WP 6 – Long Term Behavior
Update and future steps

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Experimental application

1. Microemulsion of organic solvents for cleaning of surfaces treated with acrylic emulsion

   Products to be tested: XYL, MEB, EAPC,

2. Nano-suspension of $Ca(OH)_2$ for consolidation of porous materials

   Products to be tested: 1P, E 35, MBN

Materials for cleaning

EAPC	XYL	MEB
Water 82%	Water 85%	Water 85%
Surfactant SDS* 4%	Surfactant SDS 4%	Surfactant Brij L4 6%
1-pentanol 4%	1-pentanol 8%	2-butanone 3%
Propylene-carbonate 5%	p-xylene 3%	Ethylacetate 3%
Ethylacetate 5%		Butylacetate 3%

Materials for consolidation

Type of nano-suspension	Concentration
CSGI 1P35	10 g/l
CSGI E 35	10 g/l
MBN Nf064	10 – 20 g/l
ZFB 695p	75 g/l

CLEANING OF MURAL PAINTINGS

Case study : Grabštejn Castle, orig. from 13 Cent.

Mural paintings in the Chapel of St Barbara dated 1560

Technique: fresco/secco

All surface was traeted with acrylic emulsion in 1980´s

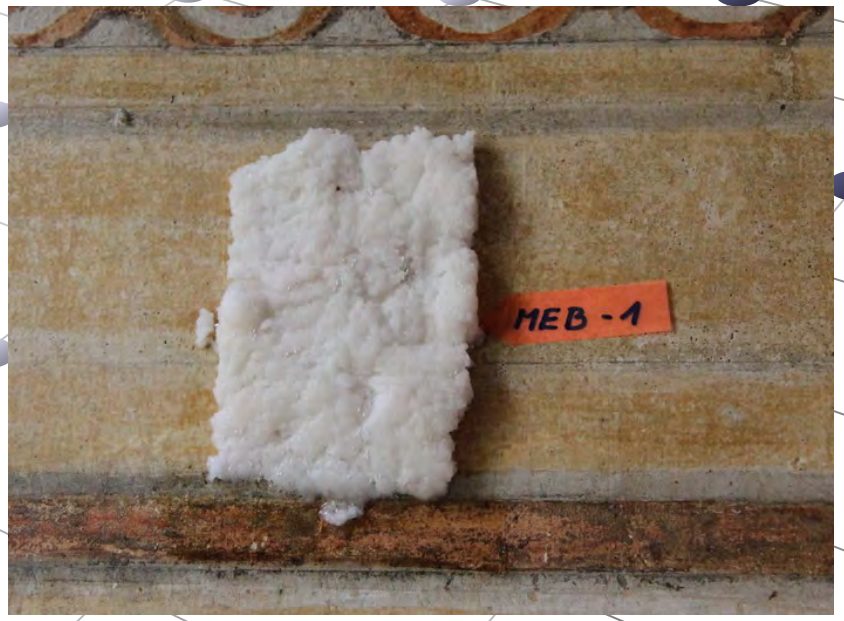
Last restoration: 2008

Testing areas

2008 treatment (in:Restoration Report by Martan, Sevcik)
Removal of fixative: aceton-ethanol 1:1 in Arbocell 200
Removal of overpaints: toluene- ethylacetate 1:3 in Arbocell 200
New fixative: : 5%- Klucel M, 2% Primal AC 35

Detail of glossy surface caused by acrylic varnish
Images in UV Light

Process of application



Testing area No.1


EAPC 2 10 min
XYL 2 10 min
MEB 1 2 x 10 min

Testing area No.2

Evaluation of dispersion removal by materials XYL, MEB, EAPC.

- XYL
- 5-minute proved to be the least agressive, no disturbance of the color layer, acrylic emulsion largely removed.

  After 7-minute exposure, minor destruction visible.

- MEB
- After 5 minutes minor damage in color layer already identified. With increasing time the damage becomes more extensive.

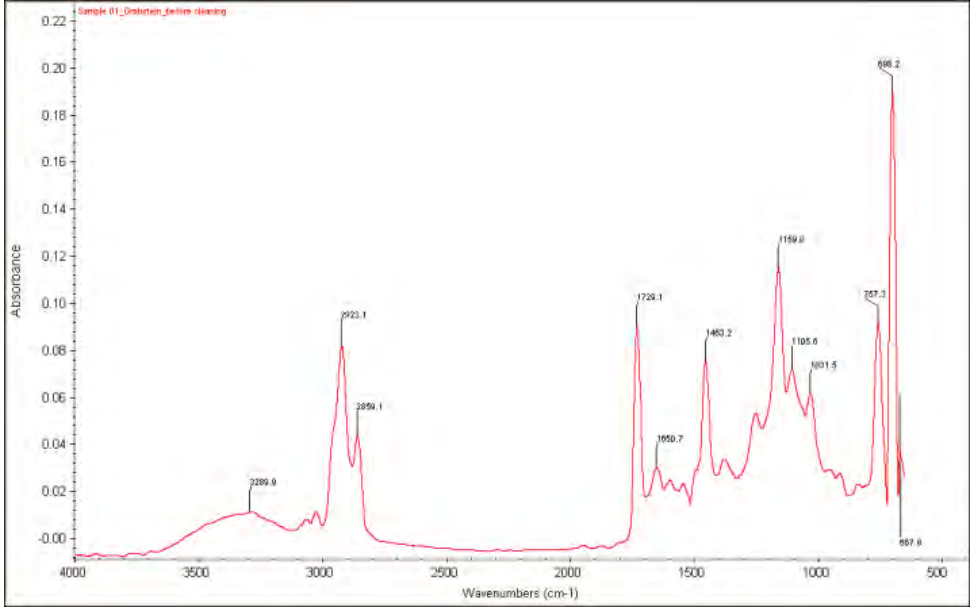
- EAPC
- Slower effect and seems to be more disturbing. 10-minute exposure visually affects the color layer.

Side effect:

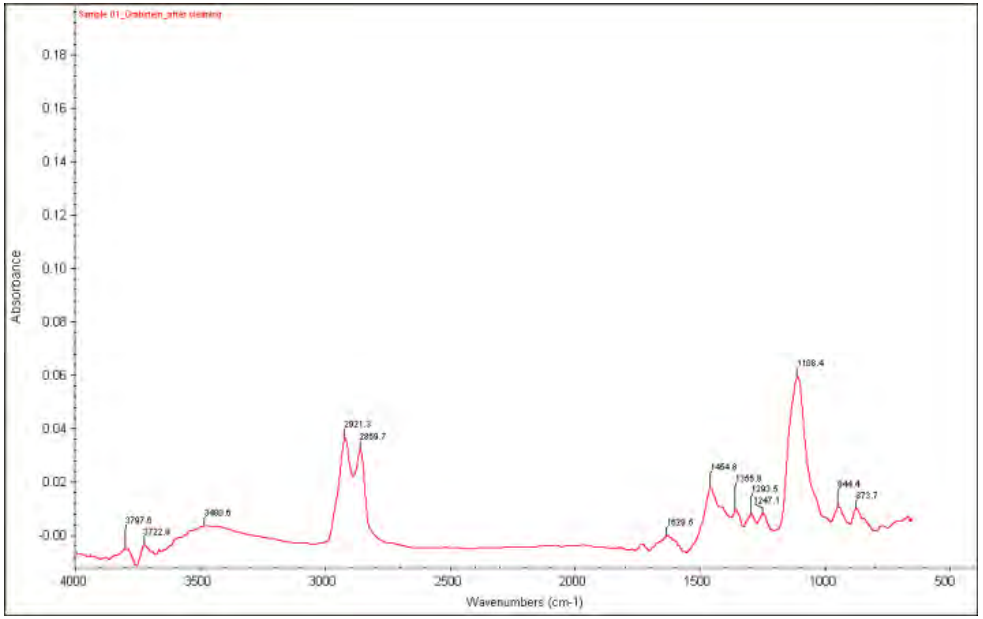
Removal of recent fixatives and retouchings in all cases

