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Original article

Research into the influence of subsoil on sulphates, nitrates and chlorides accumulated in renovation plasters used for rehabilitation of monuments in the Czech Republic

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ABSTRACT

Degradation of historical masonry and plasters is often caused by external conditions; the presented research focused on salts originating from subsoils. The content of salts: Sulphates, Nitrates and Chlorides was analysed from plasters on 5 chosen historic buildings before and after the renovation in this paper. The samples were collected three times between 1998–2018. In some cases, the Sulphates were still present or even with a higher content after the renovation in comparison with the state before renovation. That can be caused by many factors from environment and this work focused on source from the subsoil. To understand better geological background the borehole data around each object were studied. According boreholes were buildings divided in two groups: on clayey subsoil and building on subsoil without clay. By Kruskal–Wallis test was proved, that the Sulphates content in plasters was constant before and after the renovation on clayey subsoils, it didnt́ changed in a time. On subsoils without clay (mainly silty to sandy soils) the content of Sulphates declined after the renovation, what was proved by regression analyse on 95% confidence level.

1. Introduction

The issue of damage to historical masonry by salt crystallization in the pore systems of artificially made ceramic materials, natural stones or plasters has long been known as it affects historical buildings. The salts usually originate from the subsoil, from where they naturally migrate in solutions. Movement of the saline solutions depends on many factors. The essential aspect is the chemical composition of the salts, which determines their solubility, migration and conditions of crystallization in case of decreased humidity/moisture. From the geochemical point of view, the process is affected by the composition of a subsoil structure; from the hydrogeological point of view, the groundwater level and the nature of the subsoil's pore system in the capillary fringe above groundwater level and in the aerated zone dominate, and humidity varies depending on the amount of rainwater falling on the ground in the broader proximity of the structure.

Many authors have dealt with the degradation process of historical masonry, e.g., Winkler [1] provided a complex assessment of the degradation of natural stones in historical structures, Goudie and Viles [2] and Rodriguez-Navarro and Doehne [3] focused on the effect of various types of salts on construction materials, while Laue [4] assessed material erosion due to the effect of salts in relation to the climate in which the structures are located.

The most harmful salts are often highly soluble in water and are transported by water inside porous material [5]. WTA specifies the classification of the salt content in the material at three levels: low, medium and high [6,7]. Damage to porous construction material is usually caused by physical and chemical processes (especially crystallization pressure). The process is linked to decreased moisture of the porous material and fluctuation of relative air humidity in proximity to the structure. This results in a transition from liquid to solid salt state, i.e., in crystallization. Restoration procedures to renovate and protect porous materials affected by salt-related degradation

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Fig. 1. Southern wing of the castle in Valasske Mezirici not yet renovated in 2007 (left), sampling in northern wing after renovation in 2018 — humidity measurement and hight of a sample (middle), typical section and detail (right), source: photos of the author).

have been developed in the past. Most of them, however, only proved to be partially successful; they do not completely stop the salt-related process of damage [8], sometimes they even intensify material degradation caused by the effect of salts. Detail analysis of the effect of moisture rising from subsoil and construction material degradation caused by salts were presented by Lopez-Arce et al. [9] who complexly assessed these processes at 24 selected historical buildings in Adelaide. What they find essential is the process of landscape urbanization, tree felling and irrigation and the related change (increase) in the groundwater level, the transition of soluble salts into solutions and their migration through the subsoil's pore system up to the surface and foundations of structures.

Moisture in masonry appears in places where damp from the subsoil rises to the plaster and masonry due to capillary suction. The range of the rising pore water is determined by the hygroscopic indexes of the salts, the amount of water in the pores and the level of evaporation [10]. The salts precipitate and crystallize on walls at various heights in the order given by their solubility [11], temperature and relative humidity. Above the ground, the water evaporates from the walls and the solution becomes more concentrated while it is still exposed to capillary rise. As soon as the transported solution is saturated, any further evaporation results in crystallization and immobilization of the salts [12].

The aim of the article is to define the reasons for defects in renovation plasters on the basis of a description of the structure, material analysis of the plasters, available information on the subsoil and on the climate in which the structure is located. Unlike the interaction between air and soil which has been studied in the laboratory [13], the interaction between subsoil with varying content of clay and historical structures has not been studied in situ. The structures studied within this research consist of historical masonry made of solid bricks or natural stone or a combination of bricks and stones whose foundations lack a waterproofing layer [14]. When repairing the buildings, renovation plasters which – due to their porosity and other characteristics – are able to accumulate salts were used [6]. Their main component is calcium hydrate produced by slaking burnt lime gained from dolomitic limestone.

The sulphates causing degradation of construction materials include $MgSO_4$ (magnesium sulphate) or $MgSO_4.7H_2O$ (epsomite / heptahydrate). Other sulphates which, under certain conditions, can damage construction materials are mirabilite $Na_2SO_4 \cdot 10H_2O$ or thenardite Na_2SO_4. The negative effect of these salts is given by their gradual crystallization in the materials' pore systems. The crystallization force of these salts is higher than the strength of the construction materials, which is why damage appears after the pores are filled. Crystallization of some salts may partly be reduced by inhibitors. The DTPMP inhibitor changes the shape of epsomite and magnesium sulphate crystals (development of either of the forms depends on surrounding conditions such as pressure, temperature, pH...) and this modification eliminates the crystallization area and the scope of damage to the material [15]. The inhibitor is based on a phosphorus compound. "Phosphonates are known to absorb on silica and clays, barite, cassiterite, aluminium oxides, iron oxides, gypsum and calcite" [16]. The biological inhibition method is introduced in the study on carbonatogenic bacteria able to "heal" calcites contaminated with $MgSO_4$ [17]. The effect of ATMP-aminotris and DTPMP changing the shape of mirabilite crystals was described in Ref. [18]; the effect of borax as an inhibitor for thenardite under various pH conditions then in Ref. [19].

This study monitors the content of sulphates as one of the main causes, apart from chlorides and nitrates, of damage to masonry. The authors of this article studied the effect of subsoil composition on the migration and accumulation of sulphate salts in the construction materials of selected structures. The study follows an analysis carried out between 1998–2007 when plasters were sampled for a planned renovation of buildings in the eastern part of the Czech Republic and were analysed for salt content and humidity, the above tests were repeated in 2018 for selected structures.

2. Materials

Renovation plasters, due to the porous structure of dolomitic materials, are able to absorb a great amount of salts. The process is similar to the poultice method when a salinized material is lined with a poultice which is then removed after a few weeks or months [20]. Unlike the above method, renovation plasters applied on a structure remain a part of the building for the rest of its lifespan and accumulate a number of chemical elements and compounds over the years. All the structures monitored within this study lack waterproofing (both horizontal and vertical) and, as water is a medium in which salts dissolve and there is no barrier to capillary rise, humidity can flow from the subsoil to the masonry.

The issue of damage caused by the type of soil was dealt with by analysing samples of renovation plasters from the examined buildings and the subsoils on which the structures are located. Within this study, renovation plasters serve as a tool to accumulate salts and enable their further research.

Before the plasters were applied, the damaged structures had been repaired.Old plasters were scraped off and the masonry surface was thoroughly cleaned of the old salinized plasters.

