Materials and technologies of historical buildings - case study of two Danube fortresses

Prof. Dr. Jonjaua Ranogajec, Faculty of Technology, University of Novi Sad, Serbia

DANUBE RECTOR` S CONFERENCE

4-6 February 2010

In its broadest context, the preservation of the cultural heritage objects is a kind of *race against time.*

- **Protection (conservation) - trying to slow down or minimize the probability of weathering process of the exposed historical materials.**

- **When damaged historical masonry needs to be restored with a new material - good characterisation of both, new and old materials, has to be done.**

Basic levels for the examination of historical materials

- Identification of the properties of historical materials:
  - authenticity, applied technology, preservation, cultural significance
- Determination of degradation mechanisms
- Selection of adequate –”new”- material:
  - Analysis of possible application of the protective materials

Strategy → Creating an interdisciplinary team

The cultural heritage objects

National identity and spirit

Examination of historical materials

Historical data

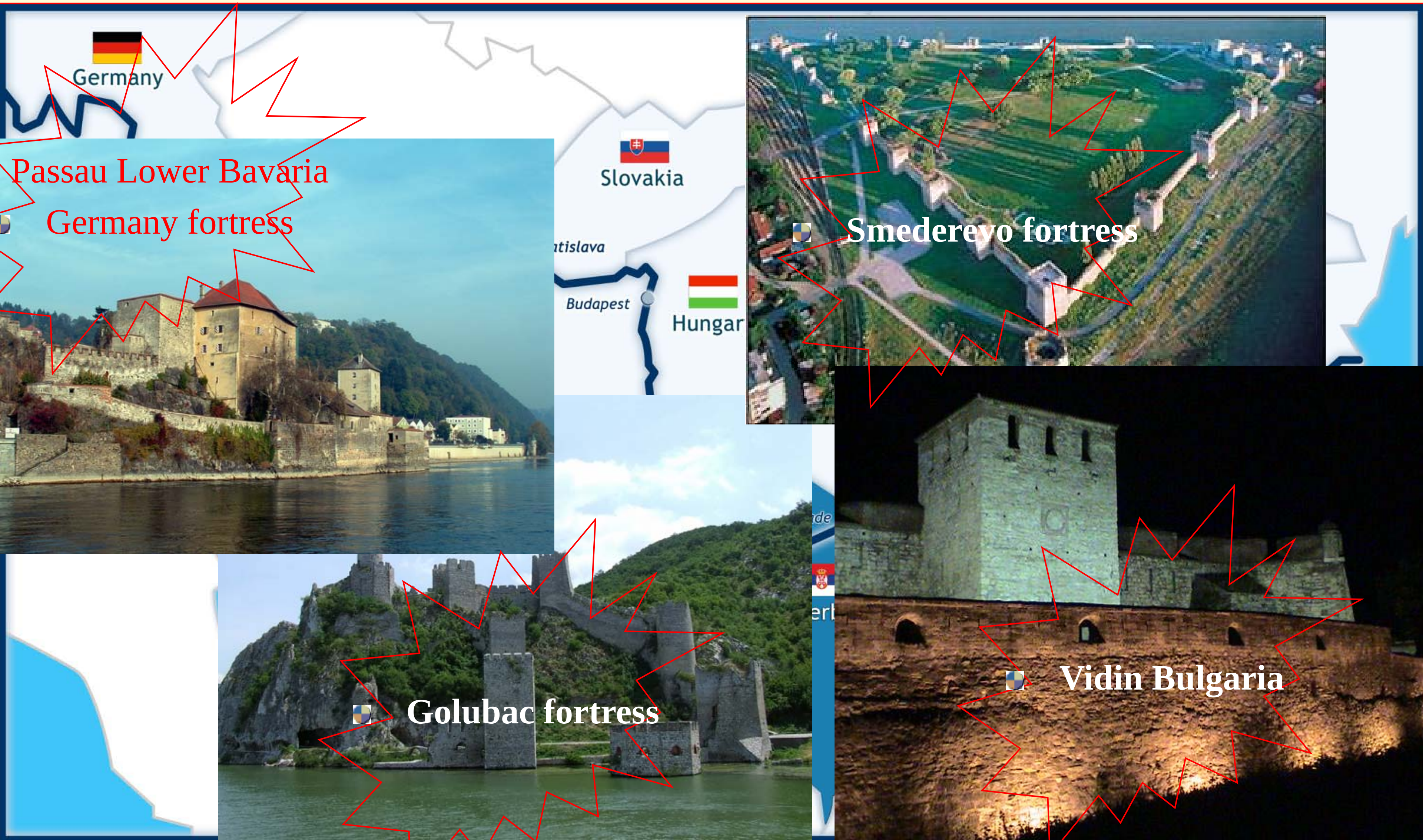
- Materials composition and properties
- Area of application
- Mechanisms and causes of degradation

- **Multidisciplinary approach**
- **Including a large number of experts**

- Long-term research Projects

The Danube is the only river in the world which connects four capitals: Vienna, Bratislava, Budapest and Belgrade and flows through 10 European countries

European Commission recognizes the Danube river as a “single most important non-oceanic body of water in Europe”, and a “future central axes for Europe”

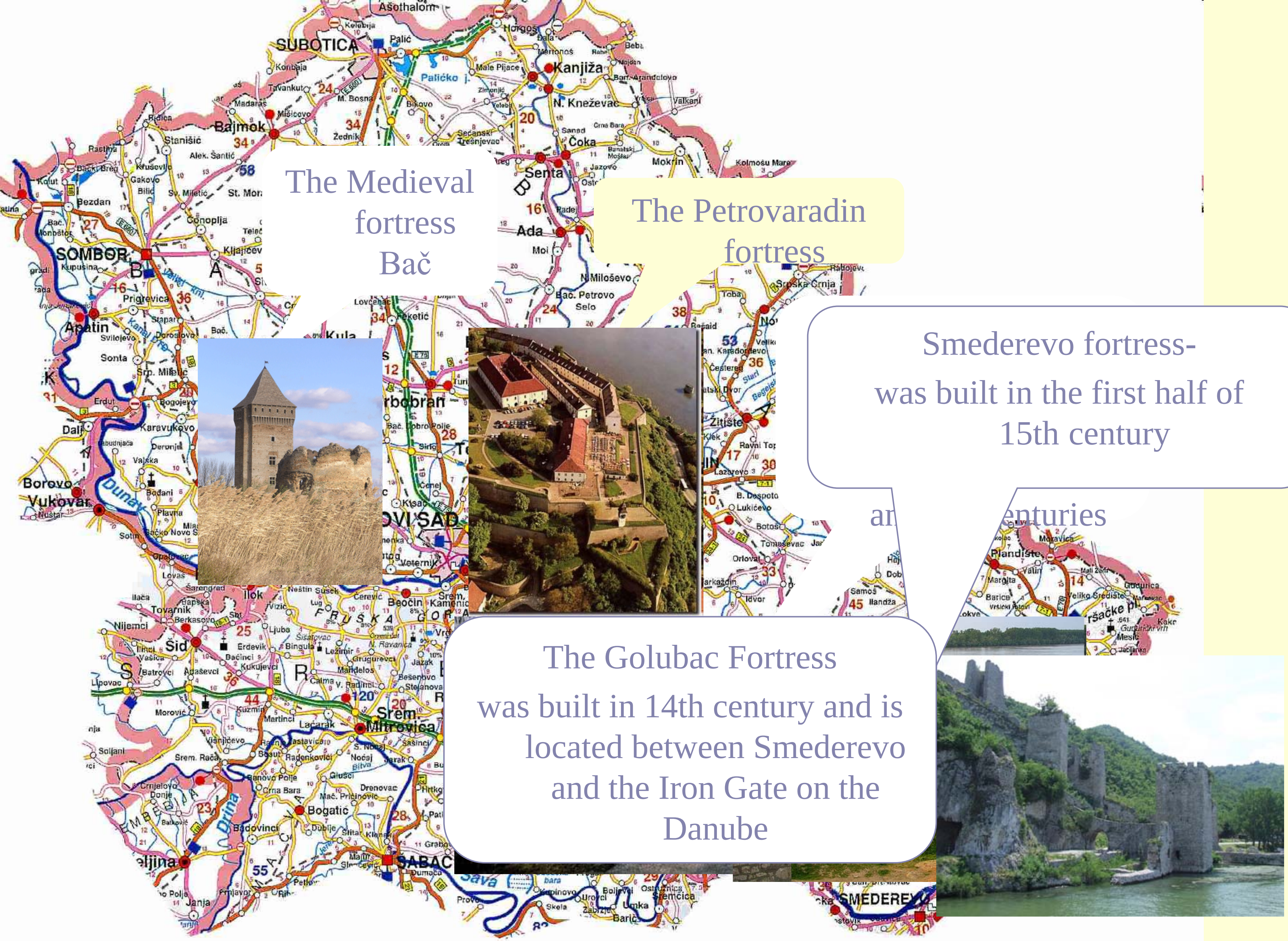


- The Danube was often the river which disconnected rather than connected territories. On the crossroads of world civilizations, between East and West, North and South, the Danube was a border between great empires. People built fortresses to protect themselves from invaders and by crossing the Danube conquered new territories.

- If you travel along the Danube you can see two thousand years of European history.