- *Grabštejn, Chapel of St. Barbara, interior*
- *Identification of organic compounds (synthetic polymers) in samples from wall paintings*
- *Method of analysis:* Fourier-transform-Infrared spectrometry (FTIR)
- *Analysis procedure:* The organic compounds were extracted by chloroform and the dried residue analysed by FTIR in Reflexion-ATR-Modus (Nicolet 380 FT-IR Spectrometer, Thermo Electron)

(FTIR Analysis Protocol by K.Bayer, 2013)



Before treatment



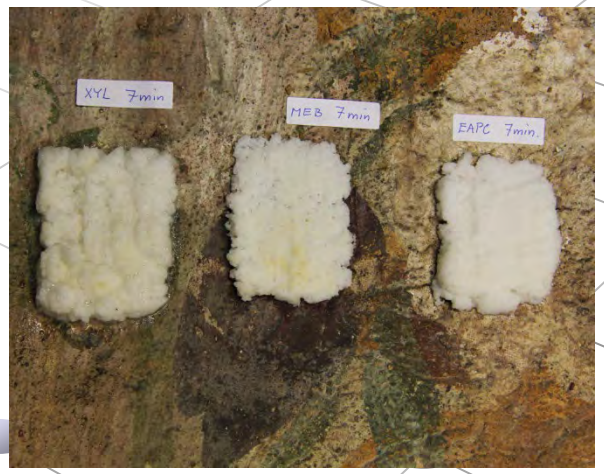
After treatment

Case study: Transfers of murals from St Wolfgang church in Doupov

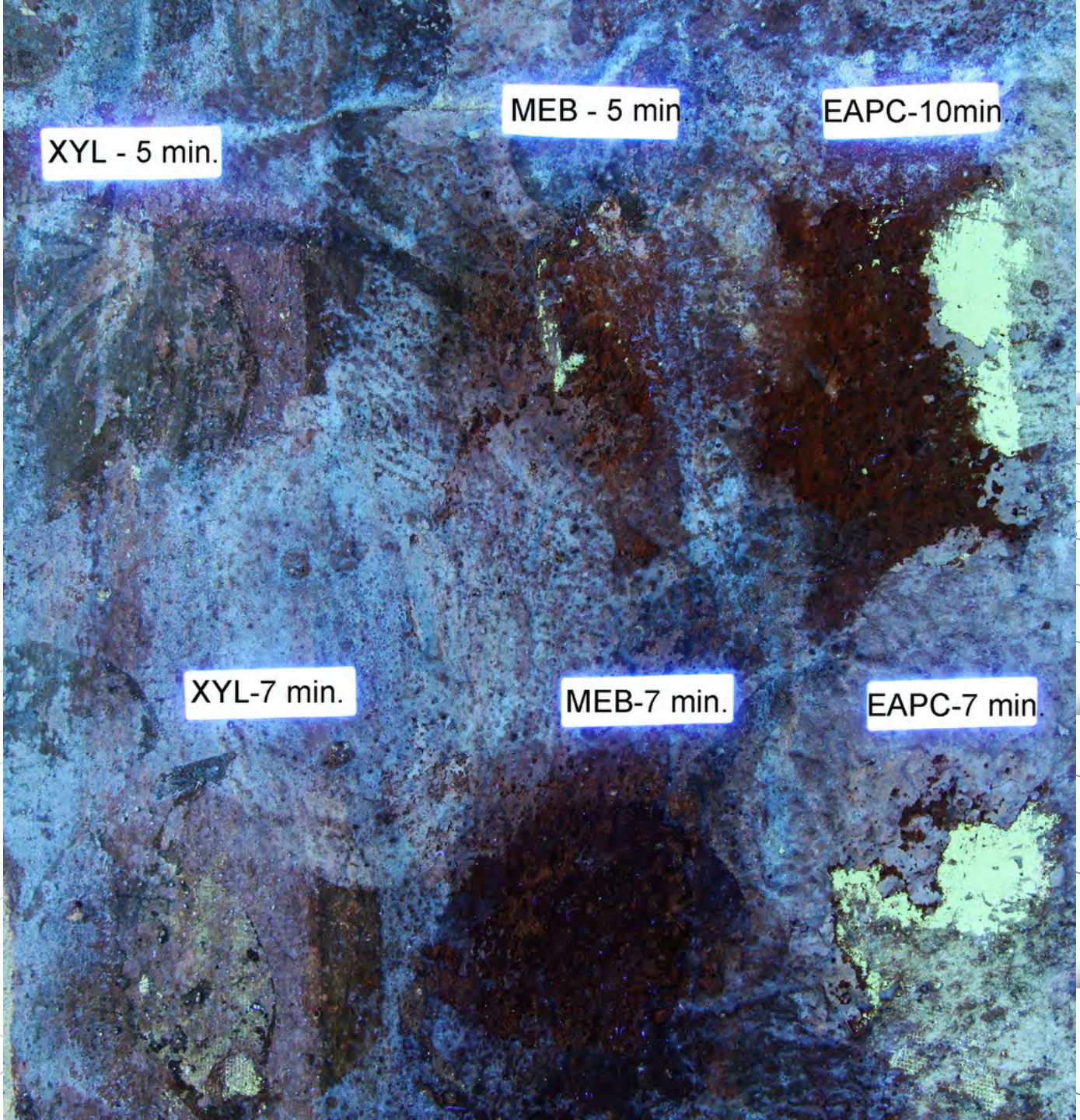
- St. Wolfgang' s Church, was evacuated in 1959 and incorporated into a new military area.
- Very short period time was given to make transfers of a part of valuable wall paintings by F.X.Palko (late18th Cent.)
- Subsequently, the church bacame a training target for tank corps and was completely destroyed.

- The designated interior paintings were fixed with Disapol (locally produced acrylic emulsion)
- Subsequently covered by three layers of gauze (light fabric with the weave of 10 x 10 threads per cm^2).
- A mixture of Lovosa (kind of CMC) and Disapol in the ratio of about 10:1 was used as glue

Transfer panel used for experiments




XYL 5 min.
MEB 5 min.
EAPC 10 min.
XYL 7min
MEB 7min
EAPC 7min.


XYL - 5 min.
MEB - 5 min.
EAPC-10min.
XYL-7 min.
MEB-7 min.
EAPC-7 min.

Evaluation of dispersion removal by materials XYL, MEB, EAPC.

XYL

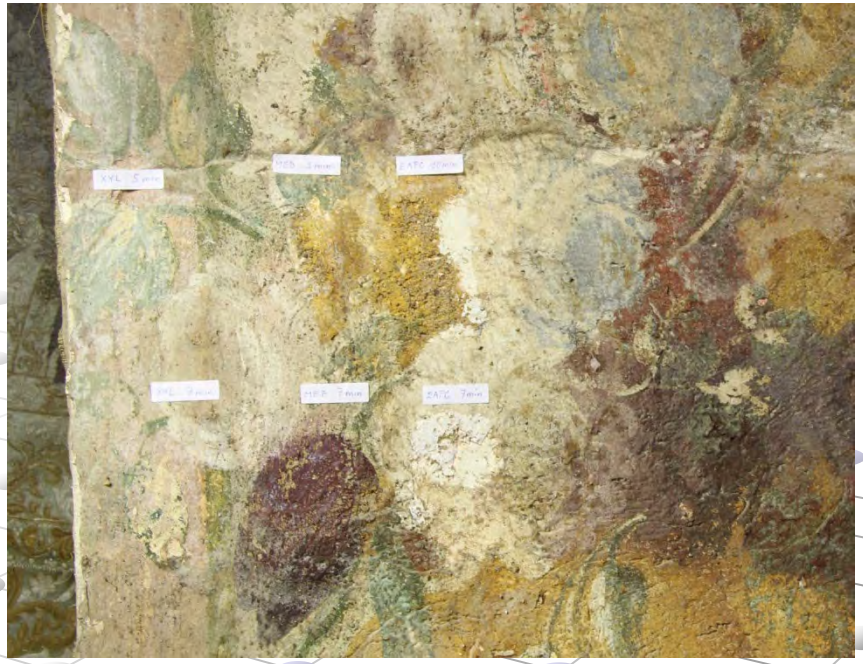
- As seen in the test field, a 5-minute exposure to the material XYL proved to be the gentlest. There is no disturbance of the color layer and the dispersion has been largely removed.