The following renovation plaster layers were used for all the examined structures: Renovation spray HASIT 205 SANIER-Vorspritzmörtel is intended for plastering of damp, salt-loaded interior and exterior masonry; its main compound is limestone

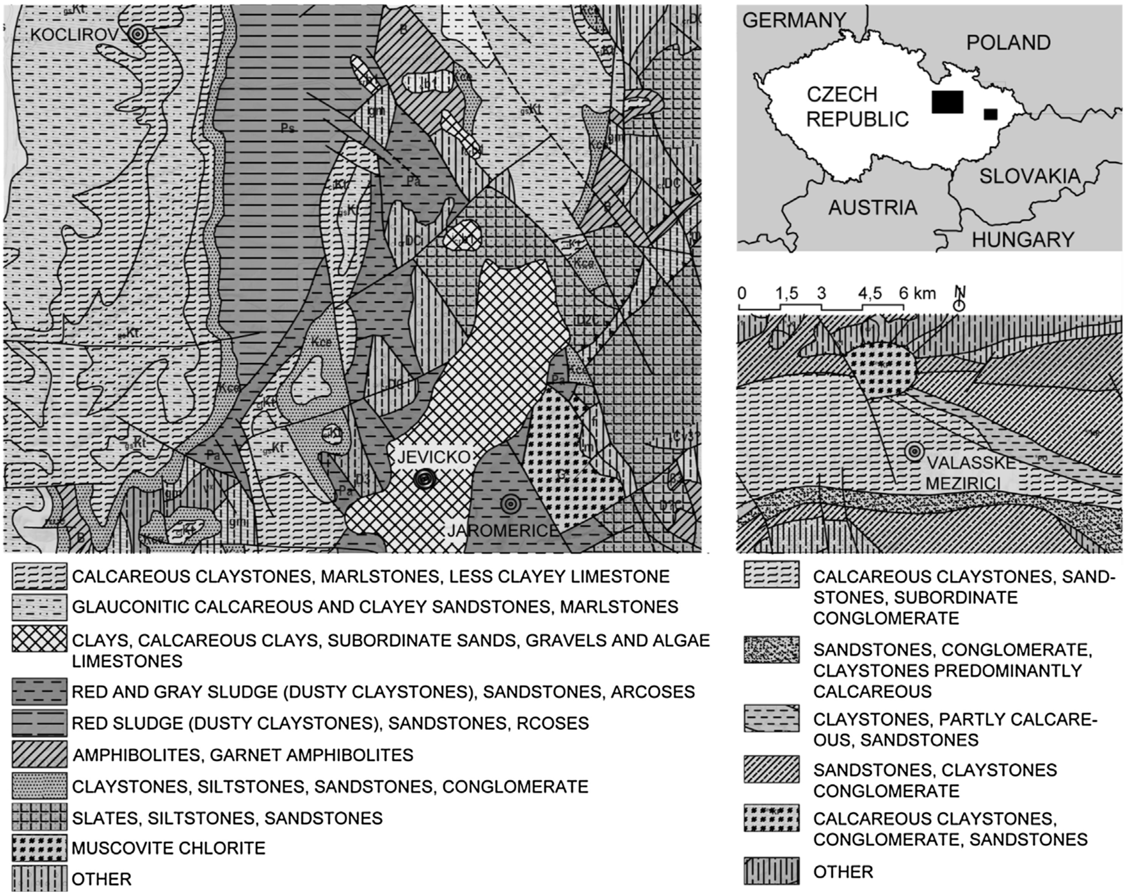

Fig. 2. Simplified geological map with positions of the selected structures in 4 towns: Valašské Meziříčí, Jaroměřice, Jevíčko, Koclířov.

sand. HASIT 208 SANIER-Porenausgleichsputz is intended to level the surface and deposit salts; its main compounds are calcium hydrate and limestone sand (minimum thickness 15 mm). The core layer HASIT 210/200 SANIER-Wandputz is designed to unify the surface and deposit salts; the main compound is calcium hydrate (20 mm). HASIT 212 Feinputz-is intended to form a fine surface texture; the main compound is white calcium hydrate (2 mm). For the final layer was used outdoor silicate coat HASIT PE 228 SILICATE SOL, indoor silicate coat HASIT PI 263 ÖKOSIL or HASIT PE 829 KALSIT — lime masonry paint made of slaked lime aged for 3 years.

The dolomitic limestone used in the renovation plasters is quarried in Velké Hydčice in the Czech Republic. It comprises approximately 70% $CaCO_3$ and 23% $MgCO_3$; the remaining compounds are impurities and other admixtures. The limestone is used to produce calcium hydrate added to plasters; its composition includes CaO (66%) and MgO (13.6%). The original percentage of magnesium is reduced to achieve a lower pH because a more acid environment is required. Dolomitic limestone and its characteristics favourable for historical masonry repairs is described in laboratory tests [21–23]. Salt deposition in the pore system of renovation plasters is enabled by porosity exceeding 40%; this value is required by the standard [24]. The requirement was checked in Valašské Meziříčí Castle 50 cm below the ground with porosity values of 42.9%, 42.6%, 42.5%, 46.0% [14]. Plasters were applied in 1998 and 2001, the analysis was carried out in 2007.

Fig. 1 (right) depicts a characteristic cross-section through historical masonry of combined stones and bricks and a new renovation plaster. Renovation plasters are applied in layers up to a total thickness of 2–4 cm, except from joints. An important detail is the enclosing of the renovation plaster with a steel profile on top of which the plaster is applied. Below the plaster, the dimpled membrane is left loose and fixed only at points to enable air circulation.

Samples of plaster, size 2 × 2 cm, depth 1–2 cm, were taken from the structures by means of a chisel and a hammer. In the course of each sampling, samples were taken in approximately the same positions. The samples were placed in airtight zipper bags immediately after collection, placed in an opaque sample box and taken to the laboratory on the day of collection. Within three days, the samples were analysed for humidity and content of the examined salts.

3. Methods

The analyses were carried out at two independent laboratories: at VSB — Technical University of Ostrava and at the Faculty of Chemistry of the Brno University of Technology. All analyses and samplings followed methodical instructions provided by the authors of this article. The first values of moisture content, mentioned in Results section — Tables 1–5, were laboratory measured by gravimetric method from samples. The second moisture values in brackets were evaluated on site around the point of sampling, with a contact hygrometer UNI 2 GANN, Germany, Hydromette UNI 2, in vertical axes always at several heights above the ground, usually in 50, 100, 150 cm. In each hight the resulting value is the average of five measurements in the immediate vicinity of point of sampling.

Samples were analysed by the same methods before renovation of the structures in 1998–2005 and after the renovation plaster was applied: in 2007 and again in 2018.

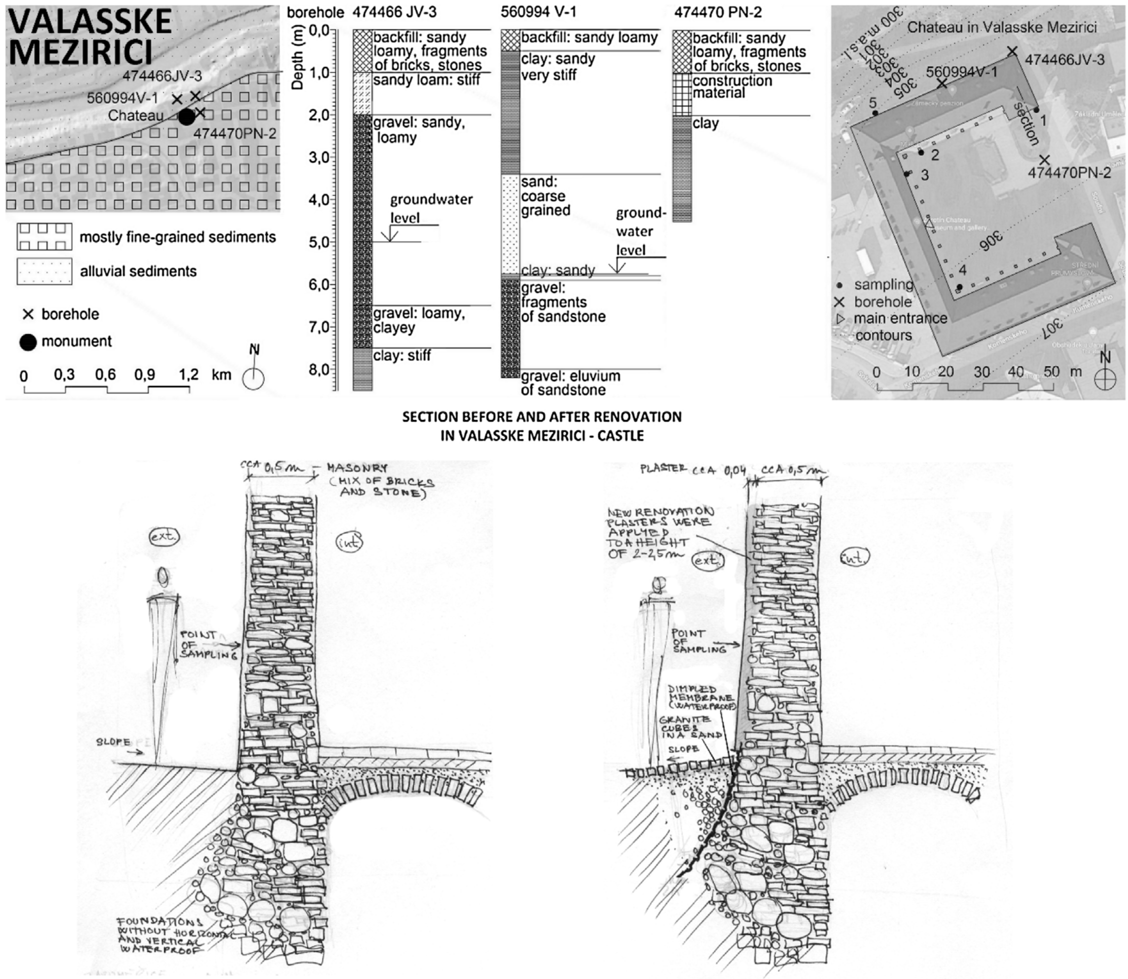

Fig. 3. Layout of Valašské Meziříčí Castle with locations of samples and geological boreholes.

