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CONSERVATION OF STONE

products and methods

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The 3 main classes of the conservation methods

1. Regular maintenance	it delays the onset of damage
2. Preventive methods	changing environmental conditions ☞ preventing degradation of materials
3. Intervention methods	direct intervention on the object ☞ limits the impact of environmental conditions on the materials

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1. Regular maintenance and precautions

Monitoring of the flow defects: roofing, joints, gutters, …

Photos C. Bläuer (Berne, CH, BE)

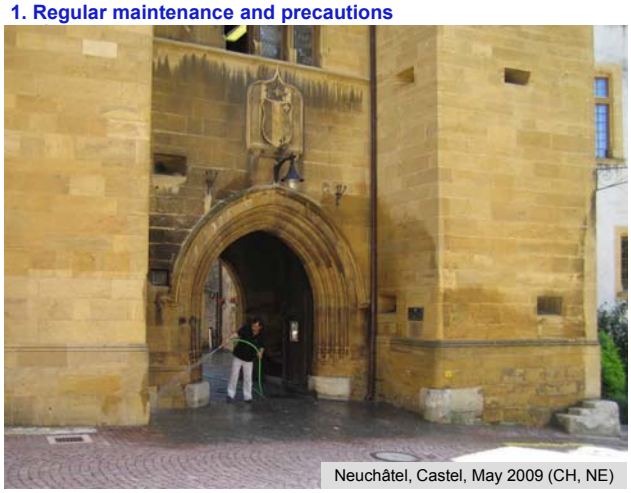
Conservation Sci

1. Regular maintenance and precautions

Monitoring of the flow defects: roofing, joints, gutters, …

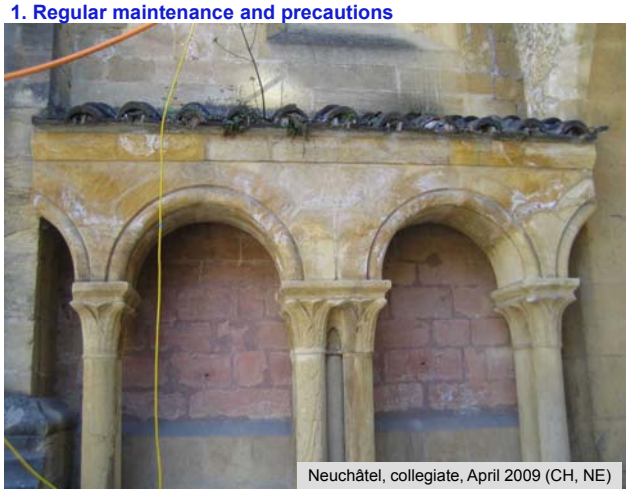
Fribourg, UNI, March 2009 (CH, FR)

1. Regular maintenance and precautions



Neuchâtel, Castel, May 2009 (CH, NE)

1. Regular maintenance and precautions



Neuchâtel, collegiate, April 2009 (CH, NE)

1. Regular maintenance and precautions

Neuchâtel, collegiate, May 2009 (CH, NE)

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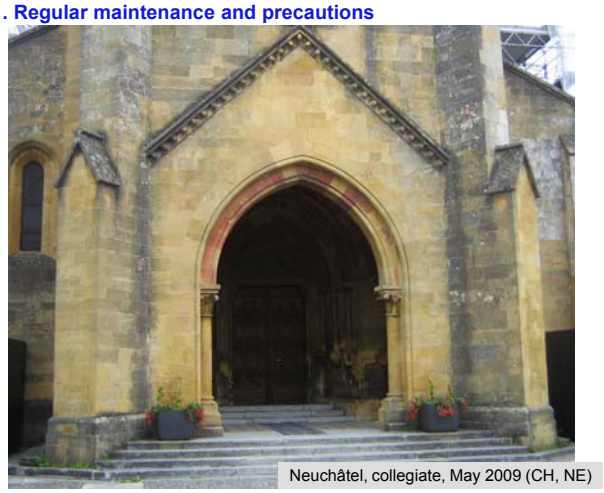

Neuchâtel, collegiate, May 2009 (CH, NE)