Fortresses in Serbia

- All Fortresses in Serbia have the status of national cultural monuments of high or exceptional importance. Some figure on the list of world heritage sites.
- Fortresses and castles were of great importance for medieval Serbia. Strong fortification guaranteed the country `s survival.
- Recently researchers have shown a heightened interest in preserving these ancient monuments.
- Their protection can be very beneficial for the local communities and an important key for cultural tourism.



The Medieval fortress Bač

The Petrovaradin fortress

Smederevo fortress- was built in the first half of 15th century

The Golubac Fortress was built in 14th century and is located between Smederevo and the Iron Gate on the Danube


SUBOTICA
Kanjiža
Bajmok
SOMBOR
Apatin
Vukovar
Borovo
NOVI SAD
Petrovaradin
Bačka Palanka
Sremski Karlovci
Titel
Zrenjanin
Žitište
Sečanj
Vršac
Plandište
Alibunar
Kovačica
Opovo
Inđija
Ruma
Srem. Mitrovica
Šid
S. Pazova
N. Pazova
Batajnica
Zemun
BEOGRAD
PANČEVO
Kovin
SMEDEREVO
Bela Crkva
ŠABAC
Sava
Dunav
Tisa
Drina

The medieval fortress Bač

- It is the most important and best preserved medieval fortress in Vojvodina province. It was built on a small hill above the town on an island between the Mostonga river and one of its tributaries.
- The fortress Bač is one of the so called ‘’water towns’’ because it used to be completely surrounded by water and the only access to it was by a drawbridge.

The Petrovaradin Fortress

- built in the 13th century. In 1526 it was attacked by the Turks, and after a two-week siege, the Turkish army resorted to underground warfare. The fortress remained in Turkish hands until 1687 when it was won by Austria during the Grand Vienna War.

The clock tower

The Royal gate

THE FORTRESS BAČ

1. Study of different types of weathering process
2. Obtain information about the degree of material destruction
3. Determine the cause of the material degradation
4. Define structure of examined materials

THE AIM

Examination of the historical materials collected from the two **Danube fortresses**

THE PETROVARADIN FORTRESS

1. Study of different types of weathering process
2. Obtain information about the degree of material destruction
3. Determine the cause of the material degradation
4. Define structure of examined materials
5. **Analyze possible application of the laboratory prepared TiO_2 suspension**

Experimental part
Methods of research - samples colected from the medieval fortress Bač and Petrovaradin fortress

- THERMAL CHARACTERISATION:
  Dilatometric analysis, Differencial thermal dilatometer

- MINERALOGICAL CHARACTERISATION:
  XRD analysis, Diffractometer PW 1050, PHILIPS, the Faculty of Mining and Geology, Belgrade

- **CHARACTERISATION OF THE TEXTURAL PROPERTIES:**
  Water absorption, JUS and ASTM methods, the Faculty of Technology, Novi Sad
  Mercury Instrusion porosimetry , Porosimeter Carlo Erba 2000, the Faculty of Technology , Novi Sad

- MICROSTRUCTURE CHARACTERISATION:
  Optical microscopy - Stereo Microscope OM99T Trinacular, Omano Lindsay Engravers, (Virtz, SAD);
  Scanning Electron Microscopy (SEM analysis) and Energy Dispersion Analysis (EDS analysis),Electron microscope JSM – 6460LV, JEOL, the Laboratory for Electron Microscopy, University in Novi Sad

Experimental – Bač Fortress

MATERIALS:

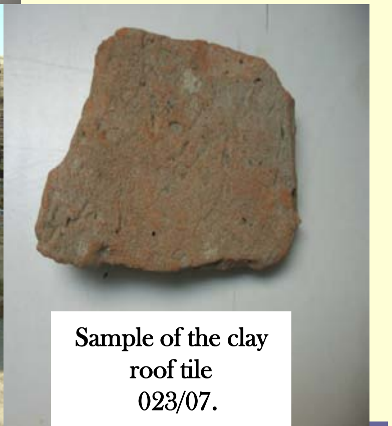
- *clay products:* samples of bricks, terracotta and clay roofing tiles

Fig. Image of *Bac Fortress*
-TODAY-

Sample of the brick 017/07

Sample of the brick 019/07.

Sample of the terracotta 020/07.



Sample of the clay roof tile 023/07.

Experimental – Chemical-mineralogical and thermal characterisation of the brick samples

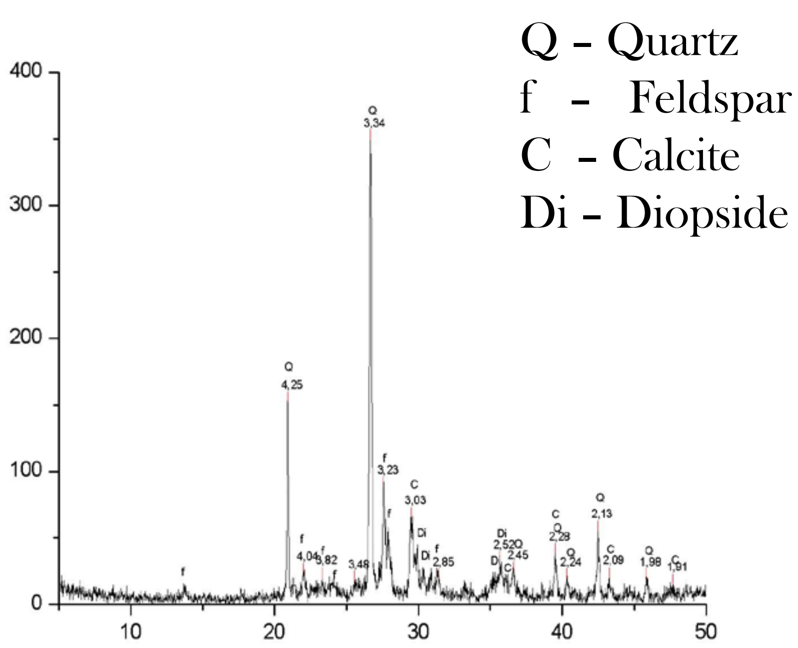


Fig. XRD pattern of the brick sample

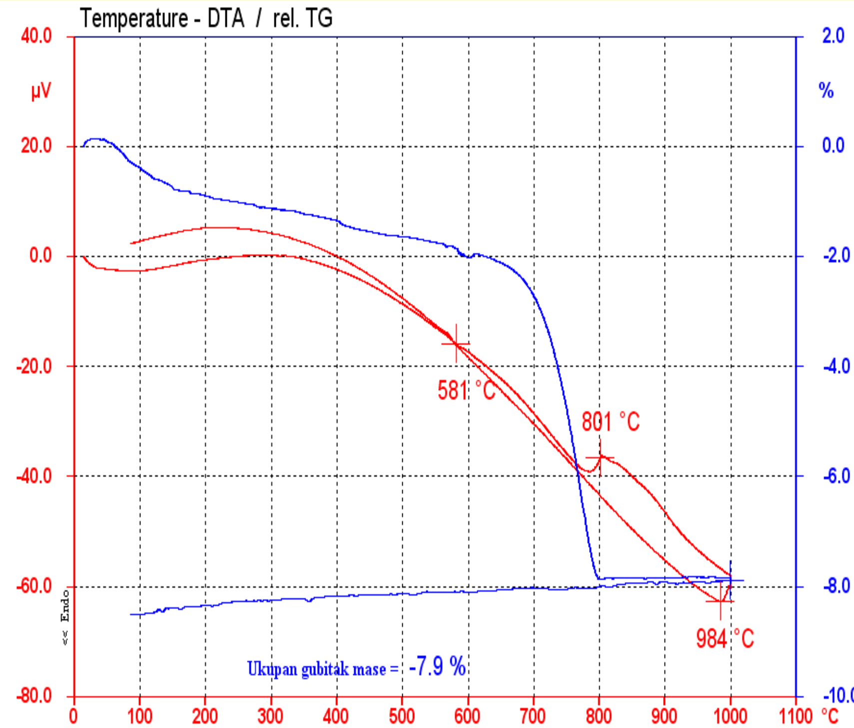
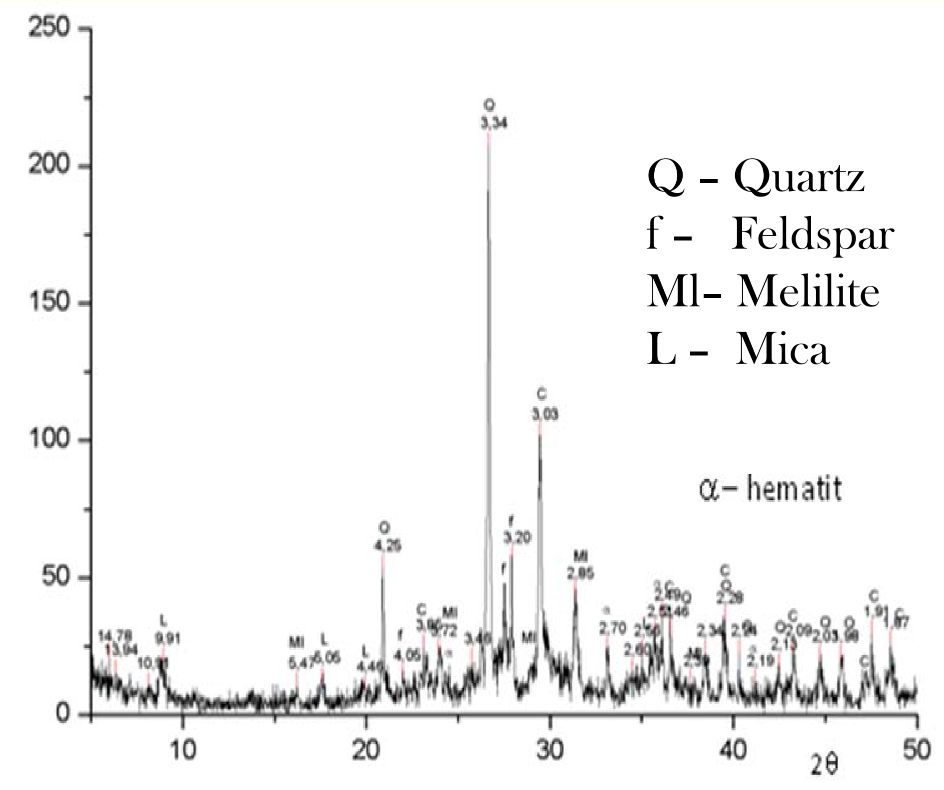