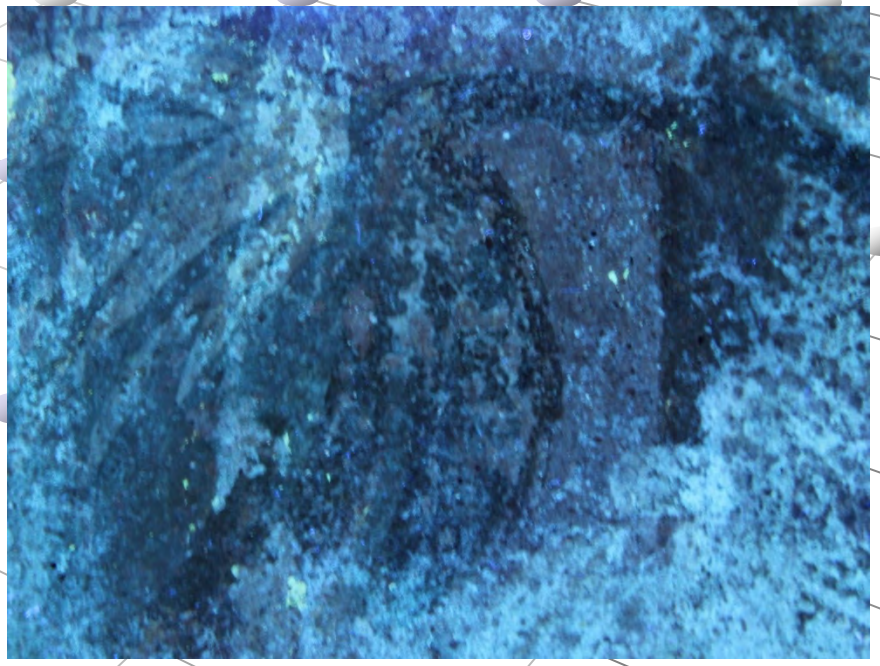
MEB

- An exposure of 5 minutes already results in minor damage to the color layer. In a longer period, the damage is more extensive.

EAPC

- During a 7-minute exposure, the dispersion layer was only removed from the putty. A 10-minute exposure strongly disturbs the color layer.





Deatil of the application of XYL for a period of 5 minutes. UV light reveals that a thick layer of glue has been removed from ca 95% of the test surface. Color layer locally came off, but due to the fact that the color layer had not been properly fixed prior to the application of the glue. This l fault is not considered to be related to the used XYL microemulsions.

CLEANING OF STONE

Case Study – Old Jewish cemetery in Prague

- marble marker
  - According to the restorer´s report covered with a mixture of PVA emulsion and beeswax in 1970´s
  - FTIR analysis of samples confirmed only presence of beeswax

Samples of micro-emulsions: XYL, MEB a EPAC

Condition of application:

- Pulp (Arbocel) saturated with micro-emulsion applied directly on the stone surface and upon Japanese paper covering of stone surface

- Covered by plastic sheet to reduce evaporation of solvents (in both cases)

- Weather condition: cold rainy day and sunny warm day

Removal of compresses:

- Surface was cleaned by excess of water and brushed after removal of compress

Evaluation

- Cleaning process was successful for all three types of micro emulsions with favourable visual effect
- Possible alteration of stone surface is still under inspection

CONSOLIDATION OF HISTORIC MORTARS

Karlštejn Castle

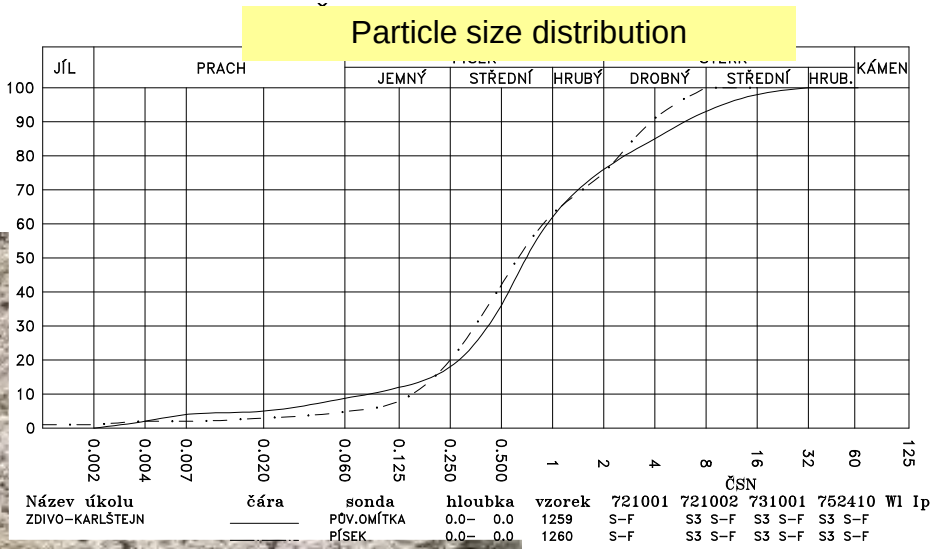
Karlštejn Castle (Central Bohemia)

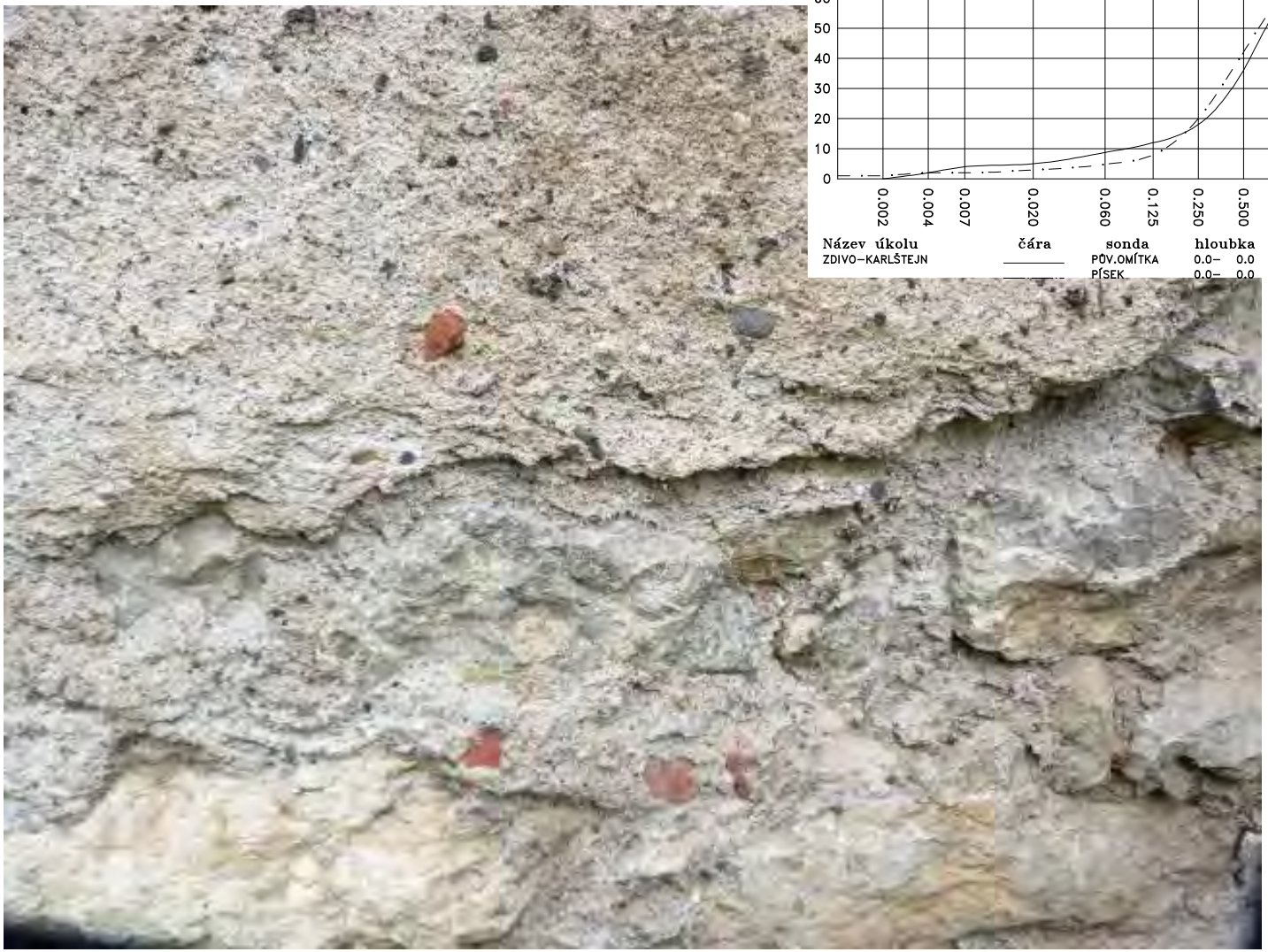
Built in 14th cent., regotized in 2nd half of 19th cent., mortars from 1890

