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APLICATION OF HIGH-RESOLUTION X-RAY RADIOGRAPHY FOR MONITORING THE PENETRATION DEPTH OF CONSOLIDANTS IN NATURAL BUILDING STONES

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Abstract: *For conservation of the built cultural heritage the application of conservation products like consolidants or water repellents is often used. A natural stone is, however, a complicated heterogeneous porous system making the process of consolidation dependent on many variables. The selection of a suitable consolidant and consolidation conditions therefore remains a complex issue. The impregnation depth is a key factor for the assessment of the treatment efficiency. So far, the methods used for monitoring the penetration depth usually require a cut of the investigated stone. These destructive approaches, however, significantly reduces the number and choice of the investigated cuts. The methods, furthermore, do not allow dynamical studies of the impregnation process. The combination of state-of-the-art hybrid pixel semiconductor detectors with newly available micro-focus X-ray sources makes X-ray radiography an ideal non-destructive tool for the penetration depth monitoring. In this contribution, we present results of high-resolution X-ray radiography applied for the penetration depth monitoring of polymer consolidants in the Opuka stone.*

Keywords: ***X-ray radiography, computed tomography, stone, consolidation, penetration depth, Opuka.***

1. Introduction

Stone impregnation with consolidating materials is an important process of stone conservation. Due to aggressive contaminants and weather effects (repeated wetting, freezing and continuous capillary action), the interaction between the building stone of monuments and the environment results in changes of the mechanical properties of the stone (Price 1996). As a result of such degradation and corrosion processes the solidness of the monument can deteriorate. The consolidation might be characterized as a targeted act leading to recovery of the mechanical properties of the damaged stone. The consolidation itself is usually realized by saturation of the damaged stone by various consolidants. The process is consequently evaluated as successful if the damaged part of the stone gains the missing binder and the part is attached to the healthy core of the stone (Bayer 2009).

A natural stone is, however, usually a complex heterogeneous porous system in which the degraded part of the stone differs from the healthy part in absorbability, porosity, composition, etc. This makes the consolidation process dependent on many variables. It is thus difficult to choose the right consolidant which will penetrate well in stone parts - both damaged and healthy (Bayer 2009). The consolidation is moreover an irreversible intervention on the stone and, if the consolidating substance does not penetrate at a sufficient depth, there is the risk of further accelerated stone degradation resulting in the loss of the valuable historic material (Pinto et al. 2007, Snethlage & Wendler 2005). Monitoring the penetration depth thus plays a key role in the assessment of the stone consolidation efficiency.

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1.1 Opuka stone

Cretaceous sandy marlstone, called in the Czech Republic and other eastern European countries "Opuka", was a common building stone in Bohemia from the beginning of stone architecture in the early mediaeval epoch. As the most ancient building stone in Prague, Opuka was used for historical monumental edifices such as churches, fortresses, castles, fortifications as well as burgher's houses. The consolidation of this stone thus plays a key role in preservation of the Czech building cultural heritage. The occurrence of this stone and the respective monuments are recorded also in Poland, Germany and France.

The Opuka stone is specific with its fine-porous structure in which the pore size with size less than 0.1 μm prevails. These small pores can even account for up to 98 % of the total pore volume. Due to very high content of small pores, in comparison with sandstone and limestone, the impregnation of Opuka stone gives the worst results (Šrámek 1992). Although the stone shows high water absorption, the speed of capillary action is very slow and in practical restoration aims the consolidation of Opuka stone still remains an issue (Kotlík 2000). For a successful consolidation of the stone it is very important to know the time needed for achieving a sufficient penetration depth and the dependence of the penetration depth on the stone type and conditions during consolidation.

1.2 Penetration depth monitoring

Most of the methods for monitoring the penetration depth of consolidants have limited use due to their destructive nature (the methods always require a stone cut). Such a destructive approach significantly reduces the number and choice of studied cuts in the sample. Moreover, dynamical studies, which are crucial for penetration depth assessment, are practically not feasible. Instrumental methods for monitoring the penetration depth in a destructive way include scanning electron microscopy, infrared microscopy with Fourier transform, micro-drilling and non-destructive ultrasonic measurement (Casadio & Toniolo 2004). Color reactions for monitoring the penetration depth include staining the stone cut with iodine vapor or specific reagents (e.g., catalyst of organosilanes can be stained with a solution of diphenylthiocarbazone, Bayer 2009). Hydrophobic properties of consolidants can be used to visualize the consolidated part by wetting.