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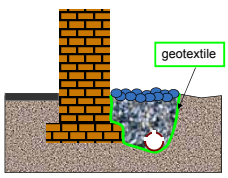
2. Preventive methods

2.1 Control of rising damp: drainages



Vuisternens-devant-Romont (CH, FR) church, 2007

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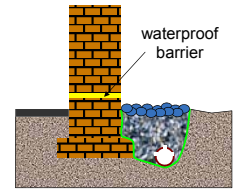
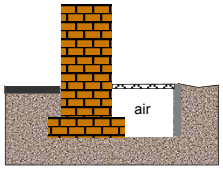
2. Preventive methods

2.1 Control of rising damp

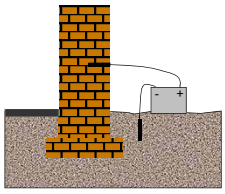
± intervention methods



drainage + waterproof barrier



ventilation gallery



electro-osmosis

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2. Preventive methods

2.1 Control of rising damp

± intervention methods


Prague (CZ), 2010

Belmont-sur-Lausanne (CH, VD), 2010

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2. Preventive methods

2.2 Protection of façades/sculptures with canopies (*auvents*), cornices, ...

Protective structures against rain and water flow


Photo C. Bläuer (Zillis, CH, GR)

2.2 Protection of façades/sculptures with canopies, ...

Fribourg, Montorge chapel, December 2009

Fribourg, Stalden, March 2010

3. Intervention methods

Treatment products must:

- **stabilize** and **improve** the current state
- **slow down** the degradation development
- have a long standing **protective effect**
- not obstruct **a subsequent conservation intervention**
- be **simple to use** and **non-toxic** to the user and the environment

3. Intervention methods

The main conservation and restoration methods

- surface protections (paints, renders, water repellants,...)
- cleaning, elimination of microorganisms
- elimination of salts, desalination
- replacement of stones and/or mortars
- consolidation

3. Intervention methods

3.1 Protection of façades/sculptures with whitewashes and paints *(badigeons et peintures)*

Functions: Formation of a **sacrificial layer** and/or formation of a **protective layer** on the surface

Binders:
- organic (oil, silicone, acrylic,… based)
- inorganic (lime or silicates)

Use: Protective paint against rain and dirt, anti-graffiti systems,…

3.1 Preventive methods: whitewashes and paints

Neuchâtel, Castel, Auguste 2010 (CH, NE)

3.1 Preventive methods: whitewashes and paints

Montheron, temple, September 2006 (CH, VD)

3.1 Preventive methods: white washes and paints

Fribourg, Rue du Tilleul, December 2009 (CH, FR)

3.1 Preventive methods: whitewashes and paints

Medieval statues, south portal, Fribourg cathedral (CH, FR)

3.1 Preventive methods: whitewashes and paints

Historic binding materials *(liants)**

slide from the course "wall paintings" of C. Bläuer

Technique	Principle / binder
Fresco	Pigment dispersion in water applied on fresh not yet set support / lime binder
Lime painting	Pigment dispersion in water or lime water applied on fresh lime wash / lime binder
Lime casein	Pigments mixed with lime casein solution
Glue	Pigments dispersed in glue water
Tempera	Binder is an oil water emulsion e.g. full egg
Oil	Binder is a drying oil e.g. linseed oil *(huile de lin)*, nut oil, etc.
Water glass (liquid silicates)	Preparation of support; application of pigment dispersions in water; fixation with water glass solution

* Incomplete enumeration; binders not mentioned here are e.g. wax, resin (natural and synthetic), many possible mixtures of binding materials, etc.

slide from the course "wall paintings" of C. Bläuer

3.1 Preventive methods: whitewashes and paints

Painting materials

Colorants (pigments and dyestuffs) and binders

Pigments: grains of coloured materials that are insoluble in the binding media

can be classified according to:

their origin: natural, artificial; organic, inorganic; from plants, from animals, from minerals or earth colours

their colour: blue, red, yellow, black, white….

