High-contrast X-ray radiography using hybrid semiconductor pixel detectors with 1 mm thick Si sensor as a tool for monitoring liquids in natural building stones

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ABSTRACT: For the preservation of buildings and other cultural heritage, the application of various conservation products such as consolidants or water repellents is often used. X-ray radiography utilizing semiconductor particle-counting detectors stands out as a promising tool in research of consolidants inside natural building stones. However, a clear visualization of consolidation products is often accomplished by doping with a contrast agent, which presents a limitation. This approach causes a higher attenuation for X-rays, but also alters the penetration ability of the original consolidation product. In this contribution, we focus on the application of Medipix type detectors newly equipped with a 1 mm thick Si sensor. This thicker sensor has enhanced detection efficiency leading to extraordinary sensitivity for monitoring consolidants and liquids in natural building stones even without any contrast agent. Consequently, methods for the direct monitoring of organosilicon consolidants and dynamic visualization of the water uptake in the Opuka stone using high-contrast X-ray radiography are demonstrated. The presented work demonstrates a significant improvement in the monitoring sensitivity of X-ray radiography in stone consolidation studies and also shows advantages of this detector configuration for X-ray radiography in general.

KEYWORDS: X-ray detectors; Inspection with x-rays; X-ray radiography and digital radiography (DR)

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1 Introduction

Hybrid semiconductor pixelated detectors (HPD) enable high-resolution position-sensitive detection of single ionizing quanta (photons [1], electrons [2], heavy charged particles [3], neutrons [4] etc.). Thanks to the unique electronics implemented per pixel in the ASIC read-out chip [5, 6], the processing of the signal generated by each individual particle is carried out without any additional noise such as dark and leakage currents and detector read-out noise. In X-ray imaging, in particular, transmission X-ray radiography and tomography, unlimited dynamic range provided by HPD enables the acquisition of radiographs even for low contrast and low absorption objects such as soft tissue samples [8]. Furthermore, when combined with novel micro-focus X-ray tubes, high-contrast radiography with spatial resolution on the µm scale has become today standardly available at small-laboratory table-top scale [9, 10].

1.1 Stone consolidation

Stone consolidation treatment is one of the key approaches used in built cultural heritage preservation, aiming at recovering the mechanical properties of the treated objects [11, 12]. In practice, the consolidation is performed by saturation of the damaged stone parts with various consolidants in the form of liquids. After penetration into the stone matrix the liquid changes state to become a solid binder (e.g. using polycondensation processes in the case of the organosilicon consolidants). The process’s success is evaluated based on the extent that the degraded stone gains the binder agent and attaches to the healthy core of the stone [13].
1.2 Evaluating and monitoring techniques

As the restored natural stones are usually very complex heterogeneous systems, the consolidation process depends on many variables. Monitoring of the consolidants inside the stone matrix thus plays a key role in the assessment of the treatment process efficiency. Evaluation of the consolidant penetration depth, visualization of the consolidant distribution inside the stone, changes of the stone capillary system, and monitoring of the water uptake in the consolidated stone sample are examples of tasks investigated using different probes.

X-ray micro-radiography stands out as a promising tool in research of consolidants inside natural building stones [14–16]. The importance of the technique is in the possibility to evaluate the efficiency of stone preservation processes in a reasonably large stone volume [15] in a nondestructive way. In comparison with established destructive techniques requiring a stone cut, X-ray micro-radiography and micro-tomography provide key features such as monitoring of consolidation as a dynamic process and measuring the 3-D distribution of the consolidant in the stone capillary system.

1.3 Current and proposed approaches

Using conventional X-ray radiography techniques, 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. Particle counting detectors can provide dynamic range limited only by the number of detected particles. However, the conventionally used 300 $\mu$m thick silicon sensor has a low detection efficiency for such a beam-hardened spectrum passing through the large stone sample. This results in unreasonably long imaging time for sufficient photon statistics. The introduction of a contrast agent enhances the attenuation properties of the monitored consolidants in the stone matrix [15, 16]. However, due to this mixing process, the penetration ability of the consolidant in the stone is altered, presenting a significant limitation of this approach (see figure 1).

As changes in behavior of the consolidation mixture in relation to the original product are usually reduced with decreasing concentration of the added contrast agent, the use of radiography setups with high sensitivity (high dynamic range of resulting radiographs) is desired. This high-sensitivity approach enables detection of very small changes in attenuation ideally without any contrast agent. In this particular application based on the use of a laboratory micro-focus X-ray tube of limited brilliance for investigation of relatively highly attenuating objects, the improved imaging performance can be attained only by increasing the detection efficiency of the used sensor. In this work, a further improvement in imaging capabilities of HPD based on the use of a 1 mm thick silicon sensor is presented.