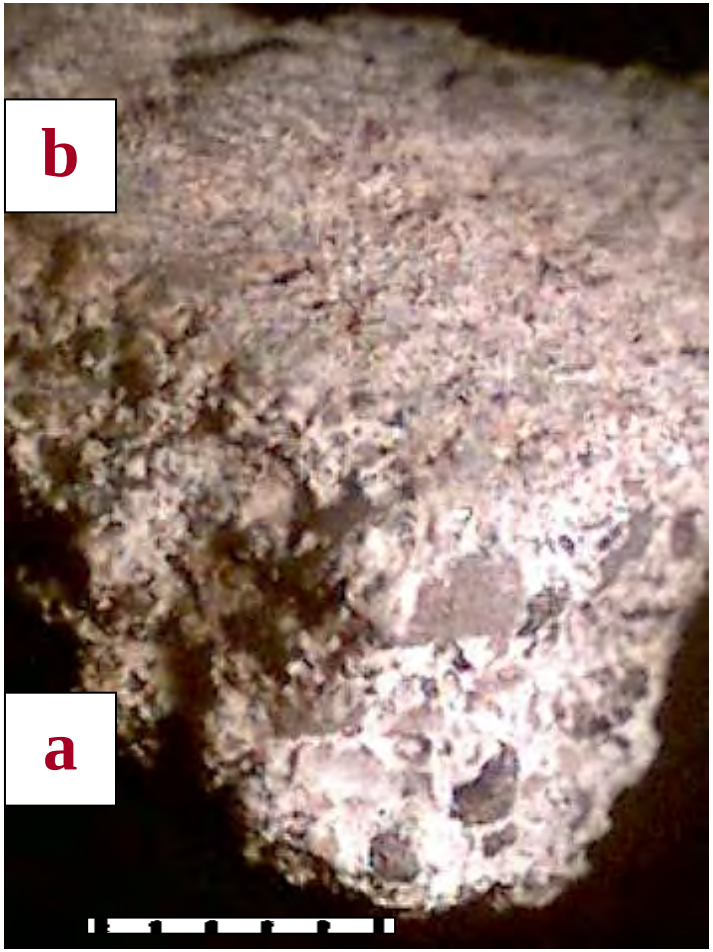
Damaged exterior plasters of the Emperor Palace, situated at the castle bailey

Weathered mortar to be tested

Particle size distribution





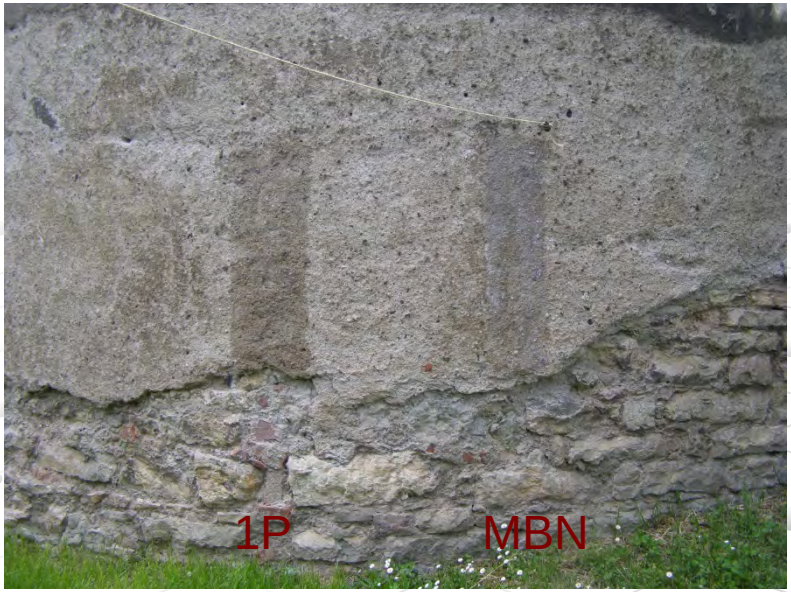


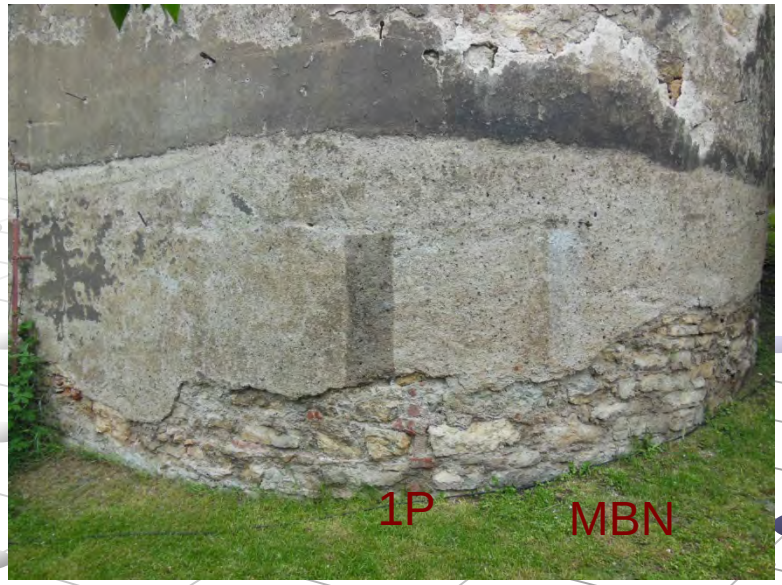
- **A – core**, 20-25 mm thick layer, coarse grain lime mortar, low cohesion and hardness , brittle, powdered. Water uptake 19,02%, Particle size distribution up to 10 mm, quartz predominantly aggregate with considerable share of unstable weathered shale up to 10 mm in diameter.
- Lime content 25 – 30 %

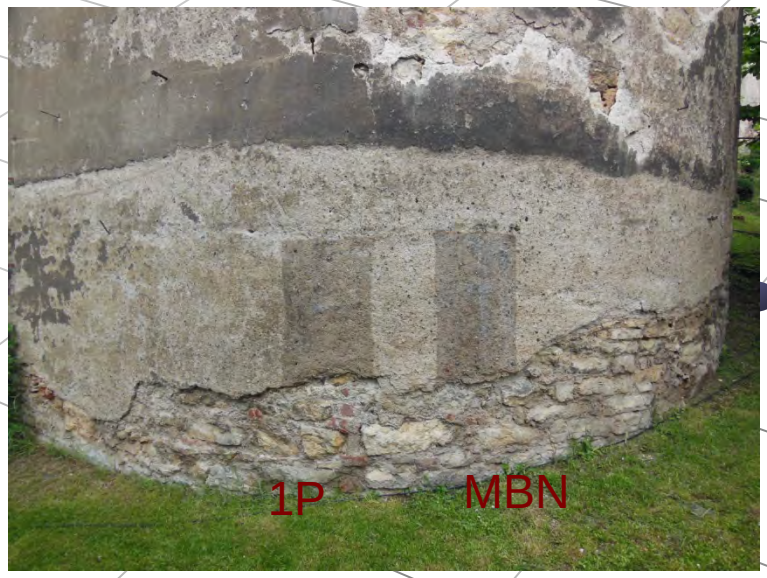
- **B – stucco**, 2-4 mm thick layer , pure lime mortar,fine to mid grained quartz sand brittle, durable ,
- Lime content 40 %