3.1. Preparation of the samples

The prerequisite for quantitative analysis of salts is a representative sample of good quality (clean solid sample, min. 10 g). The sample was dried and pulverized in a mortar-rod mill to a 0.5 mm fraction. A funnel was placed in a dry and clean measuring glass of a volume of 250 mL. A folded S.&S. 595 ½ filter of 110 mm diameter was placed in the funnel. 5 g of the pulverized sample was placed on the filter, rinsed and leached in 250 mL of distilled water heated to 40–60 °C. The funnel was then removed, water was added to the glass to an exact volume of 250 mL, the glass was capped and shaken.

pH of the leachate was checked. If the value was lower than pH 4, the leachate was modified with sodium acetate, if it was higher than pH 8, tartaric acid was added. To define the sulphates with a test strip, the value of pH had to range between 4 and 8. The content of salts was defined by the Merckoquant method; the procedure has been described, e.g., by Mills et al. [25].

SEM, Scanning Electron Microscopy, was carried out on selected samples (one from each structure, from samples collected in 2018). Photos were taken using a Zeiss Evo LS 10 (W cathode). The XRD analysis was carried out using EMPYREAN provided by the Panalytical company. The experimental conditions in the laboratory were stable, ca. 23 °C, humidity ca. 50%.

The study included research of the geological conditions in the involved locations. Data on the subsoil composition were gathered from the Czech Geological Survey [26,27], geological maps of suitable scales were used. A schematic geological map with subsoils and locations of the examined structures compiled from data gathered from the Geological Survey [22] was used as an indicative source of information (Fig. 2). Frequently occurring clay and loam differ in the size of particles and their characteristics (the size of clay particles is smaller than 0.002 mm, the size of loam particles is 0.002–0.06 mm) [28].

The statistical methods used in the final analysis were carried out in the STATGRAPHICS Plus 5.0 software. Within the conclusion of the study, the hypotheses were tested and a regression analysis of their probability expressed by P-value [29,30].

4. Results

Structures selected for this study are under preservation orders: the castle in Valašské Meziříčí, church in Jaroměřice, castle in Jevíčko and church in Koclířov; plus one non-historical monument — a school in Jevíčko. Seasonal temperatures in the examined area drop to ca. −10 °C in winter and rise to ca. 30 °C in summer.

4.1. Castle in Valašské Meziříčí

The castle is three-wing building with renaissance arcade from 1538. The first part of renovation was carried out in 1998 on the northern wing, the next one in 2001 in the courtyard (Figs. 1 and 3, Table 1), the southern wing wasn´t renovated in 2007 yet. New plasters were visually in excellent condition in both survey in 2007 and 2018.

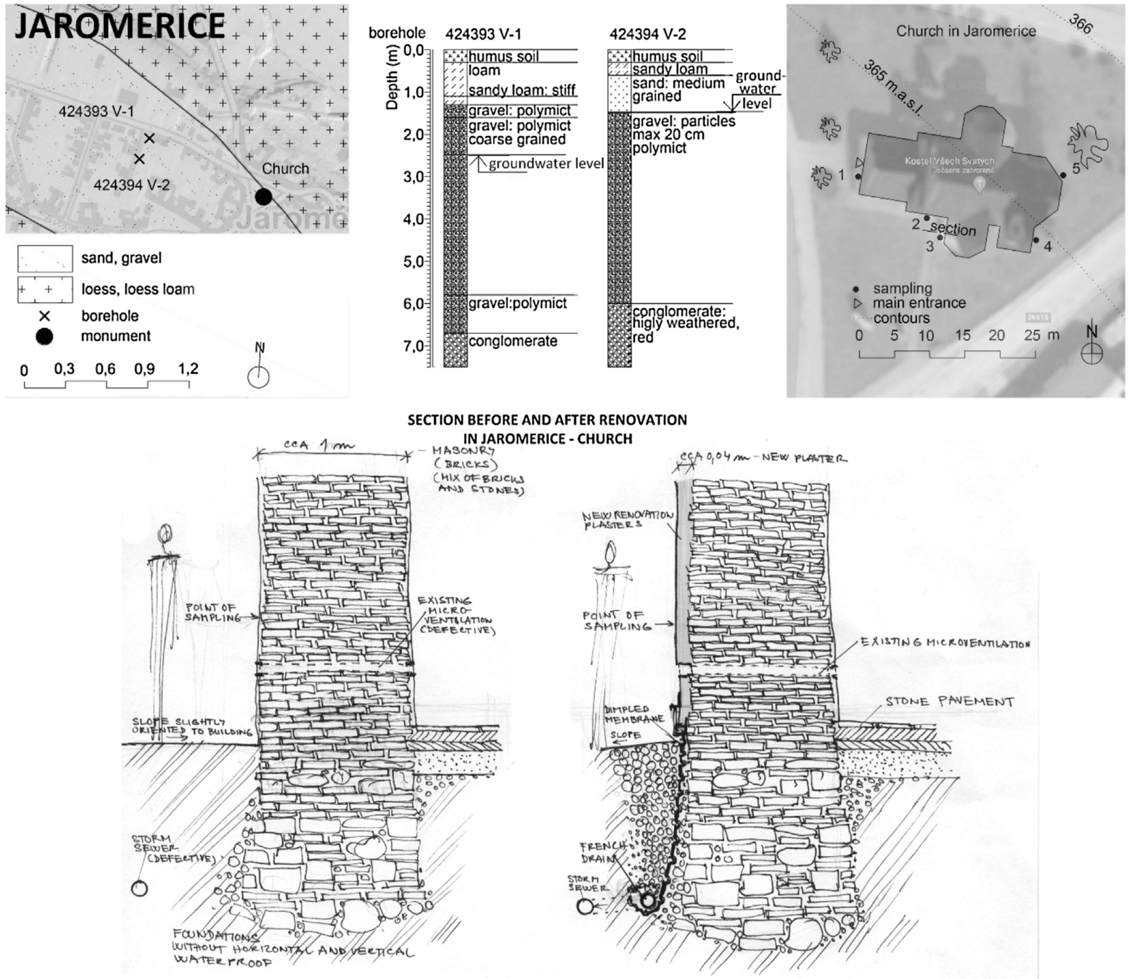

Fig. 4. Layout of the Jaroměřice church with locations of samples and geological boreholes.

4.2. Church in Jaroměřice

The masonry dates back to the 12th century, the Gothic period.

The building was in poor condition before the renovation. Defective drainpipes and drainage combined with ground sloping unfavourably towards the building caused increased humidity of the masonry up to a height of 3 m. The masonry and plasters deteriorated around the cornices. The first works focused on repairing the roof, drainpipes, gutters and good sloping of the French drain around the building that carries water away from the structure. Vertical waterproofing down to the foundation base and drainage down to the waterproofing bottom edge level were additionally applied. The outlet of the masonry ventilation system is placed ca. 1 m above ground. After that, renovation plasters were applied 50 cm above the visible masonry damp. The last step, was supposed to be a coat of Silikat 790 which is air-permeable and water-repellent. However, an unsuitable acrylic coat was used.

The survey from 2007 showed a poor visual state of the church. Coat that peels off and white patches indicate poor quality of the repairs. This was, apart from others, caused by the unsuitable final finish which prevents the renovation plaster from drying and seals the surface. Yet another mistake within this renovation was the use of gypsum for minor repairs even though it had been strictly prohibited by the contractor.

The survey in 2018 showed a similar or perhaps even worse situation than in 2007. The chapel walls are up to 1 m thick and degraded plasters and damp patches are visible in the church interior (Fig. 4, Table 2).

The exterior of the oldest part implies a more serious issue than just an unsuitable final finish. There seem to be defects of the drainage system and the ventilation system probably fails to fulfil its function.