1.3 X-ray radiography

X-ray radiography is relatively non-destructive methods newly explored for direct monitoring of the stone consolidation (V. Cnudde et al. 2004, V. Cnudde et al. 2009, Slavikova et al. 2012). The possibility of monitoring consolidation as a dynamic process and measuring a 3-D distribution of the consolidant in the stone makes the approach an outstanding tool with many advantages over other methods.

Using this technique, the visualization of the consolidant inside the stone depends on the contrast in X-ray absorption between the mineral constituents of the stone material and the consolidant itself. Besides the stone sample parameters, the quality of the resultant visualization is dependent on the CT configuration used given by the X-ray source parameters (used photon flux, tube spectrum) and in particular by the X-ray detector. In the case, when the total amount of the consolidation product applied is very small, the contrast between the treated and untreated part of the stone is very small and the exact localization of the penetration depth and the consolidant distribution in the stone remains very difficult to determine. A clear visualization of the consolidant is then often accomplished by doping these consolidation products with a contrast agent that causes a higher attenuation for X-rays (e.g. 3-bromopropyltrimethoxysilane, Brunetti et al. 2004, Slavikova et al. 2012).

By adding a product with higher attenuation for X-rays to the original conservation products, higher contrast can be created between the stone material and the conservation products. On the other hand, due to doping of the original products, the process of consolidation can be in certain characteristics significantly influenced (the penetration ability of consolidants is often not exactly the same as the penetration ability of commercial consolidation products). As these differences are reduced with decreasing concentration of the contrast agent, the application of X-ray radiography with high sensitivity enabling detection of very small variations in attenuation in the stone is desired.

Recent advances in semiconductor technology allow for the construction of hybrid planar pixelated detectors. The pixel detectors of Medipix type (X. Llopart et al. 2001, X. Llopart et al. 2007) contain highly integrated signal electronics with a digital counter per pixel. Thus, each individual X-ray photon impinging on the detector is processed independently – the signal is amplified, discriminated and counted. Moreover, the counter is incremented without any dark current and with full suppression of electronic noise. Thanks to the digital integration, the result (e.g. radiograph) is absolutely linear and the dynamic range is virtually unlimited (in practice limited just by the number of detected photons, Jakůbek 2007). Such advantages do not exist in other types of detectors such as charge integrating devices (e.g. flat panels and CCDs) which suffer from limited dynamic range, limited linearity, noise integration and non-zero dark current. In this contribution, we present the application of Medipix detector technology for monitoring the penetration depth of consolidants in the Opuka by means of X-ray radiography.

2. Materials and methods

1.4 Stone materials

Three kinds of Opuka were used for consolidation monitoring – gold Opuka from Přední Kopanina (Central Bohemia near Prague), grey Opuka from Přibylov (East Bohemia) and decalcified Opuka from Džbán (North West Bohemia). Decalcified Opuka is a special stone which has naturally lost much of its binder (calcium carbonate). In our studies, decalcified Opuka simulates a vastly degraded stone with high porosity, poor mechanical properties and low resistance to structural deterioration. On the other hand, the so called gold and gray Opuka represent a healthy rock part with narrow pore size distribution and much lower total porosity than decalcified Opuka. At present, the gold and grey Opuka is often used for restoration of stone monuments (Kotlík 2000).

The stone samples were consolidated and after seven days their radiograms were measured. The samples were stored at 20°C and 50 % air relative humidity. As the X-ray radiographic system was not able to measure large stone samples (due to limited area of the used pixel detector), stone samples were therefore cut with a diamond saw Minosecar to blocks of 0.5 × 0.5 × 4 cm (see Fig. 1). In order to prevent evaporation of consolidant from the impregnated stone and the capillary action from the side walls, the vertical sides of the samples were covered with a carnauba wax layer. The wax impregnation of the side walls ensures that the consolidation mixture penetrates only the lower sample base. Without the wax treatment the flow profile of the consolidant would be influenced by the interaction with the sample surface and would not represent the behavior in larger stone blocks.

