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Comparative Analysis of Stone Cleaning Technologies Applied in
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1. INTRODUCTION

Most of historical monuments in Budapest have been built of the
workable, very porous soft limestone of Sóska, applied for
ornate façades of public buildings, sculptures in squares, and
even in engineering structures such as pylones of the Chain
Bridge. Stone material utilized in the past 150 years is of
rather heterogeneous quality, though, data on certain build-
ing /e.g. Opera House, Chain Bridge/ confirm the utilization
of picked stone material /1/. Because of its workability,
suitability for carving, this stone type had been massively
utilized in rapidly extending Budapest on the way to become a
metropolis. On the other hand, there was little concern for
durability. This Sarmatian limestone has a porosity of 10 to
30 %, hence a high water absorptivity, making it especially
liable to destruction upon the combined effect of meteorologi-
cal factors /frost/ and increased atmospheric pollution. In
some cases the omission of maintenance /damaged gutters and
cornice covers/ accelerated this process.

In recent years, cleaning and consolidating of stone façades
has begun also in Hungary. In the previous decades, after
having repaired war destructions, in lack of stone cleaning
technologies, or better, in conformity with stone restauration
practice in this country, soft limestone carvings were mainly
replaced. New sculptures and other building ornaments carved
from fresh-water limestone are much more durable than are
those of the traditional soft limestone but this practice is
challenged by principles for historical monuments. Recently,
the demand arose to integrally reconstruct stone façades, in
addition to preserving the original stone material from
aesthetic aspects, making if indispensable to try out various
cleaning technologies, of which to select the best suitable
ones. International standards for the effectivity of stone
cleaning are still missing /2/, but anyhow, aesthetic
requirements cannot be standardized. Thus, cleaning technol-
gies for this type of soft limestone are advisably selected
upon laboratory tests. These cleaning problems being hard to
simulate, the cleaning effect has to be evaluated directly on
the surface, a fact rather restricting types and methods of
tests feasible /e.g. low sample demand/. Tests as little
destructive and as informative as possible are aimed at. Re-
results are of use for the restauration not only of monumental
buildings but also of similar /soft limestone remnants from
mediaeval buildings now exhibited in museums.
2. EXPERIMENTAL

2.1. The soft limestone under test

Originally, the tested Sőskut-type soft limestone contains 94 to 98% of CaCO₃, some 2 to 5% quartz and clay mineral and some what of iron compound. Comparison of stone samples taken from several buildings in Budapest with the same type of soft limestone now quarried shows the originally applied stone material to be of more uniform porosity, with better petrophysical characteristics. This fact argues for cleaning, on the other hand it justifies the mentioned practice of freshwater hard limestone replacement.

The SEM photomicrograph in Fig. 1 shows stone textures typical of sound structures of weathered-surface soft limestone samples taken from public buildings /Opera House, Parliament, St. Stephen’s Basilica, Hungarian Academy of Sciences/. X-ray microanalysis of this layer confirms the outlined stone composition.

2.2. Applied cleaning technologies and comparative tests

1981 to 1984, several, primarily basic /and acid/ chemical, as well as mechanical cleaning processes have been tried out on the Parliament façade parts considered to need stone replace-

ment. Cleaning by liquid chemicals and by polishing proved to be unsuitable, being either ineffective, or largely destruc-
tive. Among mechanical cleaning methods, wet sand blasting was applied on several public buildings, inciting us to involve this cleaning method among the comparative tests. Subsequently, several buildings were renovated by various, combined cleaning methods. It is a recent achievement to let technology tests performed on public buildings under Monuments Act to find the proper cleaning method. The following test methods, accepted in Hungary, involve preliminary laboratory control tests on the weathered stone material, then also the effectiveness of cleaning is checked in laboratory.

Effectiveness of cleaning is advisably evaluated from the variation of several parameters, such as colour, weathering product remains, as well as in knowledge of the surface coarseness. Another important requirement in addition to cleaning effectiveness is as little damage to the stone texture as possible, this is why morphology changes had been tracked by scanning electron microscopy and by evaluating the surface imprint. The rate of removal of weathering products has been determined from compositions of the cleaned surfaces and the underlying stone layers of a few mm.