Fig. DTA / TG analysis of brick sample

The results of chemical analysis of the brick sample

Oxide components	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	Ignition loss
mass. %	66. 24	15.71	1.44	6.59	3.91	1.81	0.91	3.52

Experimental – Chemical-mineralogical and thermal characterisation of the brick sample



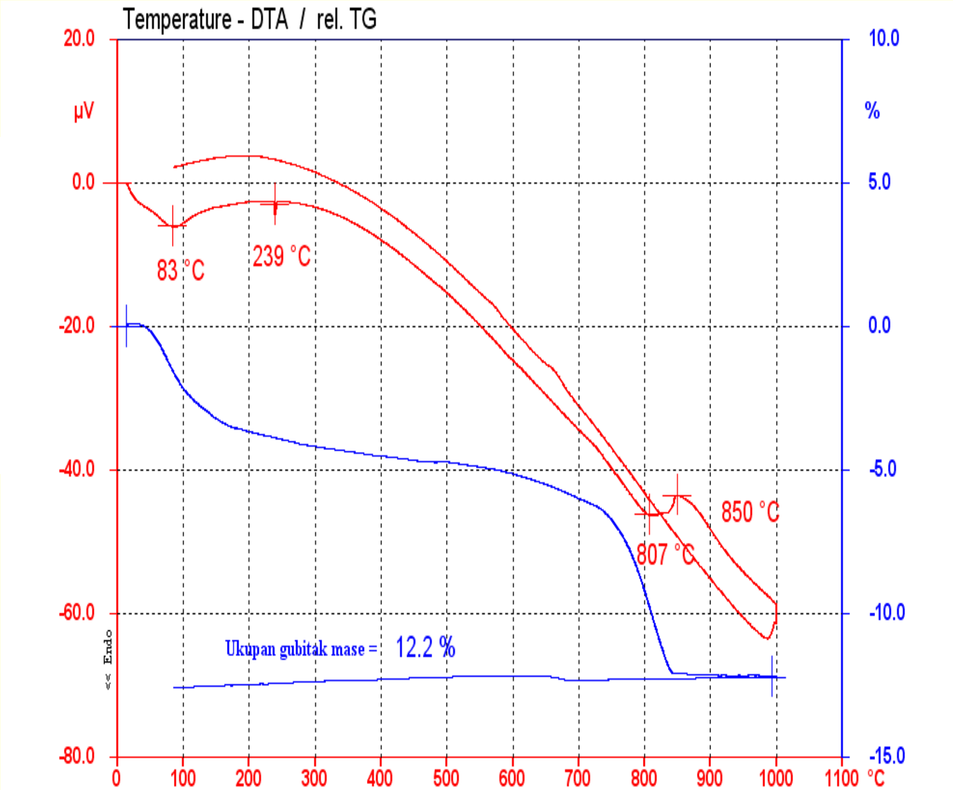


Fig. XRD pattern of the brick sample

Fig. DTA/TG analysis of the brick sample

The results of chemical analysis for brick sample

Oxide components	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	Ignition loss
mass. %	58.84	15.20	1.35	5.30	7.36	1.63	0.87	9.27

Experimental – Chemical-mineralogical and thermal analysis for the sample of terracotta

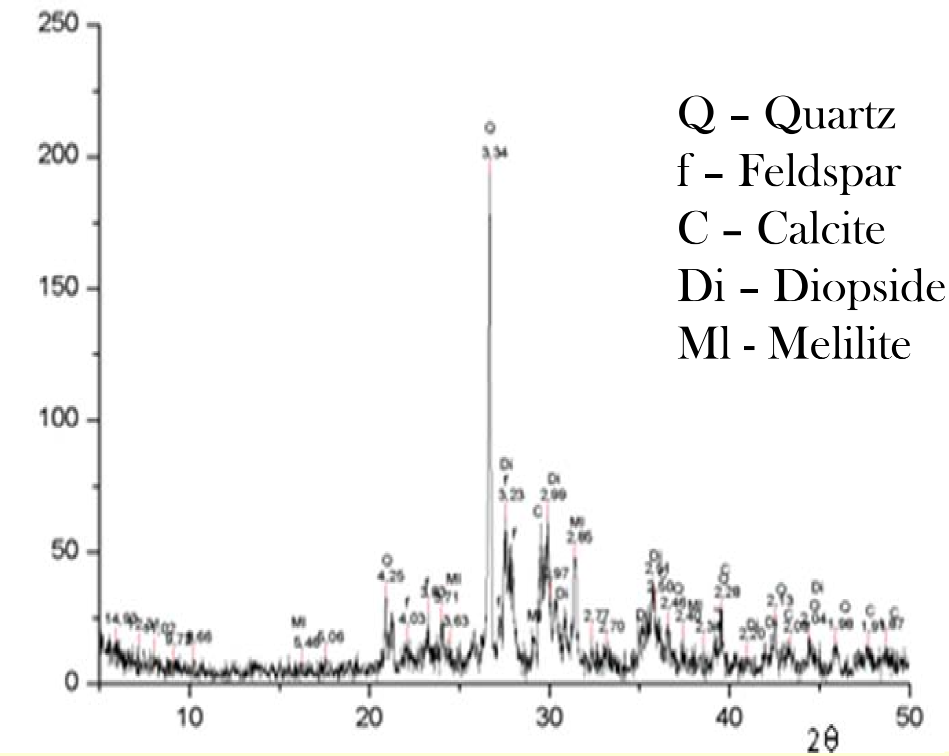


Fig. XRD pattern for the sample of terracotta

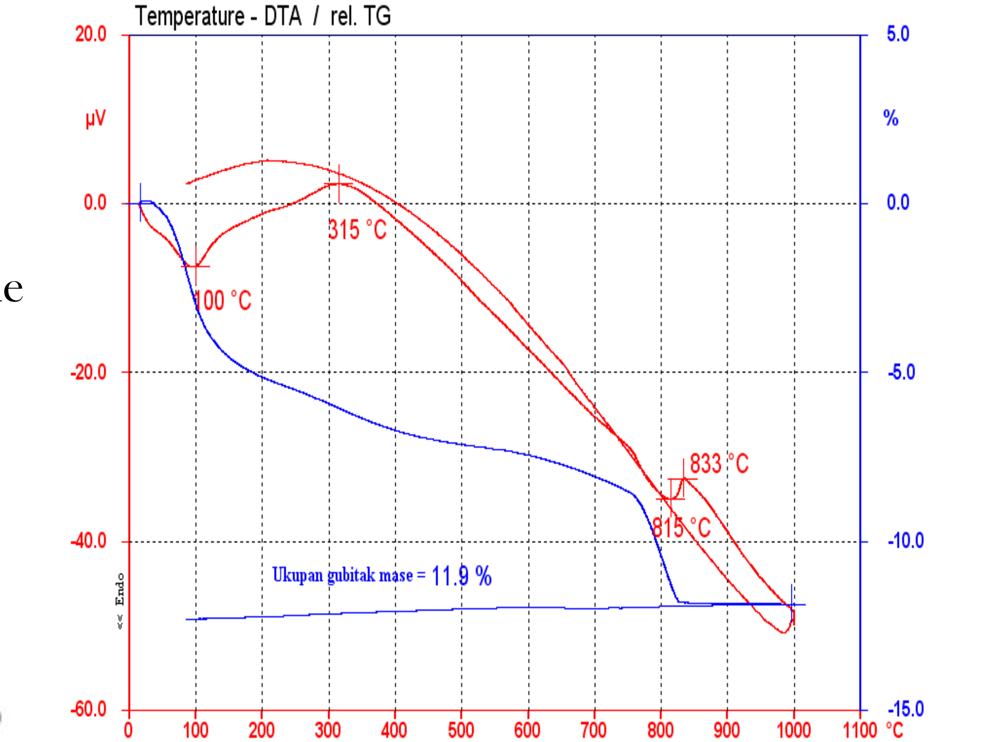


Fig. DTA/TG analysis for the terracotta sample

The results of chemical analysis for terracotta sample

Oxide components	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	Ignition loss
mass. %	55.45	11.30	trace	15.42	5.56	2.35	0.73	9.16