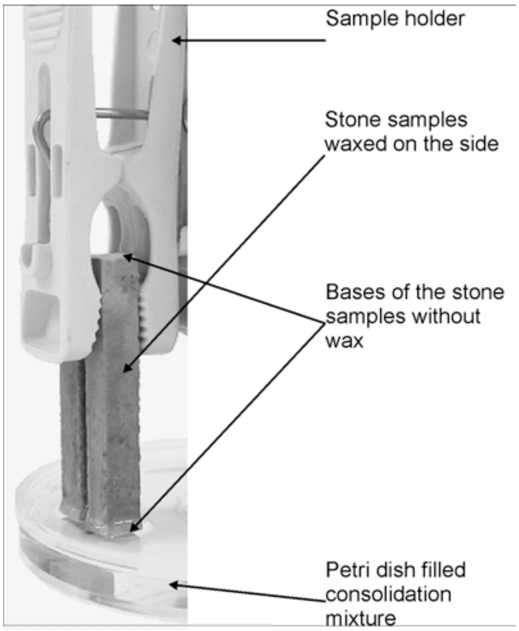

Fig. 1 Experimental setup used for the stone samples consolidation. The sedimentary layers of the impregnated sample are perpendicular to the surface of the consolidation mixture. The wax impregnation of the side walls ensures that the consolidation mixture penetrates only the lower sample base (i.e., only vertically).

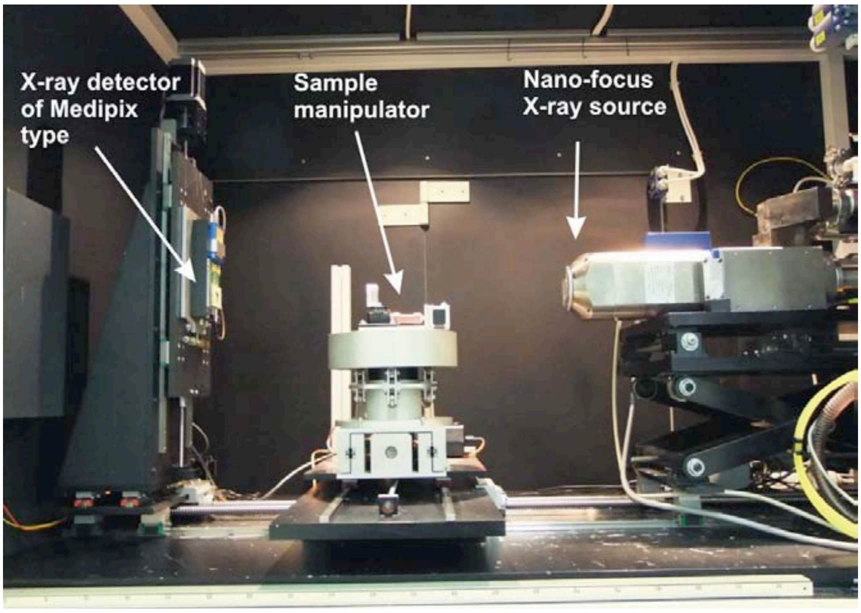

Fig. 2 X-ray micro-radiography setup at the Institute of Experimental and Applied Physics of the CTU in Prague used in the measurement.

1.5 Consolidants

For X-ray radiography measurements a commercial consolidant was mixed with a suitable contrast compound enhancing the attenuation of X-rays. To study the influence of the contrast agent to measured quantities, three mixtures of different contrast agent concentrations were prepared for our experiments. The mixtures are denoted in the text as follows: ID (concentration of the contrast agent 97 %), IED (48.5 %) and IEDE (4.3%). The consolidation mixtures were prepared from Dynasylan 40 (Et40), (3-iodopropyl)trimethoxysilane (I- MEOS) and dibutyltin dilaurate (DBTDL) catalyst which was added as an accelerator of polycondensation (Brus & Kotlík 1996),. Dynasylan 40 (Evonk Degussa Corporation) is a mixture of tetramers and pentamers of tetraethoxy orthosilicate. The iodinated silane (3-iodopropyl)trimethoxysilane is a contrast agent for X-ray radiography from Sigma Aldrich.