4.3. Castle in Jevíčko

Originally a fortress from 1559 that was converted into a castle in the 18th century (Fig. 5). The structure is built of solid bricks with a cellar under a part of the layout (Table 3).

The surrounding ground originally sloped unfavourably towards the structure and the façade had lacked maintenance. Before the renovation plasters were applied, a French drain of coarse river gravel, fraction 35–120 mm, was made to reduce rainwater backsplash on the façade and enable soaking into the soil in the proximity of the structure.

Renovation plasters were applied in the interior and the exterior plinth plasters were replaced by renovation plaster, too. Visual inspection from 2007 documented the excellent state of the structure, which was also confirmed in 2018.

4.4. School in Jevíčko

The school is located ca. 200 m from the castle (Fig. 5). The main subject of the renovation in 2003 was the basement. Construction of the school started in 1898 Plasters were disrupted and the basement masonry was damp, in some places up to the ceiling, a storm sewer was defective during the survey in 2003. Before the reno-

Table 1
Results for samples taken at Valašské Meziříčí Castle.

Valašské Meziříčí — castle		Date of sampling			
	Before rehabilitation	After rehabilitation — new plasters			
		17.4.1998	24.5.2001	25.1.2007	19.7.2018
Actual weather		–	–	Snowfall	Cloudy/rainy
Temperature		–	–	−5 °C	19 °C
1. *Courtyard (sample material: mortar)	height of sampling		100 cm	100 cm	100 cm
	humidity		5.7%	1.4%	2.9% (2.9%)
	pH		6.4	6	5
	Cl^-		<2.0 mg/g	0 mg/g	0 mg/g
	NO_3^-		3 mg/g	0 mg/g	1.3 mg/g
	SO_4^{2-}		0 mg/g	10 mg/g	2 mg/g
2. Arcade in courtyard (sample material: plaster)	height of sampling		300 cm	–	100 cm
	humidity		2.6%	–	3.0% (3.1%)
	pH		6.3	–	5
	Cl^-		< 2.0 mg/g	–	0 mg/g
	NO_3^-		1 mg/g	–	1.3 mg/g
	SO_4^{2-}		0 mg/g	–	1 mg/g
3. Arcade in courtyard	height of sampling		200 cm	–	100 cm
	humidity		10.1%	–	1.9% (2.2%)
	pH		6.2	–	6
	Cl^-		> 5.0 mg/g	–	0 mg/g
	NO_3^-		3 mg/g	–	0.5 mg/g
	SO_4^{2-}		< 5.0 mg/g	–	2 mg/g
4. The terrace side by the river	height of sampling	100 cm		100 cm	100 cm
	humidity	–		2,5%	4.4% (4.6%)
	pH	–		6	6
	Cl^-	< 2.0 mg/g		0 mg/g	0 mg/g
	NO_3^-	1.0–3.0 mg/g		1.3 mg/g	0.5 mg/g
	SO_4^{2-}	0 mg/g		15 mg/g	2 mg/g
5. Arcade in courtyard	height of sampling		–	100 cm	100 cm
	humidity		–	1.4%	2.8% (3.3%)
	pH		–	6	4
	Cl^-		–	0 mg/g	0 mg/g
	NO_3^-		–	0.5 mg/g	2.5 mg/g
	SO_4^{2-}		–	10 mg/g	1.5 mg/g

Table 2
Results for samples taken at the Jaroměřice church.

Jaroměřice — church		Date of sampling		
	Before rehabilitation	After rehabilitation — new plasters		
		1999	1.2.2007	19.7.2018
Actual weather		–	–	cloudy/rainy
Temperature		–	–	19 °C
1.	Height of sampling	–	–	100 cm
	Humidity	10,0%	7,2%	5,4% (5,1%)
	pH	–	6	8
	Cl^-	2.0–5.0 mg/g	0 mg/g	0 mg/g
	NO_3^-	1 mg/g	0.5 mg/g	0.5 mg/g
	SO_4^{2-}	5 mg/g	10 mg/g	0 mg/g
2.	Height of sampling	–	–	100 cm
	Humidity	–	–	6,2% (5,9%)
	pH	–	–	8
	Cl^-	5 mg/g	–	0 mg/g
	NO_3^-	< 1.0 mg/g	–	0.5 mg/g
	SO_4^{2-}	5 mg/g	–	0 mg/g
3.	Height of sampling	–	–	100 cm
	Humidity	–	–	6,5% (6,2%)
	pH	–	6	8
	Cl^-	–	0 mg/g	0 mg/g
	NO_3^-	–	0 mg/g	0.8 mg/g
	SO_4^{2-}	–	10 mg/g	0 mg/g
4.	Height of sampling	–	–	100 cm
	Humidity	–	–	8,2% (8,0%)
	pH	–	–	7
	Cl^-	2.0–5.0 mg/g	–	0 mg/g
	NO_3^-	< 1.0 mg/g	–	0.8 mg/g
	SO_4^{2-}	5.0–15.0 mg/g	–	6 mg/g
5.*	Height of sampling	–	–	100 cm
	Humidity	6,0%	11,1%	8,4% (8,1%)
	pH	–	6	7
	Cl^-	< 2.0 mg/g	0 mg/g	0 mg/g
	NO_3^-	1 mg/g	0.3 mg/g	0.8 mg/g
	SO_4^{2-}	< 5.0 mg/g	10 mg/g	6 mg/g

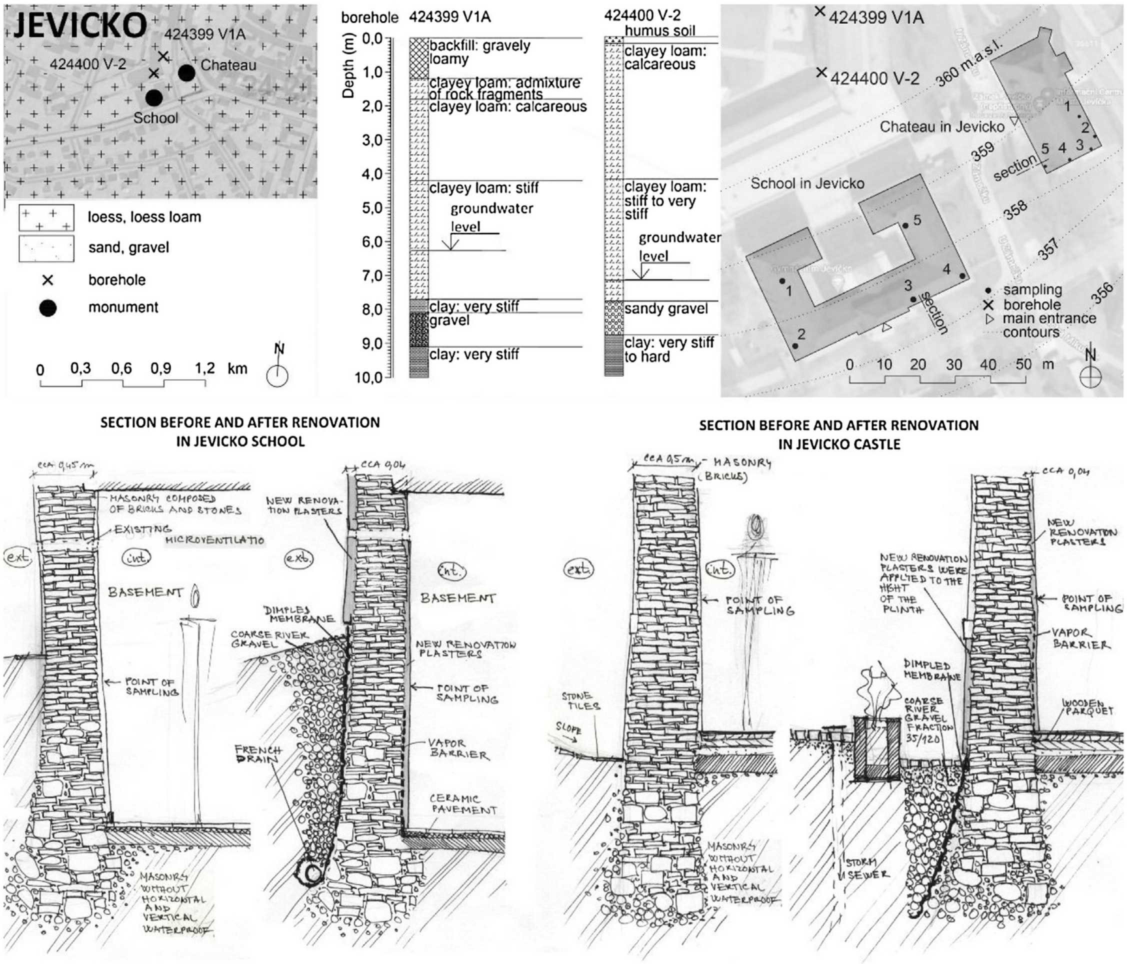

Fig. 5. Layout of the Jevíčko castle and school with locations of samples and geological boreholes.

vation, vertical waterproofing was provided on the perimeter of the building from the foundation base up to 5 cm above the new ground. New renovation plasters started on top of the enclosing profiles above the ground (Fig. 2).