Experimental – Chemical-mineralogical and thermal characterisation for the sample of clay roofing tiles

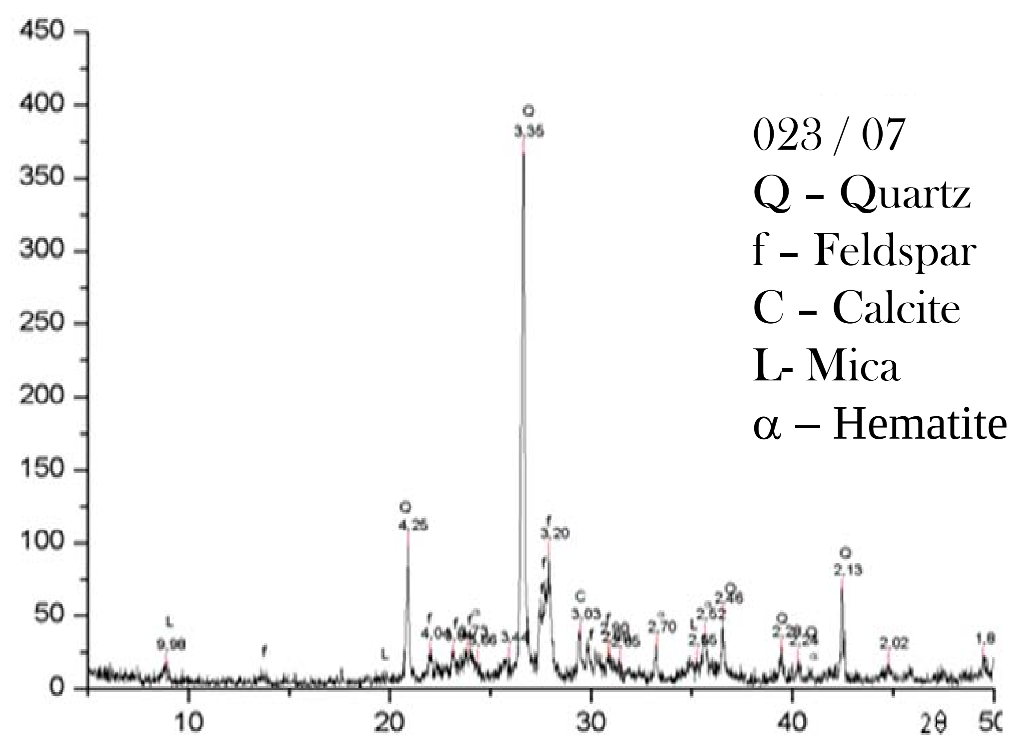


Fig. XRD pattern for the sample of clay roof tile

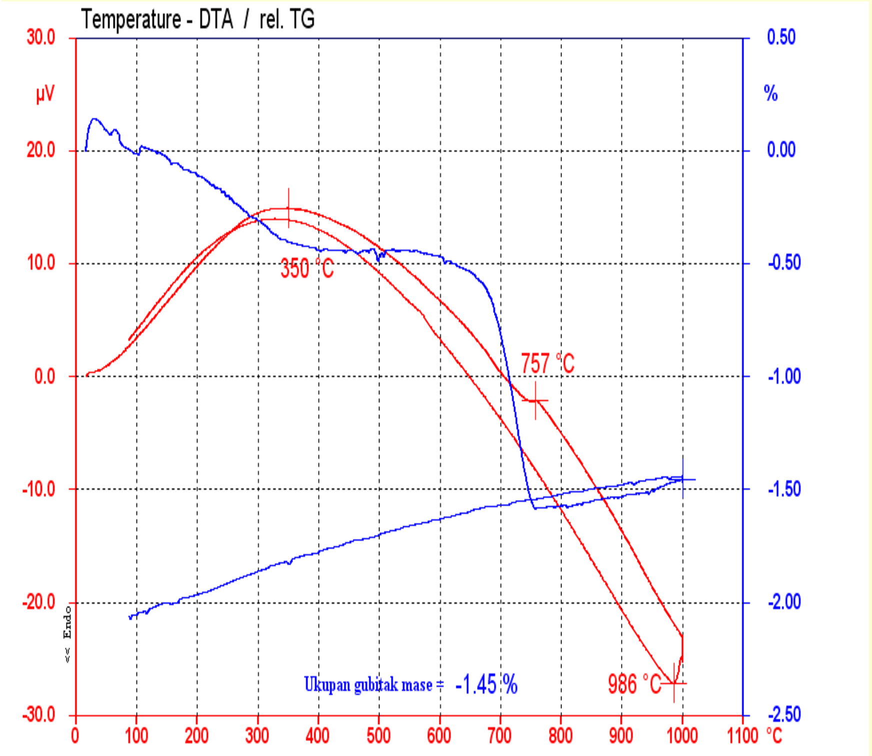


Fig. DTA/TG analysis graphical view for clay roof tile sample

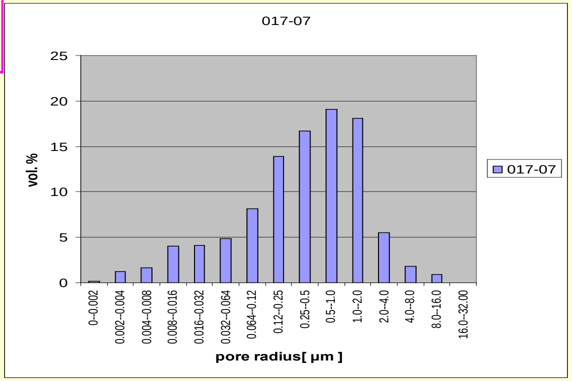
The results of chemical analysis for clay roof tile sample

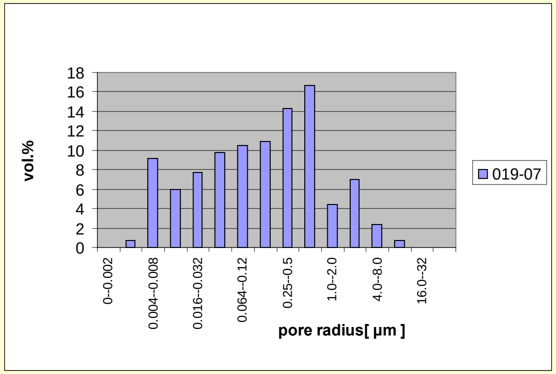
Oxide components	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**CaO**	**MgO**	**K_2O**	**Na_2O**	**Ignition loss**
mass. %	**66.18**	**12.50**	**4.80**	**7.51**	**3.30**	**2.53**	**0.84**	**2.44**

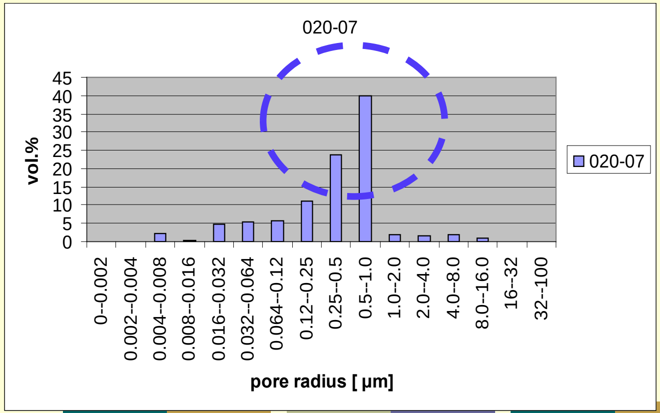
Experimental – Characterisation of textural properties of the clay products

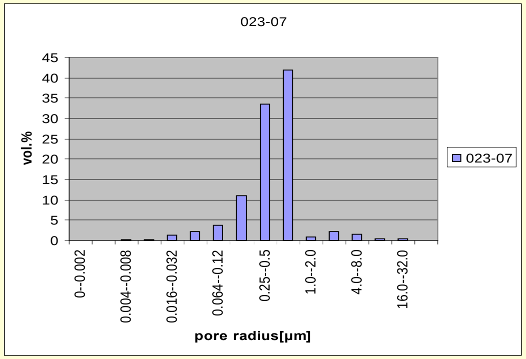
Sample designation	Water absorbtion, EN method (mass.%)	Water absorbtion ASTM method (mass.%)
Brick 017 / 07	18.74	22.72
Brick 019 / 07	16.78	18.44
Terracota 020 / 07	25.73	27.90
Clay roof tile 023 / 07	20.89	21.30

- Pore size distribution









- **The results of the examination of *the historical materials from medieval fortress Bač* can be summarized as follows:**

- **1. Brick 017/07 is a ceramic system based on quartz, feldspar, calcite and diopside. It was fired in reduced atmosphere, below 600. The interval of dominant pore radius is between 0.5 and 1 mm, with a vol. pores of 18%. The product as a hand-modeled element, possesses a low water absorbing index (18.74 mass.%).**

- **2. Brick 019/07 consists of newly formed crystal phases: mellilite (Ca, Na/K)(Mg,Al,Fe)(Si_2O_7) and hematite - Fe_2O_3, as well as mineral components as quartz, feldspar and mica originated from the raw material. It is a system fired below 800 ^oC mostly in oxidative atmosphere. The interval of dominant pore radius is identical to brick sample 017/07.**