1st application

2nd application

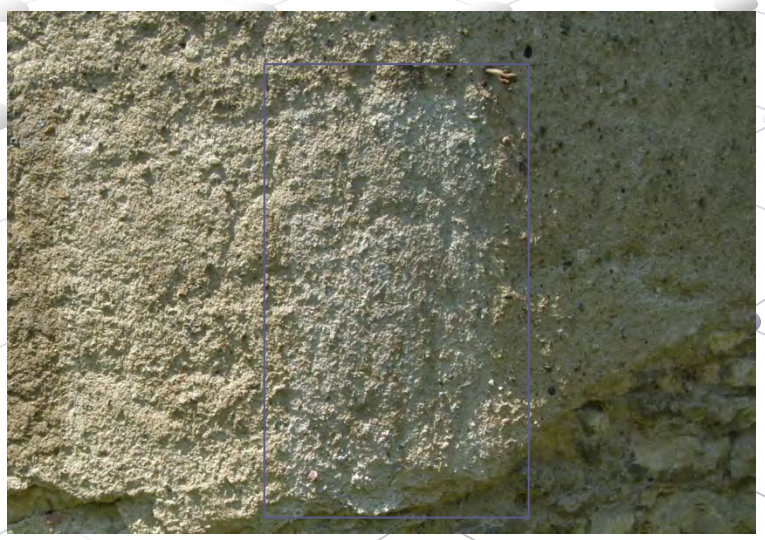






MBN

3rd application



2nd application

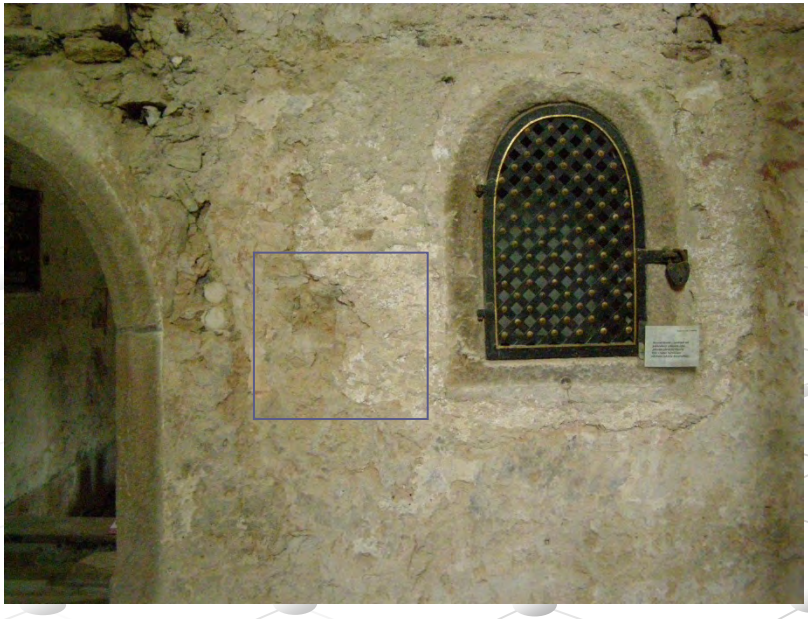
E35

CONSOLIDATION OF MURAL PAINTINGS

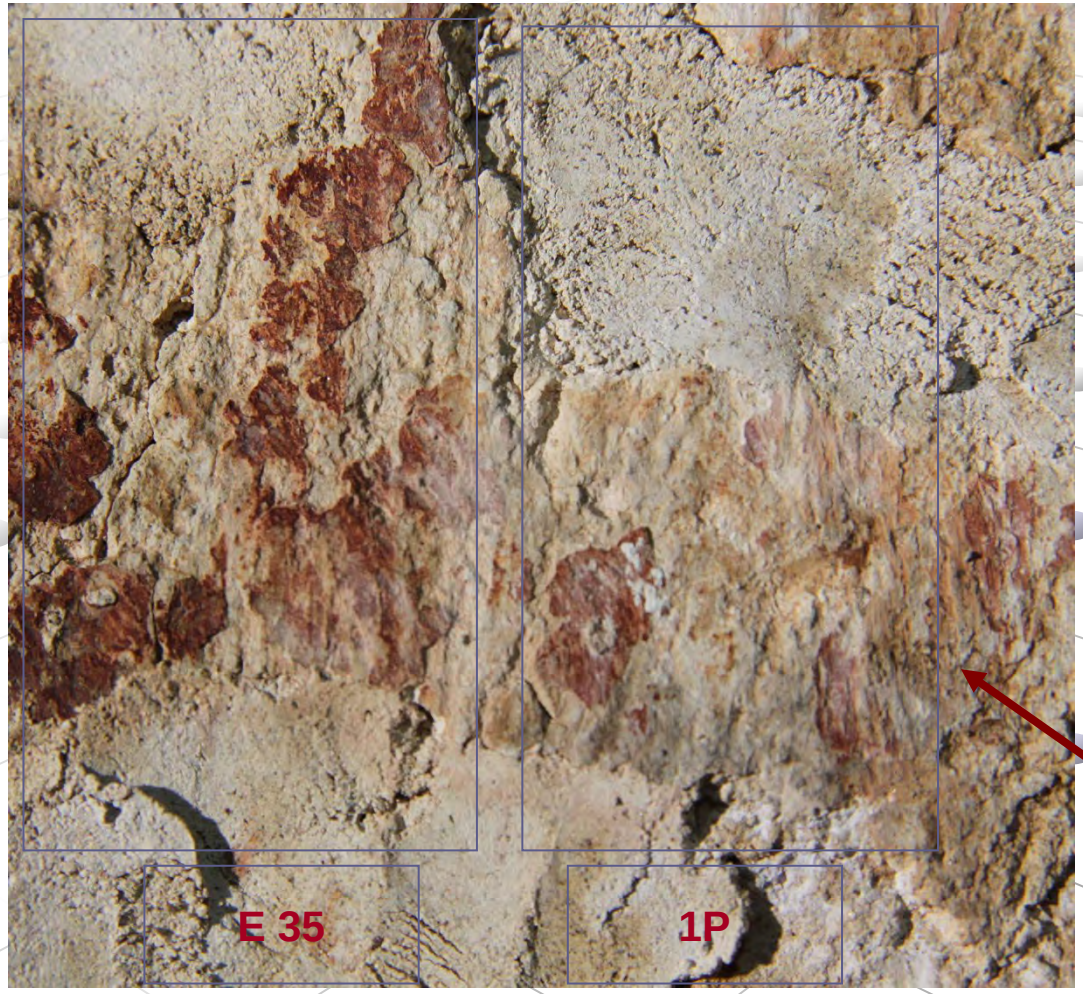
Church of st. Vitus, Zahradka, Eastern Bohemia