1.6 X-ray radiography and micro-tomography measurement

The X-ray imaging experiments were carried out in the compact radiography system developed at the IEAP CTU in Prague (J. Jakůbek et al. 2006). The setup (see Fig. 2) is equipped with a X-ray tube from Feinfocus. During the experiments the X-ray tube was operated with a transmission tube head FXT-160.51 and a broad polychromatic spectrum of a W–Be target spot at 50 keV. The size of the X-ray focal spot has of Gaussian shape with sigma ~1 μm. As an X-ray sensor, we used the position sensitive Timepix digital single photon counting device (X. Llopart et al. 2007) with a 300 μm thick Si sensor arranged into a matrix of 256 × 256 square pixels of 55 μm pitch giving a total detection area of 14 × 14 mm^2.

During all measurements the Timepix detector was operated in counting (so-called Medipix) mode. In our studies, although the number of photons reaching the detector is relatively low (mostly hard X-rays traverse the 5 mm thick stone for which the efficiency of a silicon sensor is low), sufficient contrast is achieved just by prolongation of the measurement exposure time (typically no longer than 60 s). Images were acquired at 50 keV X-ray tube voltage and 30 μA target current. The measured radiographic data were corrected for the beam-hardening effect using a signal-to-thickness calibration (Jakůbek 2007). From the measured radiographs the penetration depth of the consolidant can be directly evaluated.

By scanning the sample at many angles and by suitable image reconstruction, high resolution tomographic images can be obtained with micrometer-scale resolution. This technique allows displaying the stone structure in various virtual cuts, which enables precise monitoring of the consolidant distribution in the sample. For the studies of the consolidation on the stone capillary level,

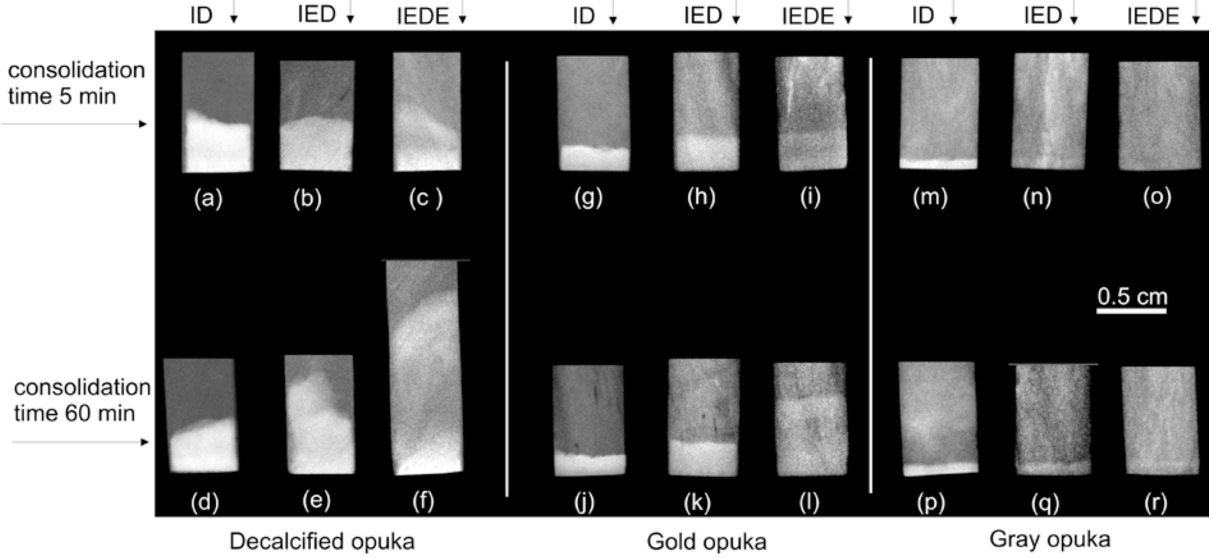

Fig. 3 X-ray radiographs of three different Opuka stone samples impregnated for 5 min (above) and 60 min (below) with consolidation mixtures ID, IED, IEDE (see text). The penetration of consolidants is visualized in white. Besides the penetration depth monitoring it is also possible to visualize Opuka stone sedimentary layers (nicely visible in radiograms (h),(n) and (e)) or consolidant distribution inhomogenities – for example, the consolidants flow is divided into two fronts in radiograms (c), (f), and (i)) (Slavikova et al. 2012).

tomography of a small sample (total imaged volume ~1 mm^3) with spatial resolution 9 μm was also measured. 3-D tomographic reconstruction was calculated from 181 projections acquired with one degree step using an adapted iterative expectancy maximization method accelerated by ordered subsets. The projection images were acquired at 50 keV with 30 μA target current and exposure time 15 s.