- ***3. Terracotta 020/07 is a creamy-white ceramic material*** **(mass.% Fe_2O_3 in traces, high mas.% CaO- 15.47), which consists of crystal modifications such as mellilite, diopside and quartz, feldspar and calcite. <u>High temperature of firing with usage of organic material</u> (probably straw) is the characteristic of this system.**

- ***4. Clay Roof tile 023/07 is an orange-red ceramic material*** **(4.80 mass.% Fe_2O_3),** ***which consists of quartz, feldspar, calcite and mica as the origin materials and newly formed phases – hematite.***

- ***The data of mineral composition, original firing temperature and the textural characteristics of the historical materials are <u>an essential background for the future production of new specific materials for the restoration of medieval fortress such as Bač</u>***

Experimental – case of the Petrovaradin fortress

Samples collected –18th century tunnel:

- bricks
- stones
- mortars

conservation strategies

Partially restored tunnel surface

Possible application of the TiO_2 suspension – designed in our laboratory

Outdoor examination

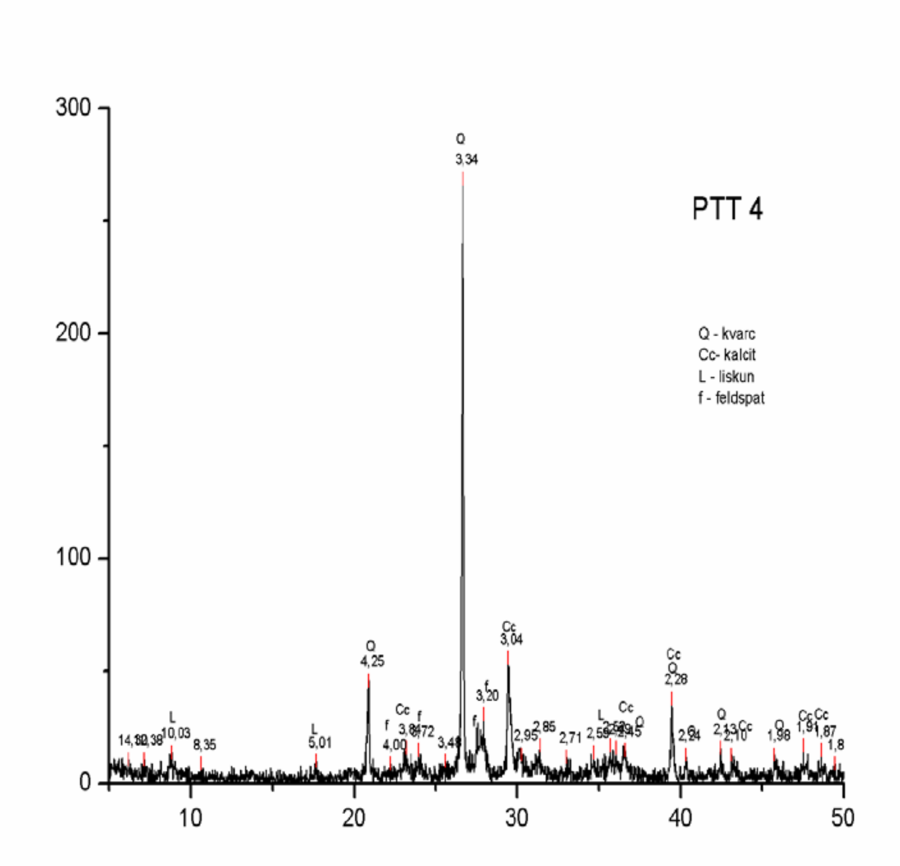
Examined materials and their location in the Petrovaradin fortress

Image of the brick PTT 4, sampling hight 1.80 m

Image of the stone PTT 10, sampling hight 1.70 m

Image of the mortar PTT 8, sampling hight 1 m

Experimental part – Mineralogical and thermal characterisation of the brick sample PTT 4



XRD pattern for the sample of the brick sample PTT 4

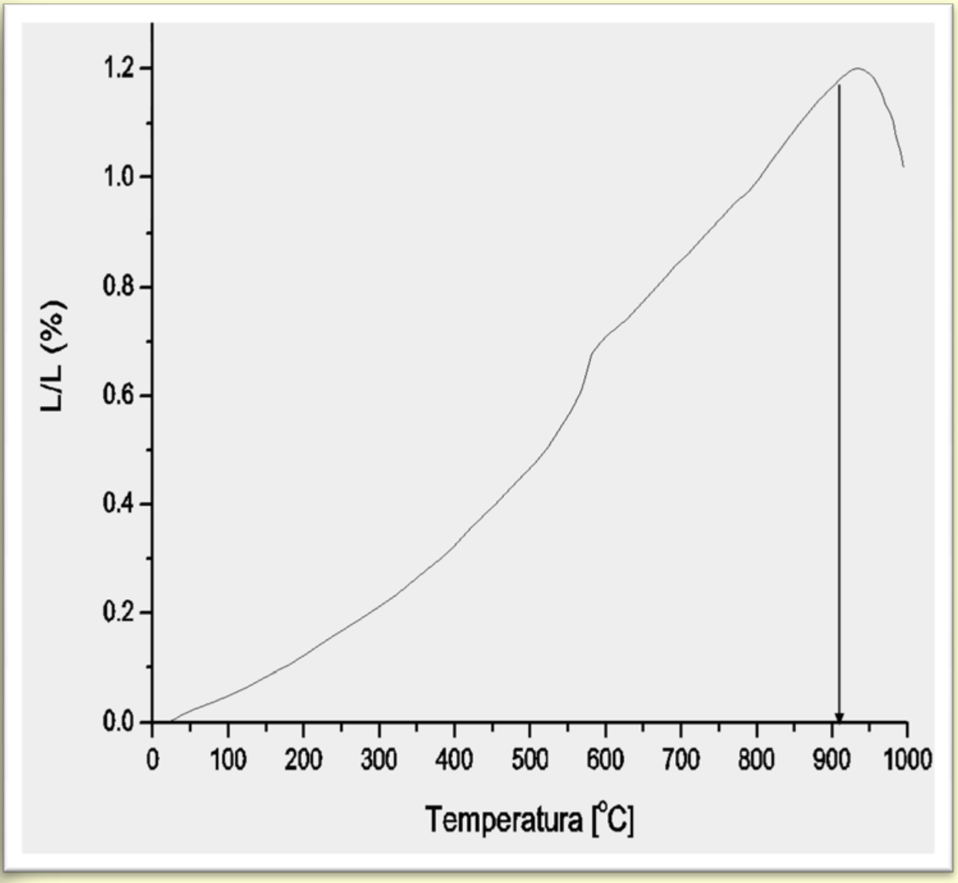


Image of Dilatometric analysis of the brick sample PTT 4

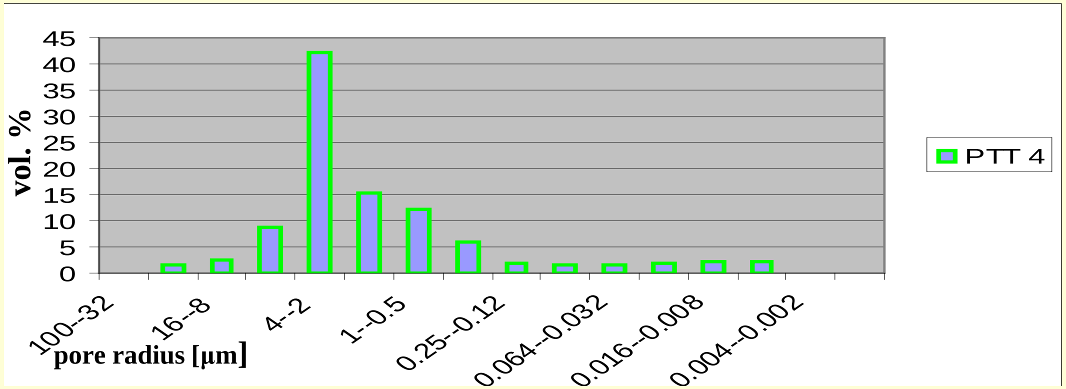
Experimental part – Characterisation of textural properties of the brick

❖ Water absorption results

Sample	Moisture determination (mass. %)	Water absorption, EN method (mass. %)	Water absorption, ASTM method (mass. %)
PTT 4	4.83	18.81	21.36

❖ Mercury porosimetry results

Sample	Cummulative volume pore [mm^3/g]	Total pores [%]
PTT 4	261.30	38.93



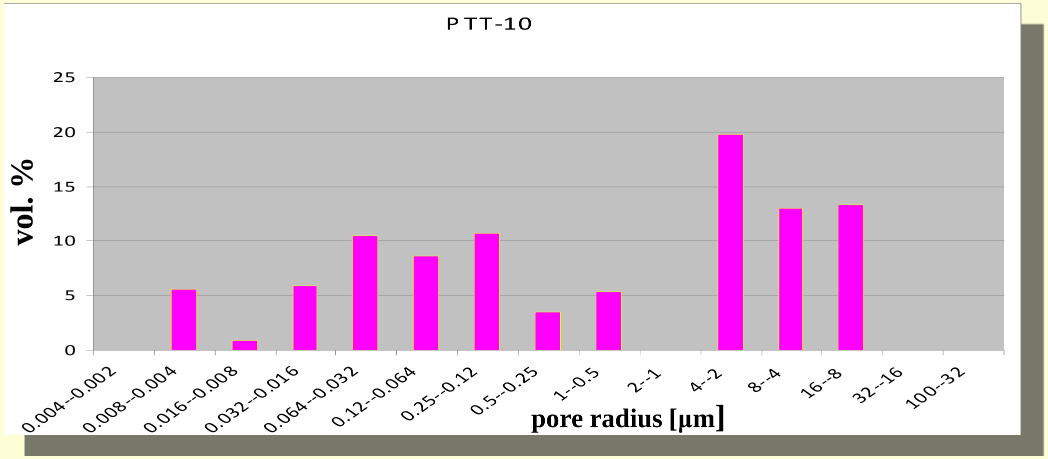
Experimental part– Characterisation of textural properties of the stone