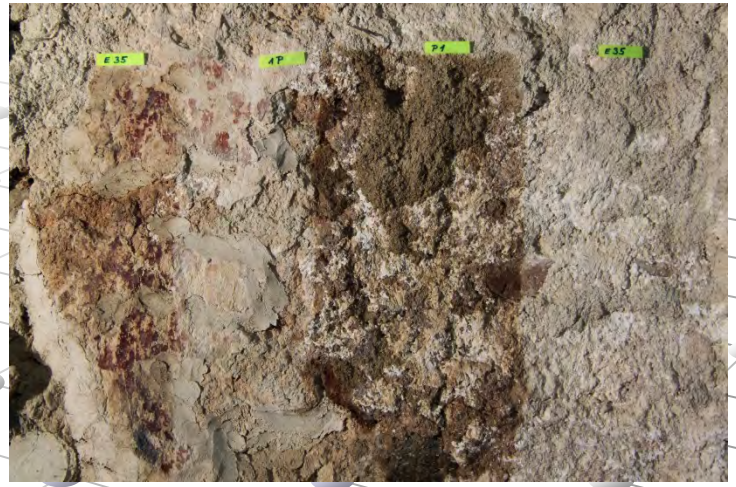
- Fragments of Gothic wall paintings (late14. century)
- Discovered in 1970´s
- Stabilized with (?) acrylic emulsion after recovery

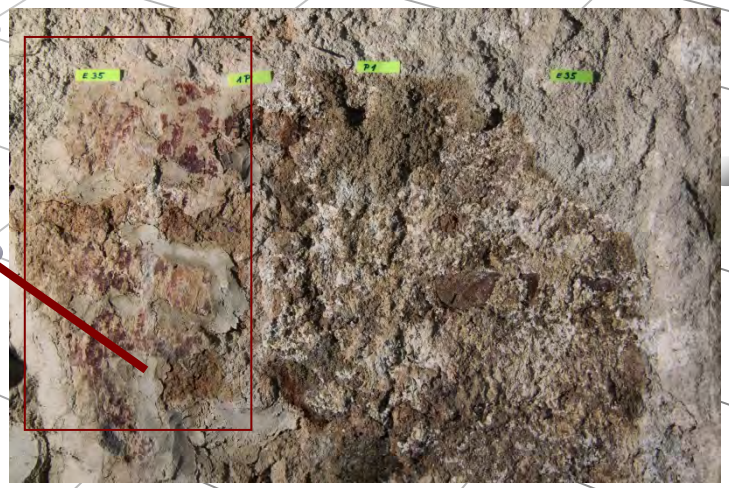
Designated testing area marked with white square,
Way of application: by brushing



Consolidation of paint layer (left image and two left stripes) and lime mortar underlayer (two right stripes)







Transfer panel used for consolidation test

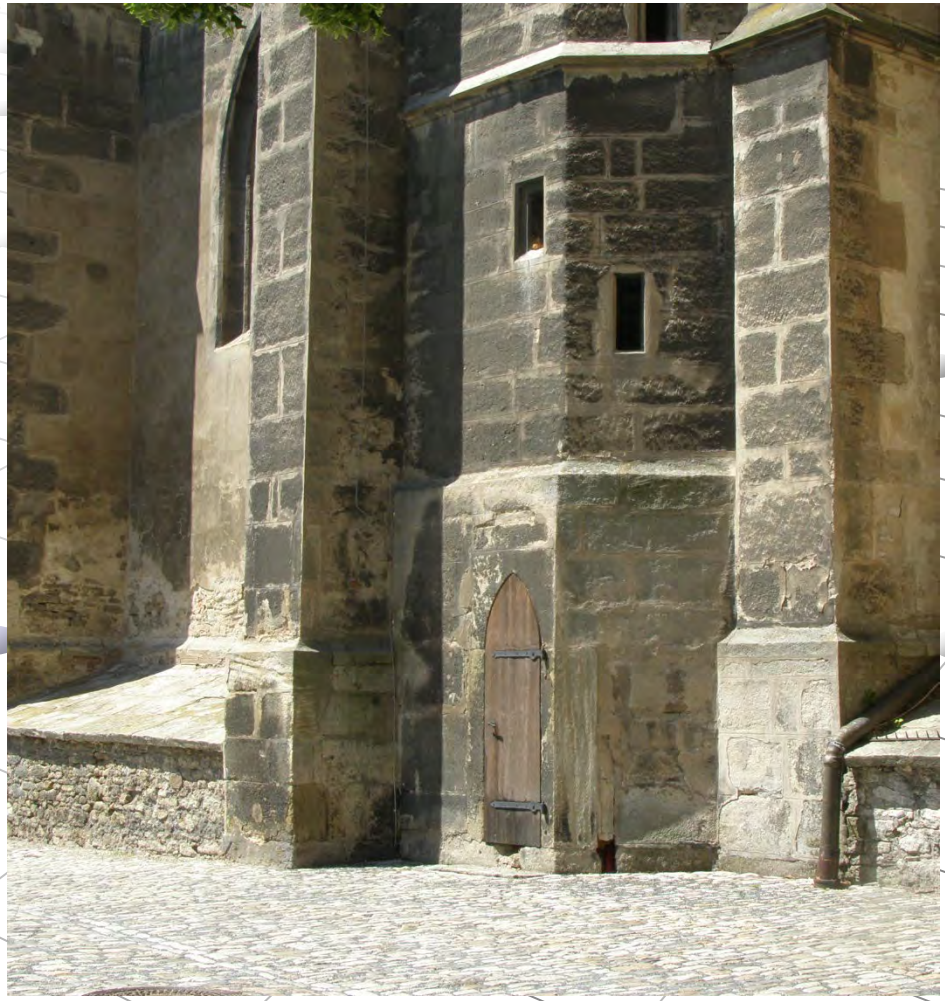
Application proceeded on the fresco layer after cleaning

Application by brushing
1 varnish – left
2 varnishes –right

Difficult to penetrate

CONSOLIDATION OF STONE

Case study: Kutna Hora
Archdean´s Church of St. Jacob



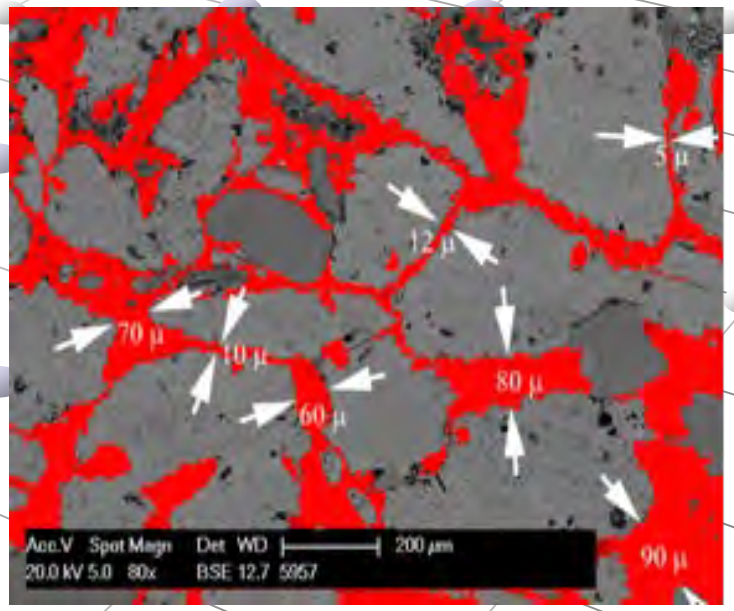
Petrographic key characteristics of Kutná Hora limestones

Material name, sample n°	Limestone Kutná Hora #CZ/11/K/1 (No. RESTAURO: K2)
Type of material	Natural stone
Geological formation	Cretaceous
Provenance	Area of Kutná Hora
Lithotype	Detritic siliceous limestone
Bulk density	?
Total porosity	?
Compressive strength	?
Absorption of water	?
Frost resistance	?
Data assessed by microscopy and SEM (IATCS)	
Structure and texture, orientation	basically compact texture of carbonate nodules of equigranular size; slight orientation at microscopic scale
Texture-supporting constituent	grain
Type of binder	contact +/- filler
Nature of binder	calcite, clay (kaolinite)
Mineral nature of grains	
main constituents	calcite, quartz
minor constituents	mica
accessories	
Average grain size	0.5 – 1 mm
Estimated degree of sorting	good

Typical shape of grains (according to Bayly 1968[1])	sphericity: low shape: rounded
quantification of visible porosity[2]	13.22 % by area (holds for the slightly weathered state, would increase significantly with progressive weathering
Classification of pores	1) Intergranular (along grain boundaries) sometimes widened by ?diagenetic dissolution 2) Irregular fissures
Description of pores and need for consolidation	Type 1 pores: partly interconnected pore system with diameter of < 1 µm to 20 µm; risk of sanding. Type 2 pores: fissures of sub-parallel orientation parallel to the texture, with diameters of 20 µm to 400 µm probably caused by weathering; risk of spalling. Both types of pores need consolidation.

