{2-} and Ca^{2+}, especially in the profile situated 2.5 m above the pavement. The relationship between concentration of different ions in profiles situated 5 m and 0.5 m above the pavement is not so clear.

The concentration of ions and conductivities increase distinctly from the inner side of the wall (i.e. that abutting the scarp) toward the outer, exposed part. In several cases the salt concentration is so high that efflorescences were found on the wall surface.

In many cases the crystallization of salts represents the major damaging factor especially in the outer part of the wall (i.e. in the evaporation zone). In contrast to most other buildings, water penetrates the retaining wall from its long „back" abutting the scarp, while capillary suction from the foundations has a minor role. This penetration has caused frost damage, most serious at a distance of ca. 20 cm from the face of the wall, where at full water saturation temperatures were low (Kozłowski & Stępień 1997), and saturated it also with water-soluble salts.

Sulphur was introduced by atmospheric pollution. The origin of chloride and nitrate is related to regional air pollution as well (Turzański 1991, 1997; Manecki et al. 1997). A high content of chlorides found close to the outer face of the wall may result from de-icing of the pavement with NaCl or $CaCl_2$ in winter. Sodium, calcium and potassium originate mainly in the process of leaching of the bricks and mortar. Air pollution could be the second source of these cations.

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