❖ **Water absorption results**

Sample	Water absorption, EN method (mass. %)	Water absorption,ASTM method (mass. %)
PTT 10	0.85	0.90

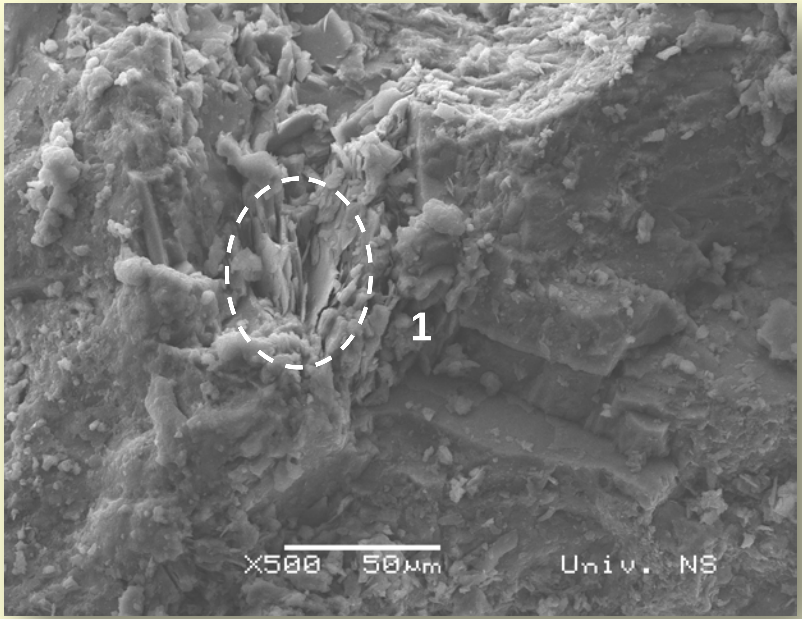
❖ **Mercury porosimetry results**

Sample	Cummulative volume pore[mm^3/g]	Total pores [%]
PTT 10	19.82	4.14

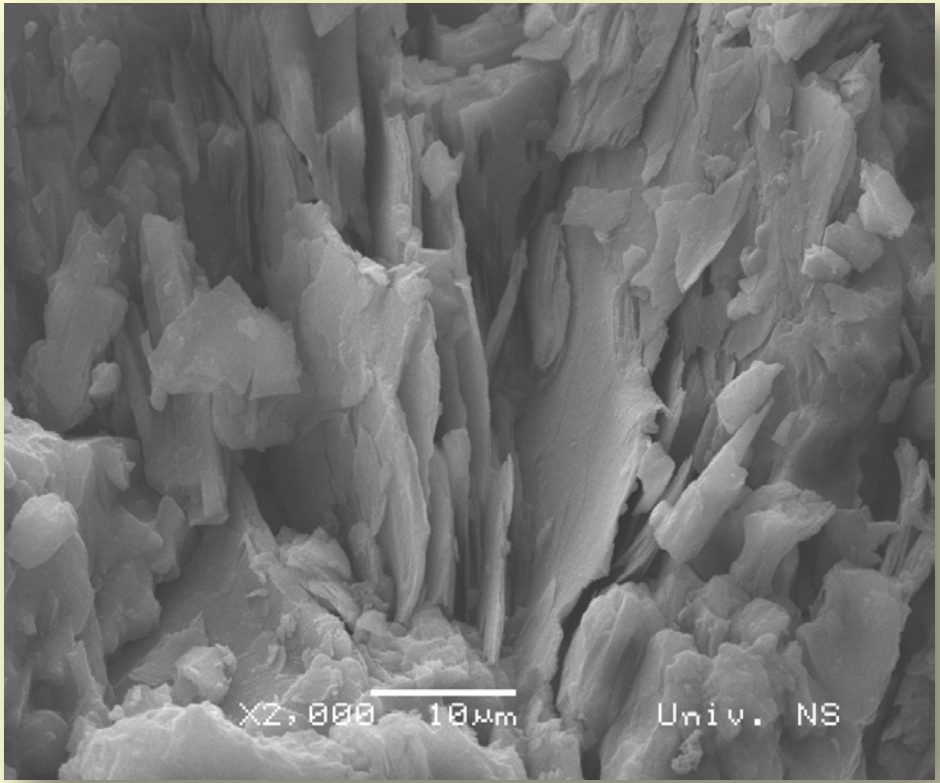


Experimental part – Characterisation of the microstructure of the stone sample PTT 10

❖ *SEM analysis*

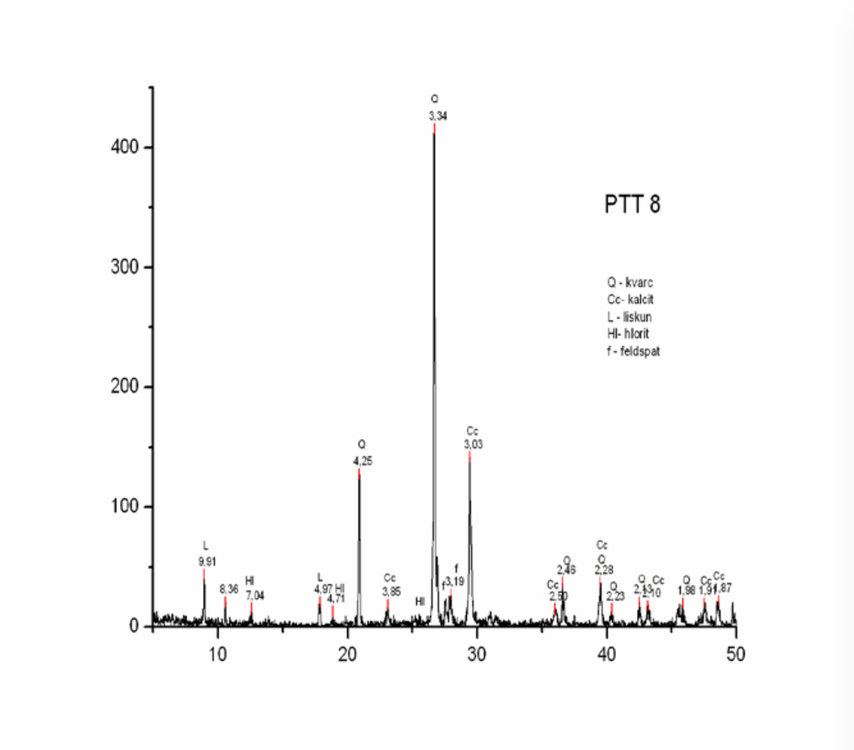


SEM micrograph of the stone sample PTT 10, x500

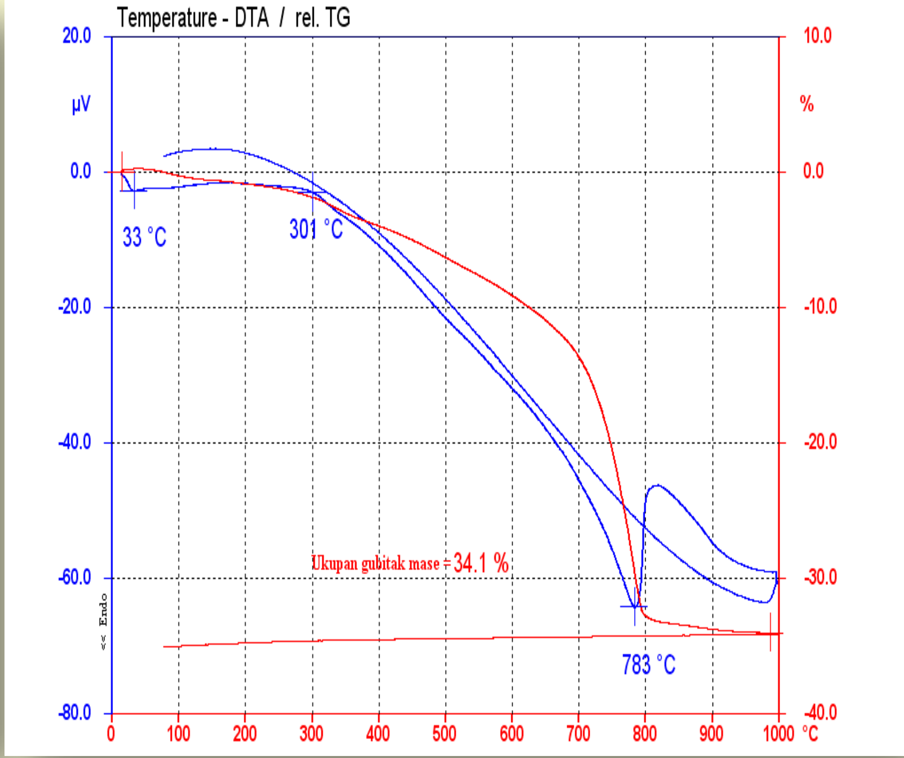


SEM micrograph of the stone sample PTT 10, x2000

Experimental part– Chemical-mineralogical and thermal characterisation of mortar sample PTT 8



XRD pattern of the mortar sample PTT 8



DTA/TG analysis graphical view of the mortar sample PTT 8

The results of the chemical analysis of the mortar sample PTT 8

Oxide components	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	Ignition loss
mass. %	45.01	0	2.56	20.92	5.97	1.17	2.01	21.93

- **The obtained results can be summarized as follows:**

1. The brick sample PTT 4 is a ceramic system based on quartz, feldspar and mica. Firing temperature of the brick sample (900 ^{o}C) was determined based on dilatometric analysis. This sample has high value of water absorption and high share of open pores (40 %).