(J.Weber, E.Ghaffari, IATCS)

- Biodetritic, cretaceous sandy limestone, coarse to very coarse-grained,
- coarse pores size 30-150 µm connected with finer pores up to 1-10 µm,
- high porosity



SEM-BEI, cross section, pore space colored red, by K. Bayer

Kutna Hora limestone

- Main results of weathering:
- loss of cohesion of the limestone particles (mainly calcite) on the stone surface;
- formation of gypsum crusts;
- exfoliation of gypsum crusts;
- deformation of stone surface due to sulphatisation
- loss of material on the surface - backweathering in larger scale;
- crack formation

LABORATORY TESTS

Materials tested: 1P and E35

Way of application: applied twice on softly dry cleaned surface by pipette

Area of application about 0.75 dm^2 in both tests

Consumption of liquid: cca 12 g (1 test), cca 16 g (2 test)

Evaluation of depth of penetration: Coloring of cross section by phenolphtalein in ethanol

Depth of penetration: very little penetration of nanosuspensions observed in both cases

Original dry surface

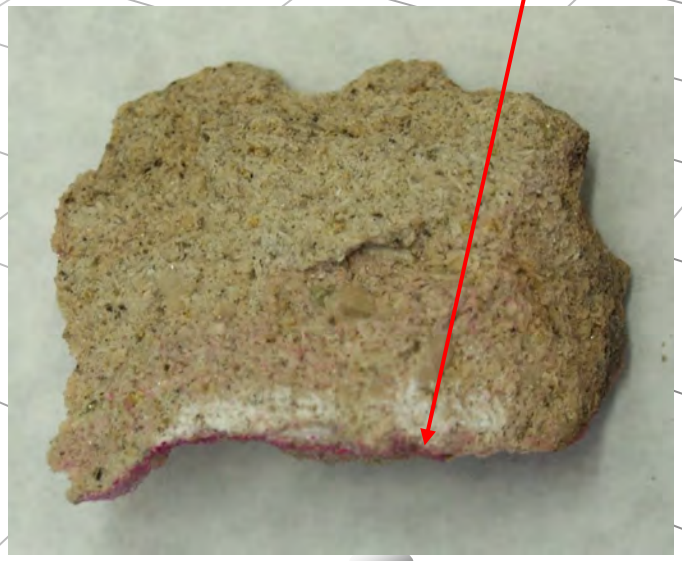
Surface after treatment

1P

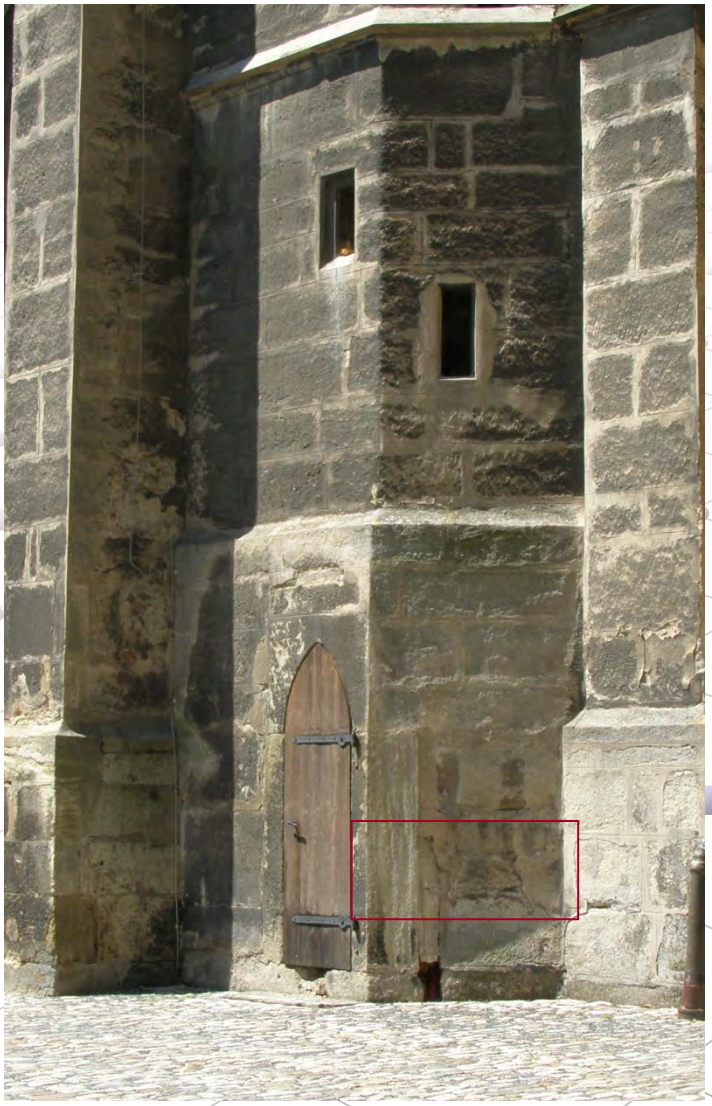
Whitening of treated surface after drying