3. Results

The resulting radiographs enable monitoring the penetration depth of the used consolidant in a very simple, reliable and non-destruction way (see Fig. 3). In comparison with most of the conventionally

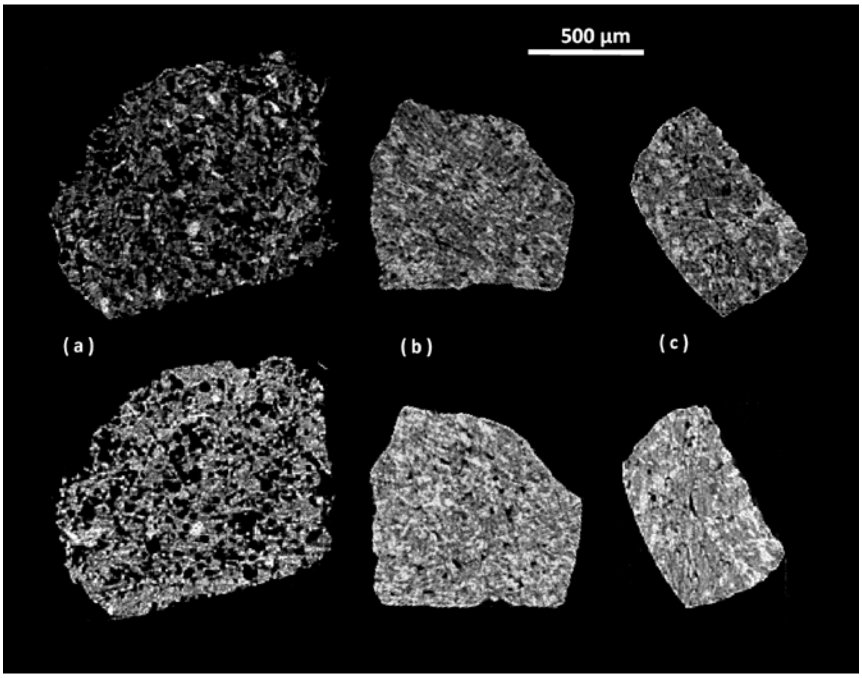

Fig. 4 High-resolution computer tomography of three Opuka stones before (above) and after the consolidation (below). (a) decalcified Opuka, (b) gold Opuka, (c) gray Opuka. All images are visualized at the same gray-scale (Slavikova et al. 2012).

used techniques, it is possible to study a large number of stone samples giving possibility to find appropriate combination of the consolidated stone, consolidant and consolidation conditions such as consolidation time. Dynamical monitoring (X-ray movie) of the consolidation process is possible as well – see Slavikova et al. 2012.

To demonstrate the feasibility of studying the consolidation on a stone capillary level, high resolution tomography of a small stone part before and after the consolidation has been carried out (see Fig. 4). This feature opens the possibility for a whole range of further studies. Topics like porosity changes visualization inside stone samples during impregnation can be investigated, as well as the investigation how the products react inside different stone types. Thanks to the quality of the measured images and their digital nature, further image analysis is possible.

4. Conclusions

We have demonstrated that the application of X-ray radiography utilizing semiconductor particle-counting detectors stands out as a powerful tool in research of consolidants inside natural building stones. The capabilities of this technique have been demonstrated on simple projections X-ray radiography as well as computed tomography used for monitoring of consolidant in Opuka. The study can provide not only a basic step for additional knowledge on the suitability of investigated products for the treatment of the Opuka stone type, but also the study can serve as an instrumental and methodological work applicable for treatment of other stone types.

X-ray micro-radiography technique appears as an ideal tool for finding appropriate combinations of stones, consolidants and consolidation time. Even though this technique cannot compete ultimate with spatial resolution, e.g., from electron microscopes, the main advantage lies in the possibility of non-destructive stone volume visualization (i.e., the method is not just superficial).

Due to mixing with a contrast agent, the penetration ability of consolidants is not exactly the same as the penetration ability of commercial consolidation products. These differences are reduced with decreasing concentration of the used contrast agent. Application of X-ray radiography demands setups with high sensitivity enabling detection of very small changes in attenuation in the stone. A further significant improvement in pixel detector sensitivity is expected with the application of novel sensor materials with higher atomic number such as CdTe and GaAs.

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