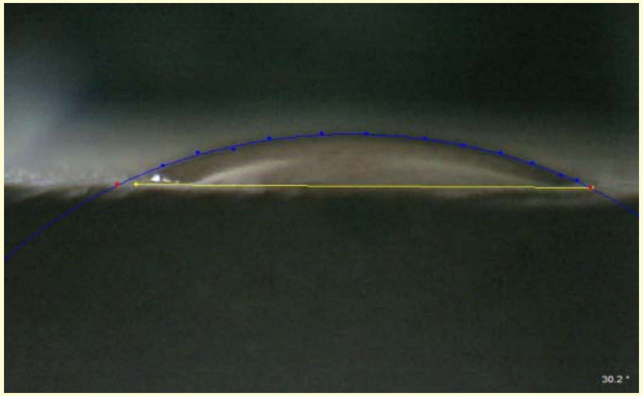
2. The stone sample PTT 10 is a metamorphyc rock material with the presence of the carbonates. The surface of sample stone is covered with a layer black patina. Low water absorption with a few open pores (20 %) is identified.

3. The mortar sample PTT 8 - inhomogenious structure with the presence of white grain (carbonates). Based on the structure characterisation the presence of lime mortar is confirmed.

Laboratory prepared and examined TiO_2 suspension

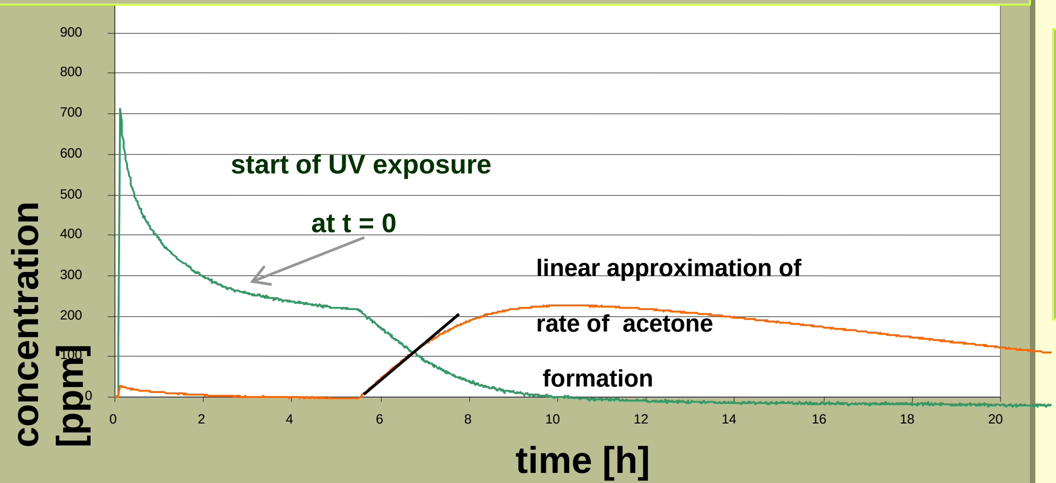
Laboratory prepared TiO_2 suspension was chosen on the basis of our previous work.
All examinations were performed on coated clay roofing tile samples – M coating.

Samples with M coatings- show very good self-cleaning (small water contact angle values) and photocatalytic properties (rhodamin B test and FTIR test) in relation to commercial coatings.



Contact angle measurements for tiles coated with M coating

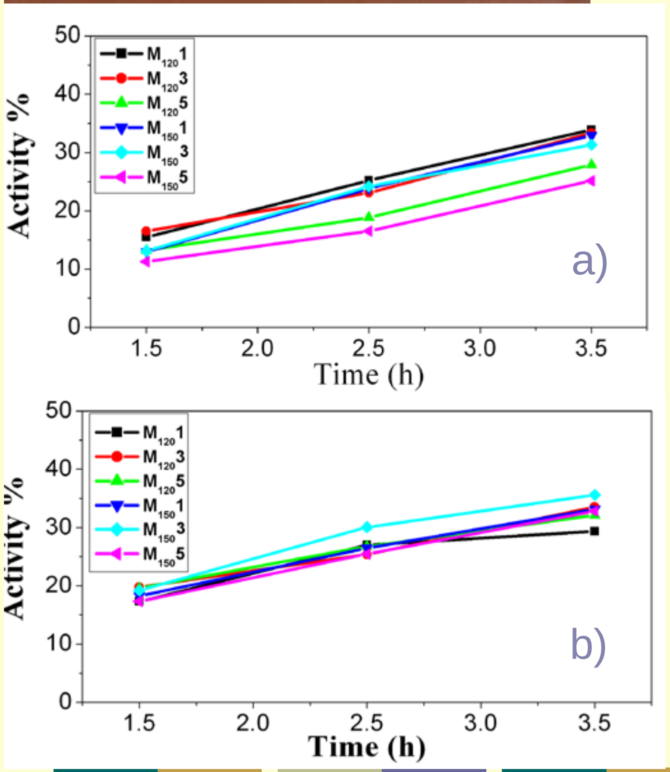
The course of photocatalytic degradation of iso-propanol



Rate of acetone formation

Conc. acetone (ppm/h) = 181.5

Photocatalytic activity-Degradation of water solution of rhodamin B



- **Photocatalytic activity of the coated tiles was examined before and after sample rinsing procedure with water (flow rate was 0.136 liters per second during 30 min. under 45º angle)**

- Photocatalytic activity of the tiles coated with M films, before (a) and after (b) water rinsing

Samples with M coatings showed great resistance to water rinsing procedure which was manifested as small or negligible decreasing of the photocatalytic activity values.

Outdoor examination

The large scale testing of photocatalytic coating in outdoor conditions provides valuable information on the behavior and performance of such coatings in their normal operating environment.

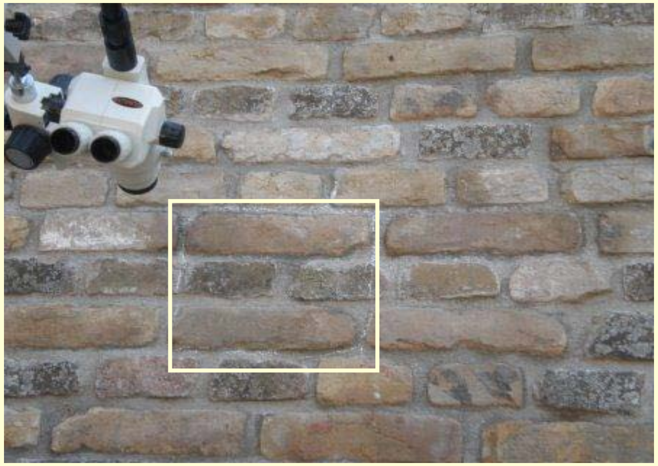
- 3 small areas (2 outside: areas I and III and 1 inside the tunnel: area II)
- already restored tunnel surface was coated with the laboratory prepared TiO2 suspension
- efficiency of this treatment was evaluated through physical investigation and surface observation

Outdoor examination

- Investigations of the chosen areas were performed after 1, 2, and 4 weeks considering suspension application
- First two weeks of investigation: sunny, average T 25^{o}C
- Third and fourth week of investigation: cloudy, 9 rainy days, average T 12^{o}C
- Changes were monitored by macroscopic and microscopic investigation, Optical microscopy - Stereo Microscope OM99T Trinacular, Omano Lindsay Engravers, (Virtz, SAD)



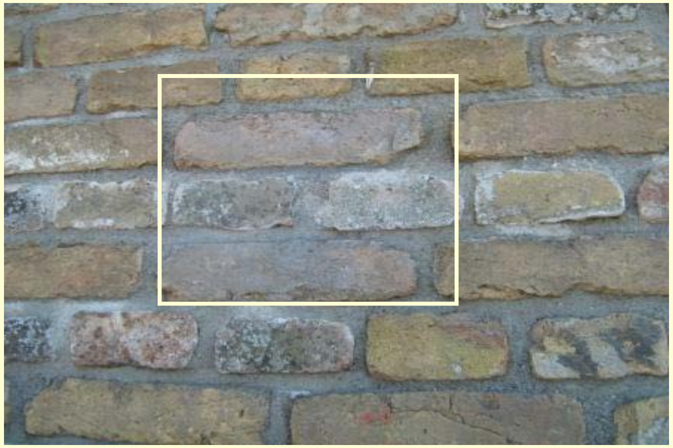
Area I – left wall outside– Application of the M coating