In 2007 not all the works had been completed. The survey in 2018 showed that radiators designed to dry the masonry had been added in the basement and patches and efflorescence appeared in some places. Boreholes into the underlying rock are identical to those for the castle (Fig. 5). An increase in sulphates was recorded (Table 4).

4.5. Church in Koclířov

The building in Koclířov was first mentioned in 1349 (Fig. 6, Table 5).

The first research of the structure was carried out just before the renovation in 2006 and proved that plasters had peeled off from both the interior and exterior walls.

Tombs adjacent to the church walls prevented exterior repairs. The renovation therefore focused on the interior, which was in a bad state. Checks in 2007 provided results after only a year of effect of the renovation plaster, which is not a relevant result. Real values were collected in the survey in 2018 (Table 5). In this case, the samples were only taken from the interior. The custodians of the church eliminated the humidity by radiators located along the walls and also by a suitably used stone pavement with joints enabling penetration of damp.

Once the data had been examined, the structures were divided into two groups according to the subsoil on which they are built. In the case of Valašské Meziříčí Castle and Jevíčko Castle and school, the soil contains clay (Tables 1, 3 and 4). Group two includes the Jaroměřice church and the Koclířov church, whose subsoils are free of clay (Tables 2 and 5). Salt contents according to this classification are shown in the box diagrams below (Fig. 7).

Nitrates increased in 2018 (Fig. 7), which may relate to the season as the samples were taken in summer when soils contain higher amounts of organic matter. The decrease in chlorides in plasters down to zero in 2018 implies that the plasters are able to rid themselves of chlorides. The previous higher content of chlorides in plasters might also have been caused by road salting (using NaCl) as gritting has prevailed in in recent winters.

Some values before renovation and in 2007 were only recorded in classes (evaluation according to WTA 2005, Table 5, [6]), not in mg/g, which is why ranges of values are sometimes provided in the tables. In the case of classes, arithmetic means were considered for boxplots; in the case of the "greater than" sign, the nearest following figure was assumed.

Further analysis focused on selected samples which were examined under a SEM microscope (Scanning Electron Microscopy) — micrographs of the plasters and diffractograms of the contents of the respective compounds (Fig. 8). One sample of plaster was analysed from each of the structures (in Tables 1–4 they are marked with an asterisk, from sampling in 2018). The Koclířov church was not accessible for a long time and taking samples for the analysis was thus prevented.

Table 3
Results for samples from Jevíčko Castle.

Jevíčko castle		Date of sampling		
		Before rehabilitation	After rehabilitation — new plasters	
		24.5.2001	14.9.2007	19.7.2018
Actual weather		–	–	Cloudy/rainy
Temperature		–	–	19 °C
Interior 1 — library	Height of sampling	–	–	100 cm
	Humidity	13,1% (in 100 cm)	–	2,1% (1,9%)
	pH	–	–	7
	Cl^-	<2.0 mg/g	–	0 mg/g
	NO_3^-	>3.0 mg/g	–	2.5 mg/g
	SO_4^{2-}	<5.0 mg/g	–	5 mg/g
Interior 2 — library	Height of sampling	–	–	100 cm
	Humidity	–	–	2,2% (2,0%)
	pH	–	–	8
	Cl^-	–	0 mg/g	0 mg/g
	NO_3^-	–	0 mg/g	7.5 mg/g
	SO_4^{2-}	–	< 5.0 mg/g	5 mg/g
Interior 3* — library	Height of sampling	–	–	100 cm
	Humidity	11,1% (in 100 cm)	–	2,7% (2,5%)
	pH	–	–	10
	Cl^-	<2.0 mg/g	–	0 mg/g
	NO_3^-	>3.0 mg/g	–	7.5 mg/g
	SO_4^{2-}	5.0–15.0 mg/g	–	6 mg/g
Interior 4 — library	Height of sampling	–	–	100 cm
	Humidity	–	–	2,6% (2,1%)
	pH	–	–	8
	Cl^-	0 mg/g	0 mg/g	0 mg/g
	NO_3^-	1.0–3.0 mg/g	0 mg/g	1.5 mg/g
	SO_4^{2-}	5.0–15.0 mg/g	< 5.0 mg/g	6 mg/g
Interior 5 — library	Height of sampling	–	–	100 cm
	Humidity	10,5% (in 100 cm)	–	2,9% (2,4%)
	pH	–	–	8
	Cl^-	<2.0 mg/g	0 mg/g	0 mg/g
	NO_3^-	>3.0 mg/g	< 1.0 mg/g	1 mg/g
	SO_4^{2-}	<5.0 mg/g	0 mg/g	5 mg/g

Table 4
Results for samples taken from the Jevíčko school.

Jevíčko church		Date of sampling		
		Before rehabilitation	After rehabilitation — new plasters	
		2003	2007	19.7.2018
Actual weather		–	–	Cloudy/rainy
Temperature		–	–	19 °C
Interior 1 — basement	Height of sampling	–	–	100 cm
	Humidity	11,6%	1,6%	4,2% (4,0%)
	pH	–	–	8
	Cl^-	0 mg/g	–	0 mg/g
	NO_3^-	1.3 mg/g	–	5 mg/g
	SO_4^{2-}	0 mg/g	–	5 mg/g
Interior 2 — basement	Height of sampling	–	–	100
	Humidity	5,4%	1,6%	4,1% (3,8%)
	pH	–	–	7
	Cl^-	< 2.0 mg/g	–	0 mg/g
	NO_3^-	> 3.0 mg/g	–	12.5 mg/g
	SO_4^{2-}	< 5.0 mg/g	–	5 mg/g
Interior 3 — basement	Height of sampling	–	–	100 cm
	Humidity	11,5%		3,8% (3,2%)
	pH	–	–	8
	Cl^-	–	–	0 mg/g
	NO_3^-	–	–	15 mg/g
	SO_4^{2-}	–	–	5 mg/g
Interior 4* — basement	Height of sampling	–	–	100 cm
	Humidity		1,0%	3,0% (2,5%)
	pH	–	–	6
	Cl^-	0 mg/g	–	0 mg/g
	NO_3^-	< 1.0 mg/g	–	1.3 mg/g
	SO_4^{2-}	< 5.0 mg/g	–	6 mg/g
Interior 5 — basement	Height of sampling	–	–	100 cm
	Humidity	–	1,9%	3,1% (2,8%)
	pH	–	–	8
	Cl^-	–	–	0 mg/g
	NO_3^-	–	–	0.5 mg/g
	SO_4^{2-}	–	–	0 mg/g