the metal they contain: Cu-, Pb-, Fe-, Mg-, Cr-, Cd-, Zn-, Ti-, Hg-pigment

Chemical compounds: metal, oxides, carbonates, silicates…

3. Intervention methods

3.1 Protection of façades/sculptures with whitewashes and paints

Lime based paints (historical paintings):

$$Ca(OH)_2 + CO_2 + H_2O \rightarrow CaCO_3 + 2H_2O$$

- good water vapor permeability and good water absorption;
- easy and reversible treatment;
- lime based paints can be modified with additions like oils, casein => increase of durability
- **need to be repaired or totally re-done regularly**

3. Intervention methods

3.1 Protection of façades/sculptures with whitewashes and paints

"Drying oils" paints:

The most common example of a drying oil = **linseed oil**
= mixture of triglycerides of long chain carboxylic acid

+ small additions of metals such Pb, Co, Mn that accelerate the drying process

The drying process is a complex one of polymerisation probably catalysed by peroxides

- good water vapor permeability,
- good resistance to UV light,
- **stop water absorption**

3. Intervention methods

3.1 Protection of façades/sculptures with whitewashes and paints

Pure silicate based paints (water glass = liquid silicates):

$K_2O(SiO_2)_4 + CO_2 \rightarrow SiO_2\ xH_2O + K_2CO_3$
$K_2O(SiO_2)_4 + CaCO_3 \rightarrow CaSiO_3\ xH_2O$
$K_2O(SiO_2)_4$ + mineral pigments/ aggregates → crystalline compounds

- good chemical resistance,
- good water vapor permeability,
- good resistance to UV light,
- do not stop water absorption

Mixtures with water repellant admixtures (like resins, silicones,...) have entirely different properties

3. Intervention methods

3.1 Protection of façades/sculptures with whitewashes and paints

Organic paints with organic solvents
- alkyd resins = glycerylphtalate resins = polyester
- silicone
- epoxy resins, ...

- they make impermeable surfaces and hydrophobic surfaces,
- they are sensitive to microorganisms,
- their reversibility depends on the nature of the treated material,
- they need solvents,
- they are sensitive to UV light,
- **they can be used ONLY in limited cases on building heritage !**

3. Intervention methods

3.1 Protection of façades/sculptures with whitewashes and paints

Emulsions: pigment and solid or semi-solid polymeric particles dispersed in water in which they are insoluble
- acrylic emulsions
and/or
- vinyl emulsions

- they make impermeable surfaces and hydrophobic surfaces,
- they are sensitive to microorganisms,
- their reversibility depends on the nature of the treated material,
- they can be sensitive to UV light,
- **they can be used ONLY in limited cases on building heritage !**

3. Intervention methods

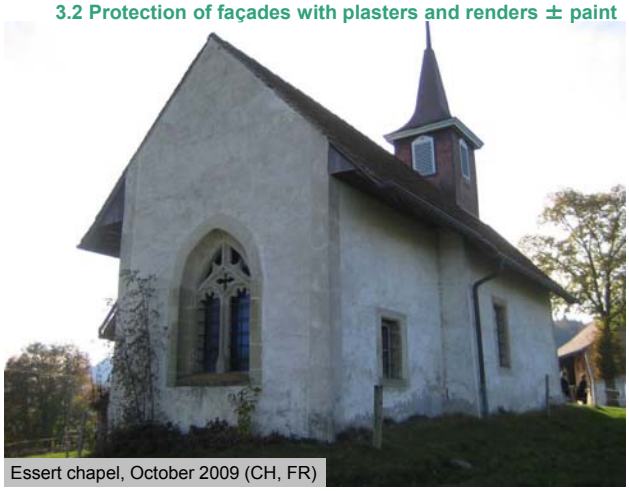
3.2 Protection of façades with plasters and renders ± paint

Function:
formation of a **protective layer** on the surface

Binders:
- inorganic (clay, lime, hydraulic lime, grey or white cement, silicates)
- organic (epoxy, acrylic,…)

Use: Protective paint against rain and dirt, anti-graffiti systems,…

3.2 Protection of façades with plasters and renders ± paint



Essert chapel, October 2009 (CH, FR)