These data may be completed by photomicroscopy, determination of the capillary water absorption and pore-size distribution of the cleaned surface. Maintenance deficiencies of old buildings may cause wet wall parts to occur in the façade. In applying wet cleaning technologies, knowledge of water and vapour migration typical of these wall structures is of im-

417
portance. Measurements of this kind of limestone and tuff masonry have been launched at the Department of Building Constructions, Technical University of Budapest.

The tested stone cleaning methods are:
   a/ cleaning with water at different temperatures and pressures /water jet/;
   b/ wet sandblasting;
   c/ ion exchange adsorption cleaning.

3. MEASUREMENT RESULTS
Semi-quantitative total analysis of elements from sodium on was made by means of a scanning electron microscope type JSM-35 and an energy-dispersive analyzer type ORTEC EEDSII. Surfaces of soft limestone samples either uncleaned or cleaned by different methods have been compared to compositions of layers 0.5 mm, 2 mm or 3 mm deep under the surface, and as a control, to those 10 to 15 mm deep. Tests over 0.9 by 0.9 mm areas were repeated three times. In the microanalysis, the microscope accelerating voltage was 25 kV, and the sample current intensity was 0.3 nA. Samples for various cleaning tests were taken from six buildings, /built in the second half of last century in Budapest/ of them about 250 microanalyses were made. Detected and identified elements are: Al, Si, S, K, Ca, and Fe. Counts for the observed elements were referred to those of calcium.

Typical cleaning problem for stone façades is how to clean effectively - but for soft limestone rather sparingly - the screened, /other than self-cleaning/ carved parts. These parts are exposed to marked stone weathering, exemplified by the main cornice of the Opera House in Budapest. The weathered layer 2.2 mm thick of the principal cornice is seen in Fig. 2. Figure 3, of the same magnification, shows the weathered surface containing chemically recombined crystals /mainly gypsum/. Texture of the same stone-sample at a depth of 15 mm is seen in Fig. 4, identical to the morphology of the quarry stone.

The high number of element analyses lead to the conclusion:
   1. surface of the soft limestone from Sóskut may contain different proportions of gypsum, maybe as high as 60 to 80 %, /crust/, depending on the location and the age;
   2. this gypsum content exponentially decreases across the upper layer of 3 to 5 mm;
   3. the polluted stone surface is enriched, in addition to in gypsum, also in other elements /3, 4/ such as iron, lending this stone type a mature yellowish hue. Similar to soot particles, ferric ions catalyze the limestone to gypsum transformation.
Figure 1: SEM photomicrograph of the sound structure of weathered surface oolitic limestone at a depth of 15 mm. Marker: 100 μm

Figure 2: The top layer 2.2 mm thick of a principal cornice /Opera House in Budapest/. Marker: 1 mm

Figure 3: The deteriorated surface of soft limestone of Sóskút. Marker: 10 μm

Figure 4: The same stone-sample at a depth of 15 mm. Marker: 10 μm

Figure 5: 3 mm below the cold water-cleaned soft limestone, ferrous compound in the middle. Marker: 10 μm
During the past 100 to 160 years, soluble iron compounds in the porous stone have migrated toward the surface. Sound stone texture 3 mm below the high-pressure cold water-cleaned soft limestone is seen in Fig. 5, with the microanalytically demonstrated ferrous compound in the middle. The cleaned surface of this is yellowish.

Effectivity of each cleaning technology has been rated by the decrease of gypsum content and by testing the cleaned stone texture.

4. CONCLUSIONS
Among the three cleaning methods, effectiveness of water cleaning much depends on parameters of the applied technology. Adequate volumetric cleaning is expected primarily from the water jet, then from a suitable water washing. Namely then, sulfur content, rather typical of weathering, is removed not only from the surface but also at a depth of 3 to 5 mm, while the original stone texture subsists.

Wet sand blasting removes a layer 3 to 5 mm thick from the stone by wearing off less adhering particles, and produces a much coarser surface layer. This phenomenon clearly appears from a surface imprint /5/.

The ion exchange absorption method essentially suits sparing cleaning of carvings and sculptures. A careful technology may effectively remove crusts on concave surfaces, without injury to form and to stone texture.