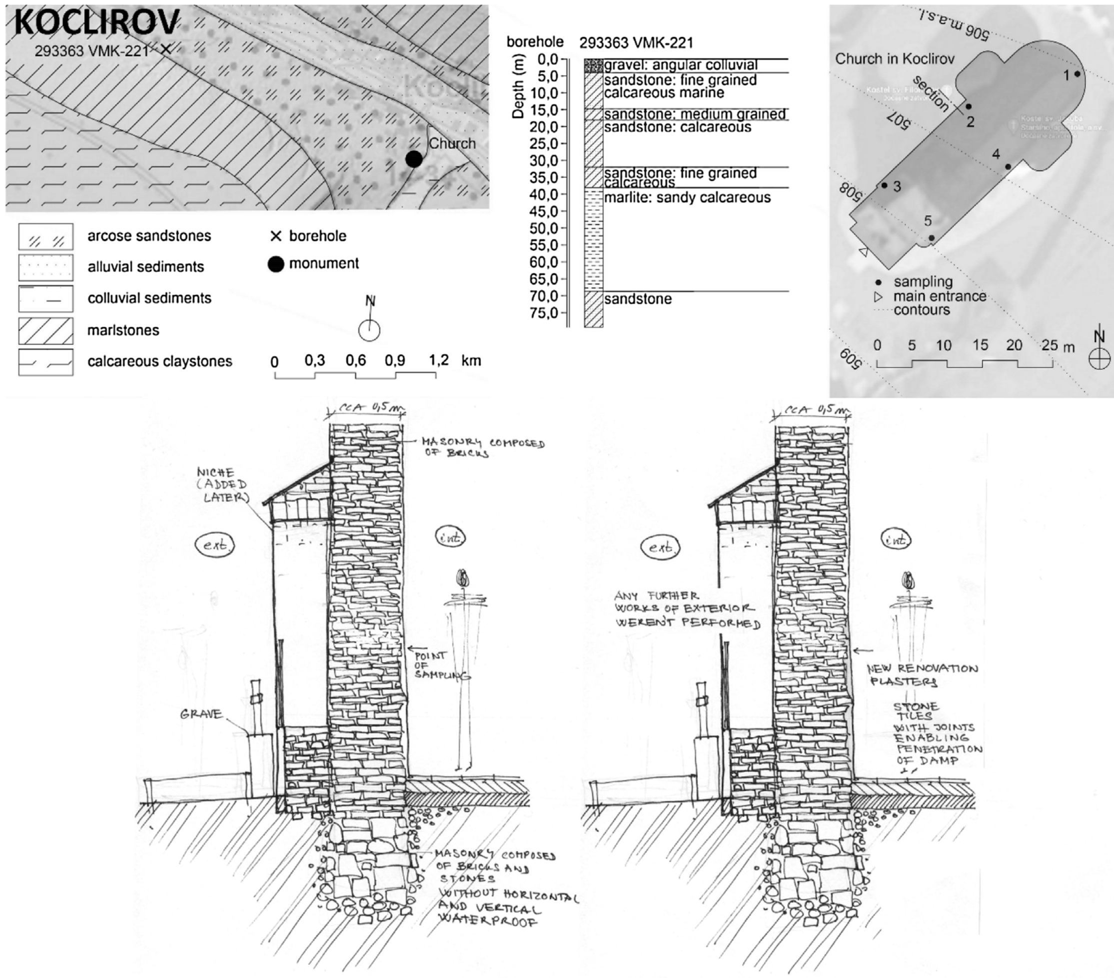

Fig. 6. Layout of the Koclířov church with locations of samples and geological boreholes.

SEM microphotographs and diffractograms show that the bearing part of the mass consists of calcite, dolomite and silicon oxide. The other elements are crystallized on their surface. Peak list showed Phyllosilicates: 7-Clinochlore (Chlorite group), 9-Muskovite (Mica group), 10-Kaolinite (Clay Minerals group), 12-Phlogopite (Mica group, metamorphosed limestone and dolomite).

The Shapiro-Wilk test for normality proved that the data significantly deviate from a normal distribution in both cases, structures on non-clay and clayey subsoils, since P-value is less than 0,05 (Fig. 9). The Kruskal–Wallis test [29] (does not assume the normality in the data) was used to detect statistically significant changes over time in the two groups of buildings. A null hypothesis on identical medians of several groups, three in this case, was tested: before

Table 5
Results for samples taken at the Koclířov church.

Koclířov church		Date of sampling		
		Before rehabilitation	After rehabilitation of interior — new plasters	
		8.9.2005	2007	6.9.2018
Actual weather		–	–	Sunny
Temperature		–	–	20 °C
Interior 1	Height of sampling	100 cm	100 cm	100 cm
	Humidity	4,9%	1,9%	1,8% (4,2%)
	pH	–	–	5
	Cl^-	< 2 mg/g	–	0 mg/g
	NO_3^-	3 mg/g	–	0 mg/g
	SO_4^{2-}	5.15 mg/g	–	2 mg/g
Interior 2	Height of sampling	100 cm	100 cm	100 cm
	Humidity	6,6%	1,6%	2,8% (4,1%)
	pH	–	–	5
	Cl^-	0 mg/g	–	0 mg/g
	NO_3^-	> 3.0 mg/g	–	0.5 mg/g
	SO_4^{2-}	15 mg/g	–	2 mg/g

Table 5 (*Continued*)

Koclířov church		Date of sampling		
		Before rehabilitation	After rehabilitation of interior — new plasters	
		8.9.2005	2007	6.9.2018
Actual weather		–	–	Sunny
Temperature		–	–	20 °C
Interior 3	Height of sampling	100 cm	100 cm	100 cm
	Humidity	6,1%	1,9%	2,4% (3,8%)
	pH	–	–	5
	Cl^-	–	0 mg/g	0 mg/g
	NO_3^-	–	0 mg/g	0.5 mg/g
	SO_4^{2-}	–	0 mg/g	2 mg/g
Interior 4	Height of sampling	100 cm	100 cm	100 cm
	Humidity	4,9%	1,8%	3,1% (3,5%)
	pH	–	–	5
	Cl^-	0 mg/g	0 mg/g	0 mg/g
	NO_3^-	> 3.0 mg/g	< 1.0 mg/g	0.5 mg/g
	SO_4^{2-}	5.0–15.0 mg/g	0 mg/g	2 mg/g
Interior 5	Height of sampling	100 cm	100 cm	100 cm
	Humidity	6,9%	1,6%	2,9% (4,1%)
	pH	–	–	5
	Cl^-	–	–	0 mg/g
	NO_3^-	–	–	0.2 mg/g
	SO_4^{2-}	–	–	2 mg/g

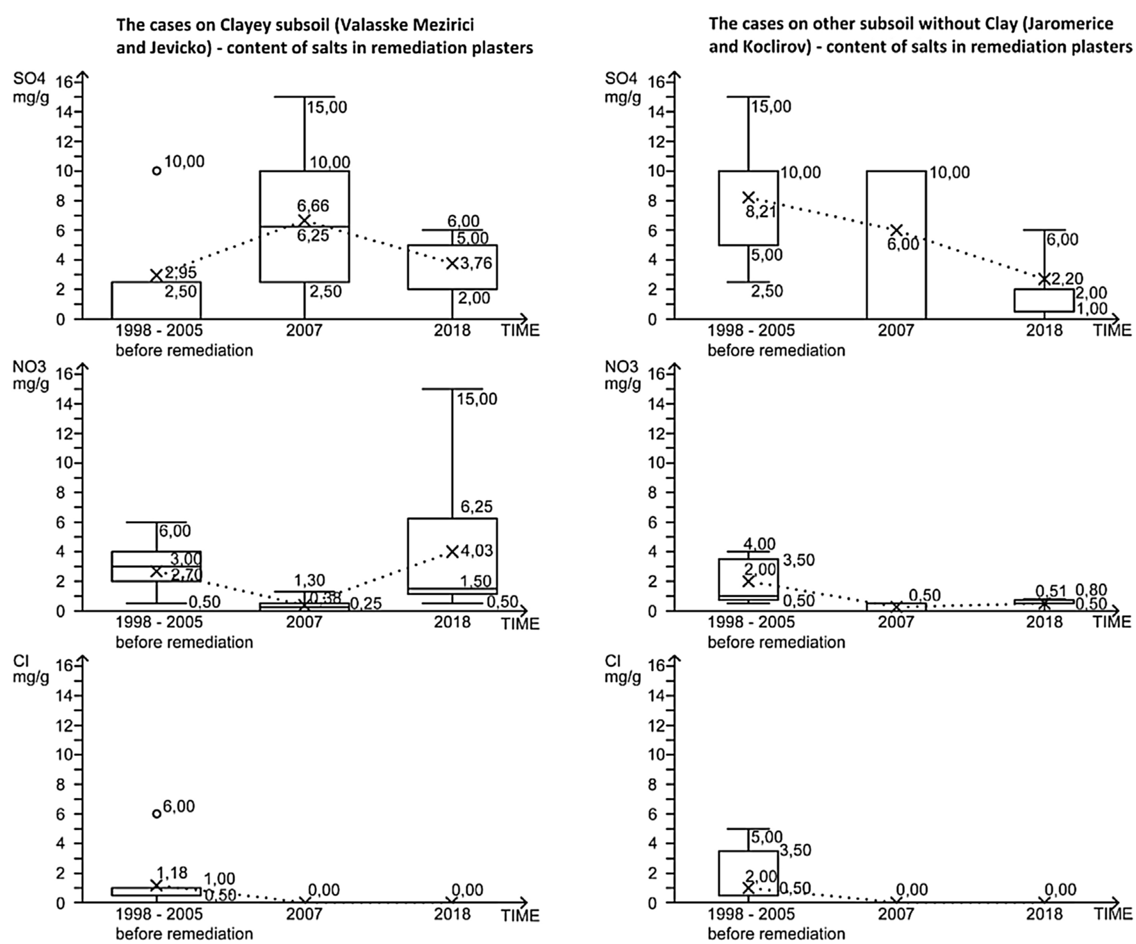

Fig. 7. Salinity box diagrams from three sampling times: 1998-2005 before renovation and twice after renovation in 2007 and 2018.

renovation and then in 2007 and 2018. The first three times groups on the clay-free soils statistically significantly differ in time. The other three times groups of sampling on clayey subsoils do not statistically differ (Fig. 9).