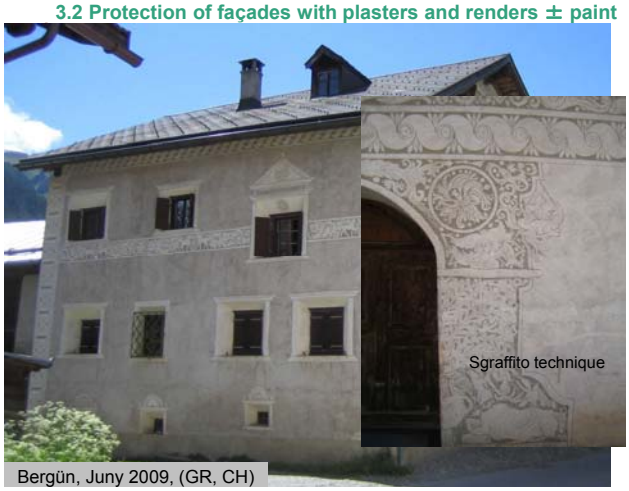
3.2 Protection of façades with plasters and renders ± paint

Vaulruz castel, July 2009 (CH, FR)

3.2 Protection of façades with plasters and renders ± paint

Grüsch GR, Haus Rosengarten, photo C. Bläuer

3.2 Protection of façades with plasters and renders ± paint



Bergün, Juny 2009, (GR, CH)

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3. Intervention methods

3.3 Protection of façades/sculptures with water repellants

Aims of making water repellant

- To protect against rain an dirt
- To limit the capillary suction
- To reduce the rate of degradation
- To reduce the impact of the air pollutants and of the biodegradation (algae, lichen, bacteria, etc.)

3. Intervention methods

3.3 Protection of façades/sculptures with water repellants

- **Silicones** – poly-organo-siloxanes or silicone resins
- **Waxes *(cires)*** – microcrystalline waxes
- **Acrylic resins** mixed with polysiloxane
- **Organofluoride resins** (urethanes, polyethers,…)

3. Intervention methods

3.3 Protection of façades/sculptures with water repellants

Berne (CH), Photo C. Bläuer

The durability of water repellants depends on the product (the chemical functional groups give their properties to the molecules) but usually at least between 5 and 10 years

Degradation :
- photo-degradation induced by photonic irradiation of polymers;
- chemical: in case of interaction with a chemical agent;
- biological

3. Intervention methods

3.3 Protection of façades/sculptures with water repellants

water repellants are not suitable for :

- horizontal areas
- areas where water infiltrations behind the treated part are possible
- supports rich in hygroscopic salts

Photo C. Bläuer

3. Intervention methods

3.3 Protection of façades/sculptures with water repellants

Water repellants disadvantages :

- irreversible
- possible chromatic changes
- development of algae
- different aesthetic changes between treated and non-treated areas
- scaling
- accumulation of the water at the lower parts of buildings

Wengi Büren an der Aare (CH), Photo H.-J. Gerber

Fribourg (CH), Rue du Tilleul, May 2008

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3. Intervention methods

3.4 Protection of façades/sculptures with antigraffiti

Role of an antigraffiti:

The aim is to make a layer between the wall to protect the graffiti, in order to prevent the penetration of the paint in the building material and to make cleaning easier

3. Intervention methods

3.4 Protection of façades/sculptures with antigraffiti

The essential properties that should have the antigraffiti:

- **safety**: should not change the colour, the microstructure, the water absorption, the water exchange kinetics of the building material;
- **durability**: must protect against graffiti long enough;
- **efficiency**: every graffiti must go away without any residues;
- **reversibility**: this principle applies to classified monuments and it implies that any treatment must be removable at any time without damage to the original building material.