2 Materials and Methods

2.1 Opuka stone samples

A cretaceous sandy marlstone, so-called Gold Opuka [18, 19] from Přední Kopanina, Central Bohemia near Prague was used (preparation samples of dimensions 0.5 $\times$ 0.5 $\times$ 4 cm). The size of stone samples was adapted to fit the single Timepix chip sensitive area 1.4 $\times$ 1.4 cm$^2$. During the consolidation process the stone sample was dipped into the consolidation mixture, consequently resulting in the capillary action through the lower sample base in the vertical direction. In order
Figure 1. X-ray micro-radiographs of three Opuka stone samples prepared from the same stone type treated with different concentration of contrast agent (I-MEOS) included in the consolidation mixture. The consolidant penetrated through the lower sample base via capillary action. The higher X-ray attenuation in the radiographs is shown by the darker regions. The images clearly demonstrate the dependency of the penetration depth on the concentration of the added contrast agent. This effect limits the possibility to monitor the original consolidation products (i.e., without any contrast agent). Image adapted from ref. [15].

2.2 Consolidation mixtures

The consolidation mixtures used in the measurements were prepared from a commercially available product Dynasylan 40 (mixture of tetramer and pentamer of tetraethoxysilane, Evonik Degussa Corporation), and dibutyltin dilaurate (Sigma-Aldrich) catalyst used as an accelerator of the polycondensation process. For X-ray radiography measurements, to study the influence of the added contrast agent, the commercial consolidant was mixed with a suitable contrast compound enhancing the attenuation of X-rays (3-iodopropyl-trimethoxysilane from Sigma-Aldrich, further in the text abbreviated as I-MEOS). To study the influence of the contrast agent to measured quantities, several mixtures of different contrast agent concentrations were prepared (0%, 1%, 4% 10%, 49%, 97%).

2.3 Table-top X-ray micro-radiography system

X-ray micro-radiography of consolidated stone samples was carried out at the compact radiography system developed at the IEAP CTU in Prague [9]. The setup is equipped with a X-ray tube Fein-focus operated with a transmission tube head FXT-160.51 and a broad polychromatic spectrum of a W-Be target spot at 50 keV and 30 µA target current. The X-ray focal spot has a Gaussian shape, sigma ~ 1 µm. The stone samples were imaged with geometrical magnification 1.5 resulting in spatial resolution of the method 40 µm (limited mainly by the pixel size). Spatial resolution at
Figure 2. X-ray micro-radiographs of an Opuka stone sample (0.5 cm thick) acquired with the Timepix detector operated in counting mode equipped with a 1 mm thick Si sensor (a) and 300 µm thick Si sensor (b). The X-ray tube was operated at 50 keV voltage, 10 µA anode current and 20 s exposure time (averaged image normalized to 1 s after flat field correction is shown). Intensities evaluated in the squared regions of approximately $40 \times 40$ pixels in the open beam area (red) and behind the sample (green) are given. The contrast-to-noise ratio given by the square orange regions demonstrates a significant improvement in imaging performance with the 1 mm thick Si sensor.

This level is fully satisfactory for most of the stone consolidation studies, such as evaluation of the penetration depth and monitoring consolidant distribution in the stone. The exposure times were typically 60 s and 30 s for the 300 µm and 1 mm thick sensor, respectively. The measured radiographic data was corrected for the beam-hardening effect using the signal-to-thickness calibration using aluminium filters [1].

As an imaging device we used and compared two single chip Timepix detectors equipped with different sensors: a 300 µm thick Si sensor, biased at 100 V and a 1 mm thick Si sensor biased at 430 V, both P-on-N type, hole collection polarity, arranged into a matrix of $256 \times 256$ square pixels, 55 µm pixel pitch giving a total detection area of $14 \times 14$ mm$^2$. The device was operated with the integrated USB-based FitPix read-out interface [20] and controlled by the Pixelman software [21]. For evaluation of spatial resolution a 50 µm thick iron edge placed with no geometrical magnification (in contact geometry with the detector) was used.

The monitoring of the water uptake inside the Opuka stone samples by means of dynamic X-ray radiography was carried out using an X-ray tube with a higher intensity output (Oxford instrument, Series 5000) operated at 50 keV and tube current up to 1 mA. The intensity provided by this tube enabled the acquisition of dynamic X-ray radiographs with sufficient contrast at time exposures up to 0.1 s which is completely satisfactory for monitoring of the processes in presented studies.

### 3 Results

To demonstrate imaging performance based on the improved detection efficiency of the 1 mm thick Si sensor compared to the 300 µm thick Si sensor, a series of comparative experiments was carried out. Basic parameters including the detection efficiency, edge response function (ERF) and...
Figure 3. X-ray micro-radiographs of a smooth iron edge (50 µm thick) measured with the Timepix detector equipped with a 1 mm thick Si sensor (top left) and with 300 µm thick Si sensor (top right). The details of the edges do not show any degradation of spatial resolution with the 1 mm thick Si sensor if proper bias voltage is used (430 V in this case). This fact is also demonstrated by the respective ERFs (bottom) obtained using the oversampling technique. For details about ERF measurement see ref. [22].