5. ACKNOWLEDGEMENTS
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6. REFERENCES


Eva Orcsik: Comparative Analysis of Stone Cleaning Technologies Applied in Hungary
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Facades of the most important public offices in Hungary - especially those built in the last 150 years - have been built of rather low-grade porous limestone. This so-called Sóskút limestone quarried in the Buda mountains when exposed to climatic effects /mainly frost/ and increasing atmospheric pollution undergoes accelerated destruction. Primarily stone carvings, in particular, sculptures, balustrades on the most exposed parts of the buildings go deteriorating, therefore since the early '60s, original sculptures of several buildings have been replaced with copies carved from fresh-water limestone /Opera House, Museum of Etnography, Parliament, etc./. This cannot go further on besides also the need for not renewing the ornaments alone but to clean all the façade arose, if possible keeping the original ornaments.

To define the adequate technologies, previous to the reconstruction of stone façades, their condition has to be determined via laboratory and field tests, made on typical surfaces of, or samples taken from stone elements of different locations. Lest adequate documentation is available, materials and rate of previous reconstructions have also to be determined /e.g. long-ago cement repairs or chemical treatments/, data to underlie trials with the expected optimum cleaning technologies. On monument façades, especially if decorated with soft limestone ornaments and sculptures, the optimum result may be expected from a combination of different technologies. The most adequate cleaning procedure for each part of the façade has to be selected on the basis of tests following trials cleaning.

Here trial cleanings on different buildings, as well as among tests previous to, or following the cleaning of stone façades, those reflecting stone cleaning effectivity the best will be outlined. Morphology changes have been tracked by scanning electron microscopy, and change of the chemical composition of the weathered limestone layer by energy-dispersive X-ray analysis. Among the three cleaning technologies of water jet and other wet technologies, mechanical cleaning /wet sand blasting/, and ion exchange absorption cleaning that one can be accepted as the most suitable one that removes as much of dirt and weathering products as possible without detriment to the stone texture.
Eva Orcsik:
Analyse comparative des technologies appliquées en Hongrie pour nettoyer les pierres
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Le façades des édifices publics de Budapest - en particulier ceux des 150, ans passés - furent bâties d’une pierre calcaire poreuse, de qualité plutôt faible. Cette pierre calcaire tendre de Sóskut, des environs de Buda, souffre d’une déstruction accélérée due aux effets météorologiques /surtout au gel/ et à la pollution atmosphérique des décades récentes. Ce sont surtout les statues et balustres aux parties les plus exposées des bâtiments qui ont souffert, c’est pourquoi après les ’60, les statues originales de plusieurs bâtiments ont été remplacées par des copies en calcaire d’eau douce. /Opéra, Musée Ethnographique, Parlement, etc./. Cette routine n’est pas à continuer, a part il y a la demande de ne renouveler les ornements seuls mais de nettoyer les façades entières, en ménageant les ornements originaux.

Pour définir les technologies correctes, avant de reconstruire les façades en pierre, la condition de celles-ci doit être déterminée au moyen d’essais de laboratoire et sur place. Les essais se font sur les surfaces les plus typiques des éléments en pierre des emplacement différents, ainsi que des échantillons en pris. A défaut d’une documentation propre, les matériaux et le degré des reconstructions préalables sont à déterminer. /p.ex. des réparations antérieures au ciment, peut-être des traitements chimiques/. En possession de ces données, les technologies optimales de nettoyage peuvent être essayées. Sur des façades monumentales, en particulier pour les ornements et sculptures en calcaire tendre l’application de technologies diverses amène au résultat optimum. Les analyses après des essais de nettoyage permettent de sélectionner le procédé de nettoyage propre pour certaines parties de la façade.

Cet article présente ceux parmi des essais de nettoyage sur des édifices différents et des examens avant et après le nettoyage des façades entières en pierre que reflètent le mieux l’effectivité du nettoyage de pierre. La variation morphologique a été observée à la microscopie électronique de balayage, et la variation de la composition chimique de la couche de calcaire effritée à la microanalyse radioscopique. Parmi les trois technologies de nettoyage par jet d’eau, et autre technologies aqueuses, le nettoyage mécanique /sablage humide/ et celui à l’échange des ions et à l’absorption celle enlevant le plus possible de la souillure et des produits d’effritement en dédommageant le moins possible la texture pierreuse sera acceptée comme convenable.

423