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3. Intervention methods

3.4 Protection of façades/sculptures with antigraffiti

Permanents systems:

Polyurethane or epoxy or acrylic or… layers, impermeable and that remain on the façade even after cleaning.
Resistant to atmospheric influences, they require little maintenance. These products are generally harmful to humans and the environment.
Risks: closing pores => limited water evaporation, colour changes

Cleaning : Hot wasser, solvent

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3. Intervention methods

3.4 Protection of façades/sculptures with antigraffiti

Partly permanent systems:

Mono-layer systems: (eg: alcoxysiloxanes based, siloxane copolymers based,… products) the protective layer is partially removed during cleaning so it is necessary to carry out a new application. Permanents residues stay on the treated material.
Cleaning: Hot water

Two-layers systems: one permanent lower layer (hydro-oleophob: oligomere siloxane) + one sacrificial layer that is removed during each cleaning (wax).
Cleaning: hot water

3. Intervention methods

3.4 Protection of façades/sculptures with antigraffiti

Reversible systems:

These products form a sacrificial layer that is removed during the cleaning of the graffitis. The layers are not much resistant to weather conditions and should be applied after each cleaning. Advantage: they influence the visual aspect and the physical properties of the façade very little.

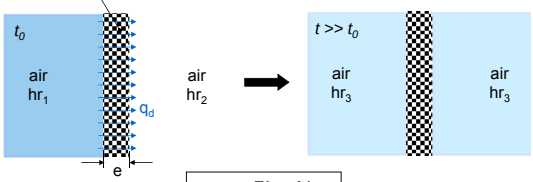
Eg.: polysaccharides, acrylate

Cleaning : Hot water

THEORIE

Protection of façades: water vapour permeability, μ & Sd

matériau poreux perméable à la vapeur d'eau

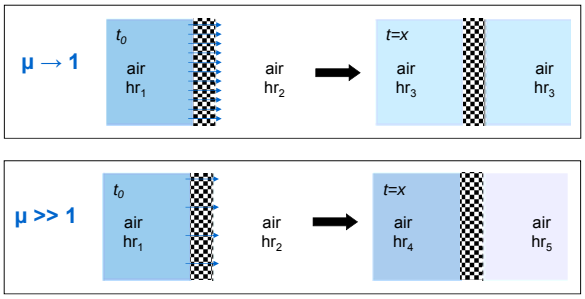


$$q_d \propto \frac{\delta L}{\mu} \frac{\Delta hr}{e}$$

q_d	densité de flux [kg/m^2.s]
δL	coefficient de diffusion à la vapeur de l'air [kg/Pa.m.s]
μ	**facteur/coeff. de résistance à la diffusion de vapeur d'eau [-]**
Δhr	hr_1-hr_2 [-]
e	épaisseur du matériau poreux [m]

THEORIE

Protection of façades: water vapour permeability, μ & Sd



Un matériau dont le facteur μ = 10 est ***en théorie*** 10 fois plus résistant à la diffusion de vapeur d'eau qu'une couche d'air qui aurait la même épaisseur

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THEORIE

Protection of façades: water vapour permeability, μ & Sd

$$Sd = \mu \cdot e$$

Sd	**résistance à la diffusion de la vapeur d'eau [m]**
μ	facteur/coeff. de résistance à la diffusion de vapeur d'eau [-]
e	épaisseur du matériau poreux [m]

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3. Intervention methods

3.5 Cleaning

Main purpose: to remove dirt deposits from the surfaces (primarily aesthetic interest! absolutely necessary only if these deposits can be harmful).

! Every cleaning must (**should!**) be done so that materials and their original surface is preserved (stones AND mortars)

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3. Intervention methods

3.5 Cleaning

The choice of a cleaning method depends on:

- the nature, the density and the adhesion of the **dirt**;
- the nature and the state of the **stones** and **joints**.

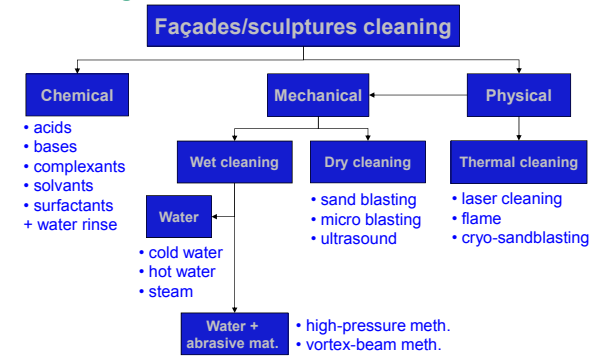
! Any cleaning must be regarded as a **special case** that requires **precedent local tests** and the job must be done by a **competent and well trained staff** !