Before application of the TiO_2 coating

Immediately after application of the TiO_2 coating

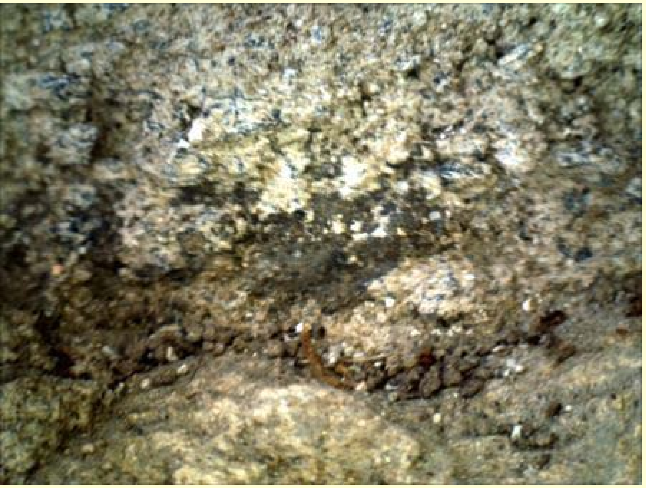
1 week after application of the TiO_2 coating



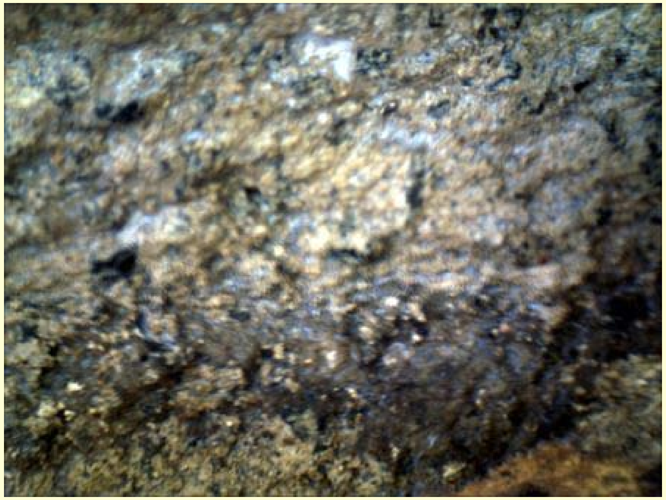
4 weeks after application of the TiO2 coating

There are no visible changes

Area I – Application of the M coating on the old mortar



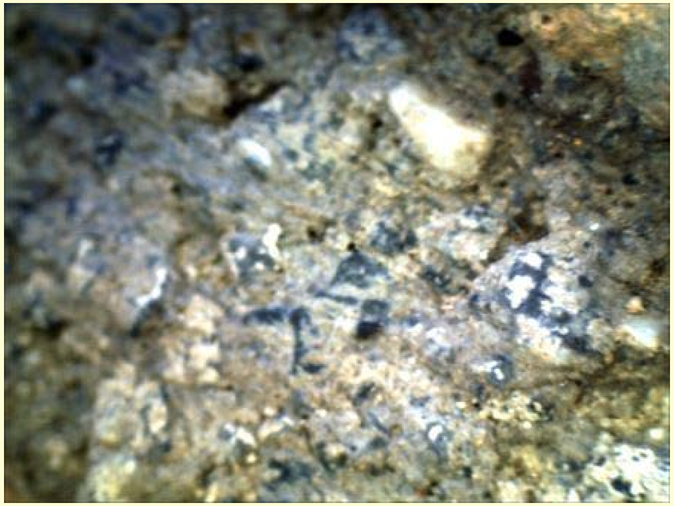
a)



b)

Optical microscopy of the old mortar sample a) ***Before application of the coating; b) immediately after application of the coating***

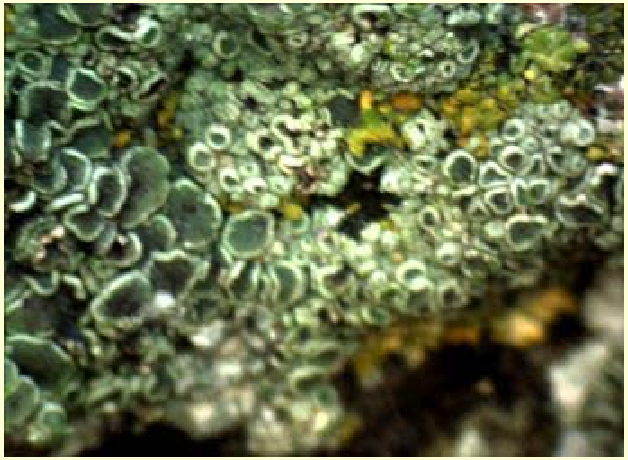
a)



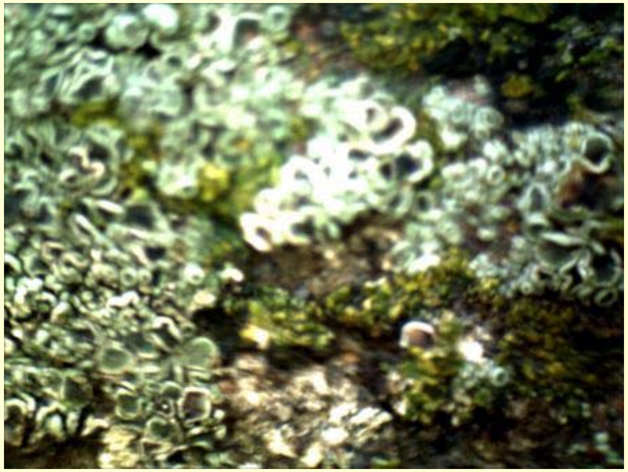
b)

Optical microscopy of the old mortar sample a) ***1 week after application of the coating; b) 4 weeks after application of the coating***

Area I – Application of the M coating on the old brick

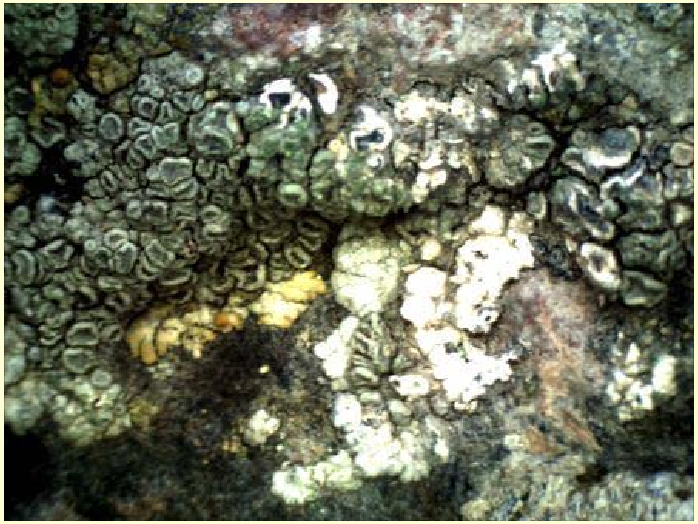


a)

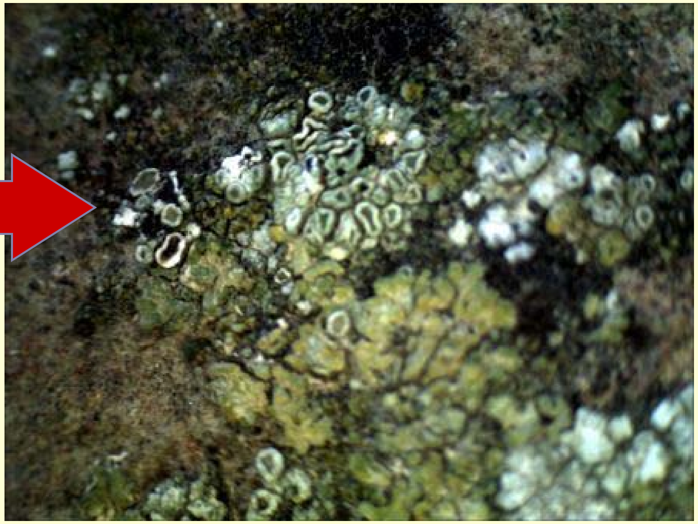


b)

Optical microscopy of the old mortar a) ***Before application of the M coating; b) immediately after application of the M coating***



a)



b)

Fig. Optical microscopy of the old brick a) ***1 week after application of the M coating; b) 4 weeks after application of the M coating***

CONCLUSION

Outdoor on-going investigation of the laboratory prepared TiO_2 coating showed the following results:

• Applied coating was stable after four weeks of advere environmental conditions.
• In the area of the inside wall of the tunnel, no visible changes connected with the photocatalytic effect (self-cleaning) were detected.
• In the areas of the outside walls of the tunnel, changes connected with the photocatalytic effect (self-cleaning) were detected → lichens were drying out.

• Fortifications and castles in European cities are the most popular tourist destinations earning their respective local communities hefty revenues.

•New programs with multidisciplinary approach to this matter will prove highly beneficial for Serbian culture and economy.

•The future network of experts should cooperate (at local, national and regional levels) in pursuing the protection and creative development of cultural landscapes of historical, technological and environmental significance.

Thank You for Your Attention