It was therefore possible to create a regression model in time for the first data set from buildings on non-clayey soils (Jaroměřice and Koclířov, 22 values of sulphate content, Fig. 9 on the left). The quality of regression model is given by number of samples and number of sampling in a time. The quality is then expressed by value of R-square, the number of data that fits the chosen model, “but R^2 based values do not clearly identify the data shape” [31], thus this value varies with a type of a model. Model should follow the nature

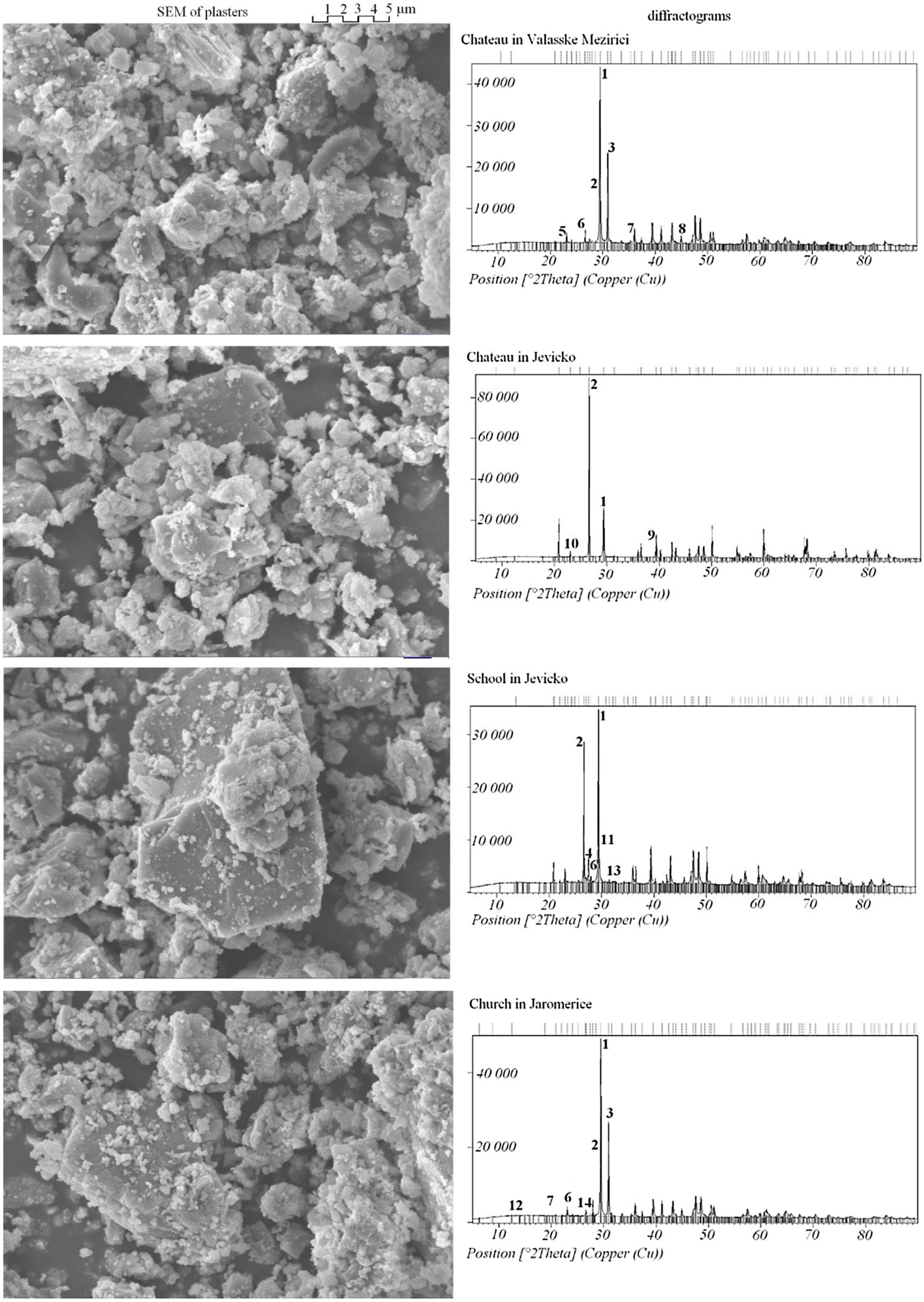

Fig. 8. SEM microphotographs and diffractograms, Peak list: 1 — $CaCO_3$; Calcium Carbonate; Calcite; Rhombohedral; R-3c; 2 — SiO_2; Silicon Oxide; Quartz; Hexagonal; 3 — $CaMg(CO_3)_2$; Calcium Magnesium Carbonate; Dolomite; Rhombohedral; R-3; 4 — $K(AlSi_3)O_8$; Potassium Aluminum Silicate; Orthoclase; SQ: 8 [%] Monoclinic; C2/m; 5 — (K0.94Na0.06)(AlSi3O8); Potassium Aluminum Silicate; Orthoclase; SQ: 3 [%], Monoclinic; C2/m; 6 — Na(AlSi3O8); Sodium Aluminum Silicate; Albite; Anorthic; C-1; 7 — (MgFeAl)(SiAlO10)(OH)8; Magnesium Iron Aluminum Silicate Hydrate; Clinochlore; Monoclinic; C2/m; 8 — $(NaK)(CaFe)(MgFeAl)(Si_7AlO_{22})(OH)_2$; Sodium Potassium Calcium Iron Magnesium Aluminum Silicate Hydroxide; Magnesiohornblende ferrous; Monoclinic; C2/m; 9 — KAl(Si3Al)O10((OH)O);Potassium Aluminum Silicon Oxide Hydroxide; Muskovite; Monoclinic; C2/c ; 10 — Al2Si2O5(OH)4; Aluminum Silicate Hydroxide; Kaolinite; Monoclinic; Cc ; 11 — CaCO3; Calcium Carbonate; Vaterite; syn; Hexagonal; F63/mmc ; 12 — (KNa)(MgAlFe)(AlSi)O10((OH)F); Potassium Sodium Magnesium Aluminum Iron Silicate HydroxideFluoride; Phlogopite 1 M; Monoclinic; C2/m ; 13 — $Ca_2(SiO_4)$; Calcium Silicate; Larnite; Monoclinic; P21/n; 14 — TiO_2; Titanium Oxide; Rutile; Tetragonal; P42/mm.

```
Plasters of buildings on subsoil without Clay
(Jaromerice, Koclirov)
N=22 samples
mean=4,03125
variance=20,39232
alpha=0,05 (95% confidence level)
Shapiro-Wilk test W=0,87168 Threshold (p=0.05) = 0.91100 --> H0 rejected
Kruskal-Walis test H=6,1043 p-value=0,04726 --> H0 retain

Regression Analysis - Linear model: Y = a + b*X
-----------------------------------------------------------------
Dependent variable: SO4 content  mg_g
Independent variable: time year
-----------------------------------------------------------------
                      Standard        T
Parameter   Estimate     Error    Statistic    P-Value
-----------------------------------------------------------------
Intercept    597,791    228,207    2,61951     0,0164
Slope      -0,294892    0,11352   -2,59772     0,0172
-----------------------------------------------------------------
                 Analysis of Variance
-----------------------------------------------------------------
Source        Sum of Squares   Df  Mean Square  F-Ratio   P-Value
-----------------------------------------------------------------
Model             108,038      1    108,038      6,75     0,0172
Residual          320,201     20     16,01
-----------------------------------------------------------------
Total (Corr.)     428,239     21

Correlation Coefficient = -0,502279
R-squared = 25,2284 percent
R-squared (adjusted for d.f.) = 21,4898 percent
Standard Error of Est. = 4,00125
Mean absolute error = 3,26161
Durbin-Watson statistic = 1,33097
   for alpha=0,05 d(L)=1,24; d(U)=1,43
   for alpha=0,01 d(L)=1,00; d(U)=1,17
```

```
Plasters of buildings on Clayey subsoil
(Valasske Mezirici, Jevicko castle, Jevicko school)
N=32 samples
mean=4,97729
variance=13,61190
alpha=0,05 (95% confidence level)
Shapiro-Wilk test W=0.86908 Threshold (p=0.05) = 0.93000 --> H0 rejected
Kruskal-Walis test H=1,9119 p-value=0,38444 --> H0 rejected

Regression Analysis - Linear model: Y = a + b*X
-----------------------------------------------------------------
Dependent variable: SO4 content  mg_g
Independent variable: time year
-----------------------------------------------------------------
                      Standard        T
Parameter   Estimate     Error    Statistic    P-Value
-----------------------------------------------------------------
Intercept    320,848    240,815    1,33234     0,1939
Slope      -0,157217   0,119894   -1,3113      0,2008
-----------------------------------------------------------------
                 Analysis of Variance
-----------------------------------------------------------------
Source        Sum of Squares   Df  Mean Square  F-Ratio   P-Value
-----------------------------------------------------------------
Model             39,4779      1    39,4779      1,72     0,2008
Residual          619,884     27    22,9587
-----------------------------------------------------------------
Total (Corr.)     659,362     28

Correlation Coefficient = -0,244689
R-squared = 5,98728 percent
R-squared (adjusted for d.f.) = 2,50533 percent
Standard Error of Est. = 4,79152
Mean absolute error = 4,10363
Durbin-Watson statistic = 1,06219 (P=0,0017)
   for alpha=0,05 d(L)=1,37; d(U)=1,50
```