3. Intervention methods

3.5 Cleaning


Florence (I)

3.5 Cleaning



According to L. Goretzki, prof. at the Weimar University

3. Intervention methods

3.5 Cleaning

Cleaning with laser (wavelength 1064 nm IR):

Interaction between the laser beam and the dark dirt absorb radiation => photoablation: combination of thermal and mechanical interactions between the absorbed radiation and the matter

Advantages: targeted cleaning (sculptures)

Disadvantages: not usable on large areas, interactions with matter not yet fully understood, yellowing of clear substrates

3. Intervention methods

3.5 Cleaning

Cleaning with laser

3. Intervention methods

3.5 Cleaning

Application of impregnated poultice:

Absorbent material (Japanese paper, rice paper, pulp of paper or pulp of cellulose, carboxy-methylcellulose, clay, sepiolite, etc.) impregnated with water or chemicals (acid, alkali, surfactants, complexing agents like EDTA)

Advantages: targeted cleaning, without any pollution if only water is used

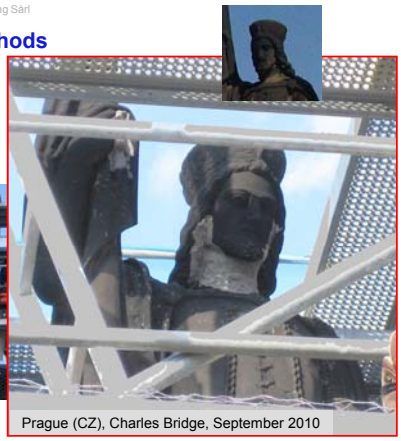
Disadvantages: not usable on large areas, pollution caused by chemical additives

http://upload.wikimedia.org/wikipedia/commons/e/e9/Prague-charles_bridge-hradcany.jpg

3. Intervention methods

3.5 Cleaning

Application of impregnated poultices



Prague (CZ), Charles Bridge, September 2010

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3. Intervention methods

3.5 Cleaning

Cleaning with scalpel

ONLY FOR RESTORER !!!

Müstair, Heiligkreuzkapelle (CH), 2007

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3. Intervention methods

3.6 Elimination of microorganisms and plants

- **Biocides**: treatment with chemical agents (bactericides, algicides, fungicides, lichenicides, herbicides, etc.);
- **Antibiotics**;
- **U.V treatment:** treatment using an ultraviolet ray generator;
- **Mechanical methods**: elimination with tool (brush, scalpel, saw *(scie)*, vacuum *(aspirateur)*, etc.).

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3. Intervention methods

3.7 Desalination

- Desalination *(désalinisation ou dessalement)* = only a REDUCTION of the content of soluble salts
- The desalinations are superficial and selective => changes in the system

Photos Steffen Laue

3. Intervention methods

3.7 Desalination

Always avoid water which would re-mobilize the soluble salts!

Mechanical desalinations:

vacuum cleaner, dry brushing

Photo C. Bläuer

3. Intervention methods

3.7 Desalination

Desalination poultices:

1. Application of Japanese paper
2. Application of wet compress
   - of cellulose;
   - of newspaper;
   - of clay;
   - of ion exchange resins…

3. Intervention methods

3.7 Desalination

- **Successive water baths** (for movable objects with a limited size)

- **Electrochemical desalination**: highly controversial; it works "in theory"; the materials change of colour in the vicinity of the electrodes

- **Chemical transformation**: transformation of soluble salts in non- or very poorly soluble salts (ie : transformation of calcium sulphate into calcium carbonate by application of ammonium carbonate then baryum hydroxide)

3. Intervention methods

3.8 Replacements / *rhabillages ou ragréages*

Remodeling of small deteriorated stone surfaces with suitable mortars: same appearance than the remodeling stone, similar hardness

In case of deep remodelings or remodeling of large surfaces a structural support is necessary (small pegs *(chevilles)* and stainless wire network)