Figure 3. X-ray micro-radiographs of a smooth iron edge (50 µm thick) measured with the Timepix detector equipped with a 1 mm thick Si sensor (top left) and with 300 µm thick Si sensor (top right). The details of the edges do not show any degradation of spatial resolution with the 1 mm thick Si sensor if proper bias voltage is used (430 V in this case). This fact is also demonstrated by the respective ERFs (bottom) obtained using the oversampling technique. For details about ERF measurement see ref. [22].

Contrast-to-noise ratio (CNR) for the case of used stone samples were evaluated for both detectors. In more complex experiments, the technique of X-ray micro-radiography with the used detectors was applied for monitoring organosilicon consolidants and for dynamic studies of the water uptake in the Opuka stone samples.

3.1 Detection efficiency and CNR

The micro-radiograph of a natural Opuka stone sample measured with the 1 mm and 300 µm thick Si sensor is presented in figure 2. The improved efficiency for the more energetic part of the used X-ray spectra (a non-filtered W-Be spectrum with 50 keV accelerating voltage used) significantly enhanced the imaging capability for this kind of objects (compare, for example, the contrast-to-noise radio parameter in figure 2). Consequently, in this particular experimental condition, monitoring of the consolidation products in these stone samples without any added contrast agent is now possible (not feasible with conventionally used 300 µm thick sensors [15]), see below.
Figure 4. X-ray micro-radiographs of several Opuka stone samples treated with consolidant modified with different concentration of the contrast agent 1-MEOS (given in % below each respective sample). Images acquired with the Timepix detector equipped with a 1 mm thick Si sensor (right) and with a 300 $\mu$m thick Si sensor (left). The consolidated parts (higher attenuation) appear in the darker regions. The usage of the 1 mm thick Si sensor enables to monitor the consolidant even without any contrast agent.

3.2 Spatial resolution

A natural concern arising from the use of a thicker sensor is degradation of spatial resolution resulting from a higher spatial spread of the signal created from the interaction of the detected photon in the sensor material. In the case of direct conversion semiconductor detectors, the signal which spreads is the electric charge. The initial charge cloud created during the particle interaction is broadened due to various physical phenomena such as thermal diffusion, electric field drift, etc. and the extent of the processes is often directly related to the collection time (proportional to the sensor thickness) [17]. The characterization of the detector edge response function (ERF) by imaging a smooth iron edge placed in contact geometry onto the sensor was carried out (see figure 3). The presented results show no degradation of spatial resolution throughout the whole detector matrix.

3.3 Consolidants and water uptake monitoring in Opuka stone

Even though the visibility of a particular consolidation product depends strongly on the stone type, consolidation conditions etc., in previous studies based on the use of a conventional 300 $\mu$m thick silicon sensor the addition of a contrast agent for the reliable recognition of the monitored substances was necessary [15]. The improvement in the detection efficiency of the 1 mm thick Si sensor provides the possibility to monitor the consolidant in the stone matrix without any contrast agent which brings a major improvement in the performance of the method. X-ray micro-radiographies of several Opuka stone samples treated with the consolidant modified using different concentrations of the contrast agent obtained using both detectors are presented in figure 4.

A similarly challenging issue from using a 300 $\mu$m thick Si sensor and conventional X-ray tube was the monitoring of the water capillary rise in the discussed stone samples. Such dynamic studies are desired in many cases related to cultural heritage preservation. Due to the intrinsic difficulty of X-ray radiography given by the poor contrast of liquids (containing typically low Z elements) in the highly attenuating stone matrix, these studies have been carried out using neutron radiography [22]. Even though this technique is a great tool yielding unique information especially
Figure 5. Dynamic X-ray micro-radiography of Opuka stone samples immersed in water acquired with a Timepix detector equipped with a 1 mm thick Si sensor. The container with water was displaced towards the lower stone base and stopped upon the water surface reaching the stone. The radiographs clearly demonstrate the possibility to monitor water uptake in the given stone samples.

Concerning hydrogen distribution in the sample, the main disadvantage is its inadequate availability. The possibility to carry out these studies using X-ray radiography, therefore, significantly simplifies the situation. The results of dynamic X-ray radiography of water capillary rise in the Opuka stone acquired with the 1 mm thick Si sensor is shown in figure 5. The acquired X-ray radiographs clearly demonstrate the position of the water level inside the stone.

4 Conclusions

The enhanced application of the hybrid pixel semiconductor detectors Timepix equipped with a 1 mm thick silicon sensor for monitoring consolidants and water in the Opuka stone was demonstrated. Compared to thinner silicon sensors used previously (in the last decade Medipix assemblies with silicon sensors has been almost solely used with thickness 300 µm), the technique shows significantly enhanced sensitivity. This study has shown that the use of contrast agent is no longer necessary for stone consolidation monitoring which improves the overall ease of use and reliability of the method. The possibility of dynamic monitoring of liquids in reasonable large stone samples opens the way to many other studies in stone preservation aims. Consequently, studies such as evaluation of effectiveness of various water repellents in stones can be carried out in a table-top X-ray micro-radiography setup instead of a limited-access neutron source facility. As the enhanced detector efficiency is achieved without any degradation of detector spatial resolution, our approach including the use of thick silicon sensor is advantageous for imaging with X-rays in general.

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