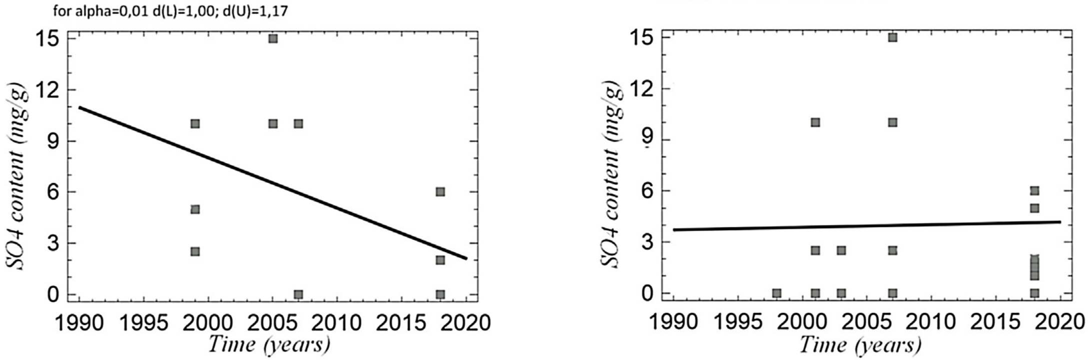

Fig. 9. Statistic data and model of the regression analysis of sulphate content over time in plasters.

of data. R-Square value is then relative to chosen model, variance of data (σ), number of data (N) and also chosen significance level (α) [31–33]. The quality of the model is also expressed by F test, F-Ratio and its P-value (Fig. 9 left). Since the P-value in the ANOVA table is less than 0.05, there is a statistically significant relationship between SO4 content and time in year at the 95% confidence level. Durbin-Watson statistic tests the residuals to determine if there is any significant correlation based on the order in which they occur in a data file. The D–W value is 1,33097 and for alpha = 0,05 lies inside the interval (1,24;1,43) and the test is therefore inconclusive. For alpha = 0,01 is D–W value higher than the upper critical value (1,00;1,17), what means that there is no statistical evidence that the error terms are positively autocorrelated. It indirectly confirmed that the model used is adequate.

The general notation of the function course is $Y = a + b \times X$, where Y is the dependent variable (content of SO_4 in mg/g) and X is the independent variable (time in years) (Fig. 9).

For comparison purposes, a regression model of the other group of buildings on clayey soils was also created (Valašské Meziříčí and the two structures in Jevíčko, 32 values of sulphate content, Fig. 9 on the right) though it is illogical in terms of the statistics because the Kruskal–Wallis test proved that the medians are identical. Sulphate dependence on time was therefore rejected and sulphate content is constant in time. This is also proved by the Intercept and Slope coefficients which are, in this case, zero on a 95% confidence level (Fig. 9).

5. Discussion

Analyses (boxplots in Fig. 7) imply a significantly different content of sulphates on clayey soils, where an increase was recorded; on the other hand, on soils with a low share of clay compound, the values decreased. By means of the boxplots, a variation of values was documented in 2007 for structures on clayey soils where the values increased considerably compared to the previous measurements and then decreased again in 2018. The variation could have been caused by other sources of sulphates from the atmosphere or hydrosphere or by pure fluctuation in the humidity of the subsoil and the implied change in conditions for salt transportation. Clayey soils have a specific structure of particles (elements smaller than 0.002 mm), which may retain sulphate salts and may, under favourable conditions, migrate to the foundations of buildings. As for the processes, the process of water absorption in the mineral structure (swelling and shrinkage) needs to be considered on clayey subsoils with a high content of a smectite group clayey mineral (as for example montmorillonite). Another process which may take place in them is cation exchange within which specific cations from solutions may replace the original cations of the clayey mineral.

Apart from these specific processes related to the smectite, usual adsorption of water or solutions on the surface of clayey mineral particles shall be assumed as well as potential salt crystallization among clay particles.

The linear regression model of samples from Jaromerice and Koclirov (Fig. 9 left) showed F-test with P-value less than significance level α (0,05) and so the data provide sufficient evidence to conclude that regression model fits the data better than the model with no independent variables. The number of samples is N = 22, what is relatively enough data to prove this analysis, on the other hand the Variance is quite big σ = 20,39232, what means the data are very spread out from the Mean x− = 4,03125. R^2 value is 25,2284%, what means, that a quarter of the data fits the model, what is suitable, when statistically significant coefficients of variables on 95% confidence level (Intercept with P-value = 0,0164, Slope with P-value 0,0172, Fig. 9) continue to represent the mean change in the dependent variable given a one-unit shift in the independent variable [29,30]. F-test confirms that the independent variable in the model improve the fit and the model is adequate for the data. Durbin-Watson statistic also indirectly confirmed, that the model used is adequate for alpha = 0,01.

6. Conclusion

Geotopographic position and the type of subsoil on which the structures are built were researched in this study as a reason for damage to the buildings by analysing the salts deposited in renovation plasters on two types of subsoils — clayey soil and silty to sandy soil. The results of salt content analyses before renovation of the buildings and twice after the renovation (time period of 1998–2018) were compared as well as profiles of the subsoils on which the structures are situated.

The difference in salt content indicates a different migration of solutions depending mainly on the different capillary rise of moisture. The rise of moisture is conditionally based on the content of pore water in the foundation soil. It depends on precipitation, humidity, sunlight, soil and building materials temperature, pore system etc. Based on the research, it seems to be a significant influence, among other things, the type of foundation soil, which conditions the further spread of moisture and thus salts in the masonry of the studied buildings.

Renovation plasters may be used as a tool to retain and subsequently research the salts and elements originating from the surrounding of buildings. Salt accumulation is ensured by their required 40% minimum porosity and the technological process of their application in layers.

The regression analysis proved independence of time for sulphate content in plasters on structures built on soils containing an increased share of clayey minerals while in plasters of structures on subsoils with a low content of clayey minerals, sulphate content decreased between 1998 and 2018. Use of the regression analysis is a very suitable method in the case of salt content in plasters and is also predictive; in this case it predicts the results for 2020. The regression analysis is moreover robust for the statistical condition of normal distribution so the data do not have to meet the presumption. Normal distribution is mostly met by data sets with a large number of values; this analysis is therefore also suitable for smaller data sets. The study evaluated a total of 54 samples taken in situ, divided into two groups.

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