Maximum remodeling surface: 30 cm^2 – Beyond=> yokes *(empiècements)* according to the ARMP (association romande des métiers de la pierre) charter

3.8 Replacements / *rhabillages ou ragréages*

Münster of Berne, 2005

3.8 Replacements / *rhabillages ou ragréages*

Münster of Berne, 2005

http://www.omnium-facades.com/omnium/img_catalogue/1114521050_1.jpg

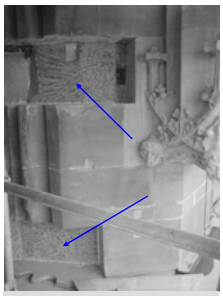
3. Intervention methods

3.9 Replacements / yokes *(empiècements)*

Holes are made in the degraded stones, then new yokes (*empiècements*) of the original stone material –or of a similar stone (juged suitable after laboratory tests)- are placed.

If this work must be done on protruding parts or on parts exposed to splashing (rejaillissement), better resistant stones are accepted.

Minimum thickness: 10 cm for hard limestones; 15 cm for soft limestones, sandstones and molasses (according to the ARMP charter).



Münster of Berne, 2005

3. Intervention methods

3.10 Consolidation

The consolidating agent must:

- Restoring the link between grains
- penetrate the matter along a sufficient depth to establish the link between the healthy and impaired parts
- not form harmful compounds such as salts
- not change the color of the stone
- not prevent subsequent treatments
- not accelerate degradation
- not modify the permeability to water vapor

3. Intervention methods

3.10 Consolidation

The reasons why one consolidates:

a few cm to a few mm
- contour scaling *(décollement de plaques)*
- render detachments

≤ 1 mm
- granular disintegration of stones
- consolidation of too soft renders
- detachments of polychrome layers

3.10 Consolidation

≥ a few cm	A few cm to a few mm	≤ 1 mm
mortars	**washes, suspensions**	**solutions, melted products**
Inorganic materials		
Lime mortars, mortars with mixed binder *(bâtard)*, cement mortars, pouzzolanic mortars	Lime putty *(chaux en pâte)*, whitewash *(lait de chaux)*, cement milk *(Schlämme ou lait de ciment)*	Water lime *(eau de chaux)*, Water glass *(verre soluble, Wasserglas)* Fluates
Synthetic organic materials		
Synthetic mortars Synthetic resins + aggregates		Synthetic resins
Synthetic inorganic materials (silans, silicic esters)		
Organosilicates based mortars	Materials with quick hydrolysis	Silicic esters
Shortlived consolidants		
		Non-polar cyclic compounds, hydrocarbons
Natural resins, tar *(goudron)*		

3. Intervention methods

3.10 Consolidation, methods:

- With poultices: regular impregnation of the compress with treatment solutions;
- With a brush: the consolidant is applied on the degraded stone surface with a brush;
- By spraying: using a sprayer to spread the consolidant on the surface (until refusal!) *(jusqu'à refus !)*;
- By injection: to fill voids in depth;
- By immersion: for movable objects with a limited size that can be treated in the laboratory within a consolidant bath

3. Intervention methods

3.10 Consolidation

Example: Application of Funcosil (silicic ester) on a molasse sandstone façade from the Berne cathedral

3. Intervention methods

3.10 Consolidation

Example:
Application of Funcosil (silicic ester) on a molasse sandstone sample from the Berne cathedral

3. Intervention methods

3.10 Consolidation, history of materials

... - ...	Limewater
1850 - 1960	Alkaline potassium silicate
1900 - 1960	Fluosilicates
... - 1930	Paraffin
... - 1930	Oil linseed
1960 - 1972	Polyester
1952 - ...	Acrylic resins
1960 - ...	Silicic acid esters
1990 - ...	Bio-remineralization
~2010 - ...	Nano-lime
~2011 - ...	Hydroxyapatite (+ $CaCl_2$!!!)