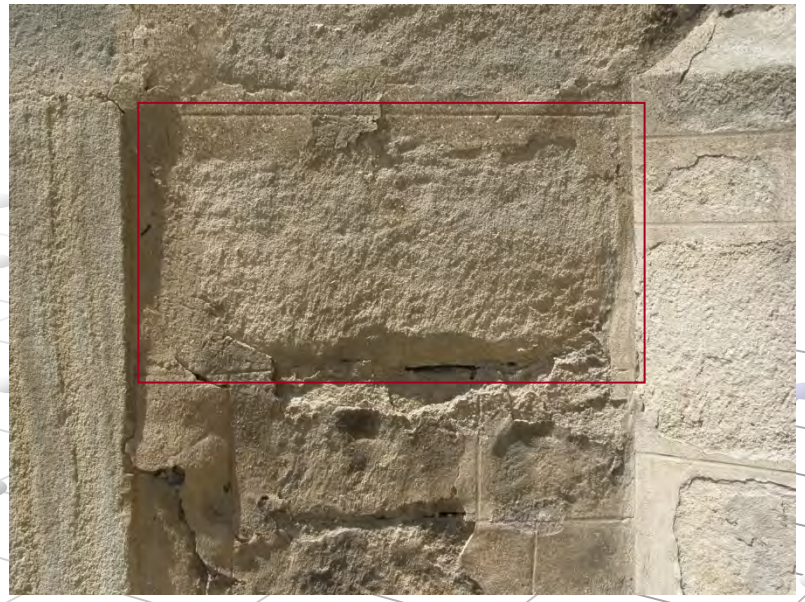
Cross section-phenolphtalein test

E35

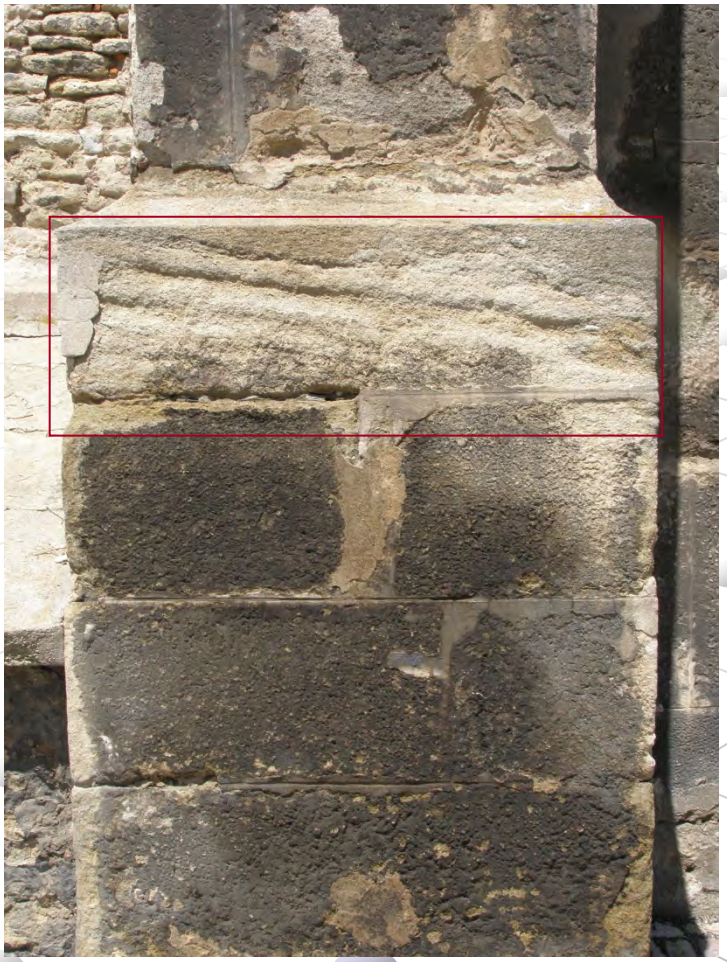


ON SITE TESTS





Test 1: homogeneous stone ashlar



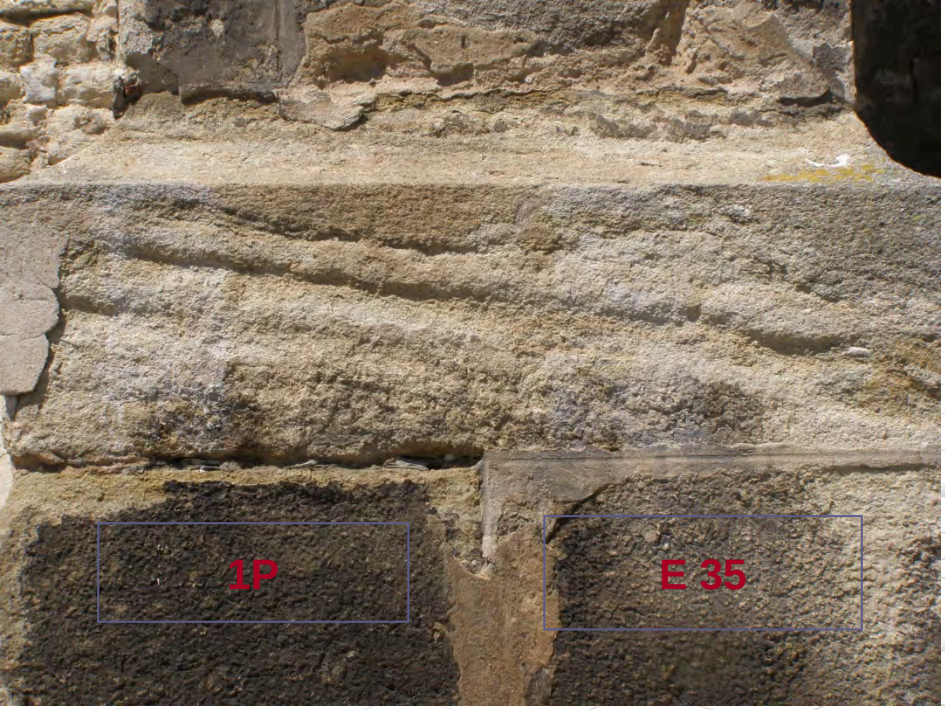
Test 2 : stone ashlar with weathered sedimentary layers

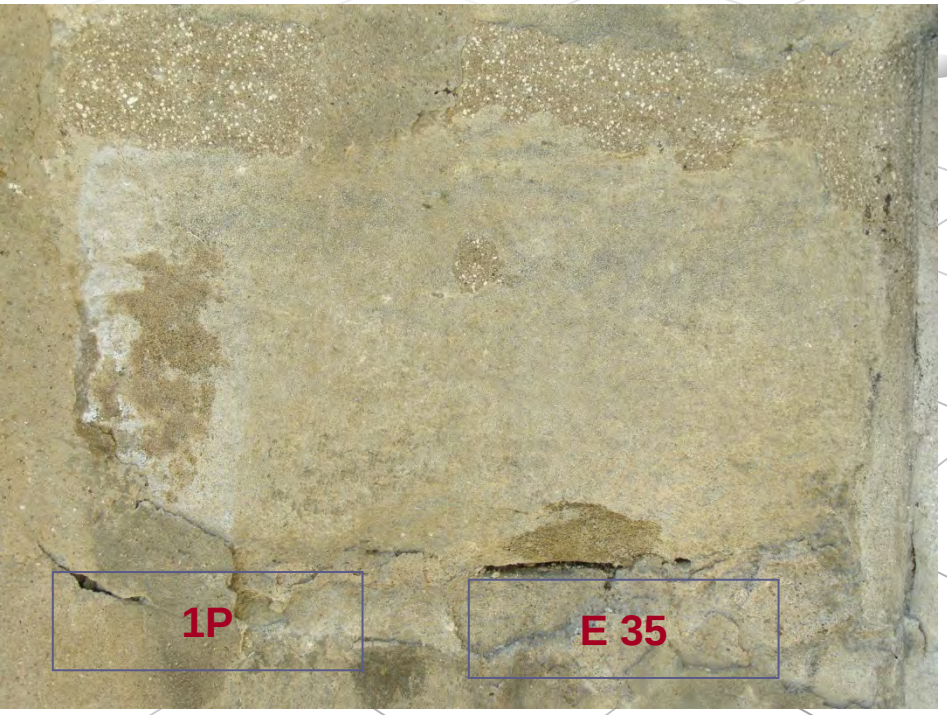
Way of application in all cases: continuous pouring till the substrate accepts consolidant

Testing areas after drying

P1

E 35





Comparison of the extent of white haze of both consolidants after drying

Calculated consumption was roughly 1,5 l per square meter

Preliminary conclusions

- CLEANING (AGED EMULSION REMOVAL)

- MURAL PAINTINGS
- Removal of aged layers of acrylic emulsion from murals was effective in all cases in spite of mentioned interactions with the substrate
- 5 min application of XYL proved to be relatively best option for the removal of acrylics from tested mural paintings provided that the secco layer is well connected with the support
- Problem is low possibility to control the speed of cleaning and to stop possible negative effects
- Additional retouchings after treatment is essential

- STONE
- Cleaning of organic layers from marble samples is visually acceptable. More research is needed to prove the safety from point of view of possible interaction between organic layer and substrate. Best results shown with XYL product

Preliminary conclusions – Consolidation I

- MURAL PAINTINGS
- White haze identified both after application of 1P (more) and E35 (less)
- No other nanosuspension tested so far
- Murals must be slightly washed after treatment to prevent the creation of white haze
- Re-washing endanger unstabilized secco layer, traces of released pigment identified
- Facing problems in identification of the depth of penetration

- HISTORIC MORTARS
- White haze appears increasingly in the row: E35 → 1P → MBN
- Consumption approx. 2,5 l /m2 per each application
- Feel of certain consolidation effect is recognizable
- Machanical tests delayed due to late arrival of nanosuspensions

Preliminary conclusions – Consolidation II

STONE (on site tests)

- White haze seems to be essential problem of the application
- Consumption approx 1,5 l/m2 when heavily weathered surface

STONE (lab test on authentic stone ashlar)

- White haze appears after 1st application
- Very low penetration of nanosuspension into tested stone ashlar

PROBLEMS TO BE SOLVED (IN GENERAL):

- Sedimentation of nano-suspensions (possible agglomeration of nanoparticles)
- After-treatment to prevent white hazing (reverse migration)
- Control of the depth of penetration
- Test methods for treated samples with good interpretive value (mechanical tests, depth of penetration in historic objects)

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RESTORATION monuments buildings CONSTRUCTION CONSERVATION landmarks