3. Intervention methods

3.10 Consolidation, example of consolidants

The alkali silicate solutions
Water glass
(verre soluble ou Wasserglas – Me_4SiO_4, Me = K, Na, Li):

Known since antiquity, largely used in the second half of the nineteenth century until 1930

Disadvantages of this type of treatment:
- formation of soluble salts and efflorescences
- bad penetration
- formation of ± hard, ± insoluble and waterproof crusts

3. Intervention methods

3.10 Consolidation, example of consolidants

The alkali silicate solutions
Water glass *(verre soluble ou Wasserglas – liquid silcates)*:

$Me_4SiO_4 + 3H_2O \leftrightarrow 4Me^+ + 3OH^- + H_3SiO_4^+$ (solution pH > 12!)

Me = sodium, potassium, (lithium)

Setting reaction:

$2Me^+ + CO_2 + H_2O \leftrightarrow Me_2CO_3$

3. Intervention methods

3.10 Consolidation, example of consolidants

The silicic acid esters = ethyl silicates (very often employed!)

Used since 1960

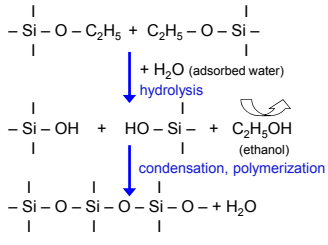
Classic products: Wacker OH, Wacker OH 100, Motema 28, Motema 30, TEOS, Keimsilex OH, Tegovakon V, Funcosil, Steinfestiger OH/OH 100,…

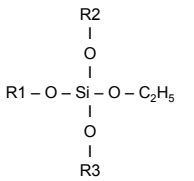
Usable on: sandstone, terra cotta, brick,… (siliceous materials)

3. Intervention methods

3.10 Consolidation, silicic acid esters

tetraethoxysilanes (TEOS): R1=R2=R3=C_2H_5





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3. Intervention methods

3.10 Consolidation, silicic acid esters

Photo S. Mühlhaus Ebersole

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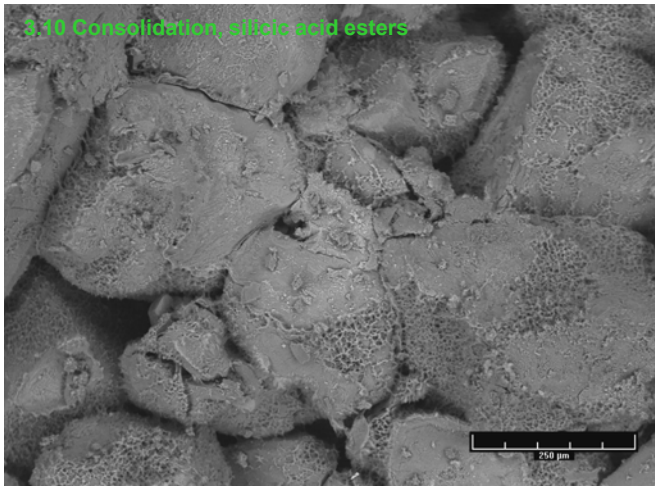
3. Intervention methods

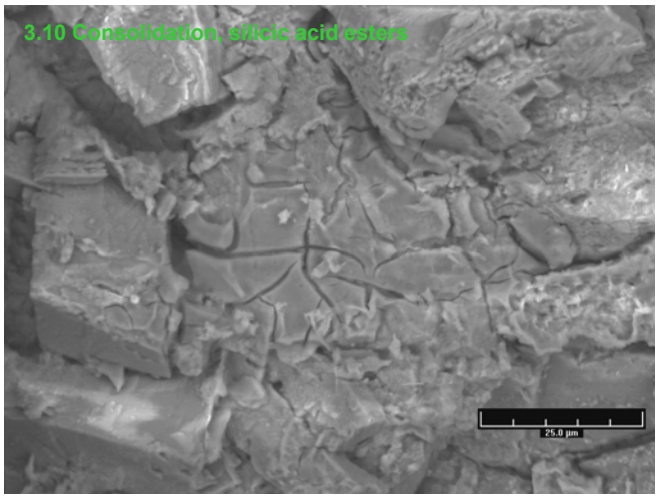
3.10 Consolidation, silicic acid esters

Laboratory tests / Ethyl silicates

Photo C. Bläuer

3.10 Consolidation, silicic acid esters





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