Imaging and elemental analysis of porous materials at the BNC

Zoltán Kis, László Szentmiklósi, Boglárka Maróti, Veronika Szilágyi

Nuclear Analysis and Radiography Department
Centre for Energy Research
• Introduction
• Instrumentation
• Case studies:
  • Imaging of static systems
  • Dynamic imaging of processes
  • Elemental analysis for quantification
• Conclusions
Usually means a complex material mixture = PARTICULATE COMPOSITE

e.g. concretes/mortars, ceramics, natural/artificial stones

They have to be characterized for
(1) the **distribution** of their constituents (spatial composition, porosity, etc.) **(static)**

(2) the propagation rate (**time dynamics**) of a certain agent (moisture, chemicals)

http://umich.edu/~waascsl/LeeProj.html
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→ **IMAGING**

Neutron Imaging: NR, NT

X-ray Imaging: XR, XT

→ **DYNAMIC AND POSITION SENSITIVE COMPOSITION DETERMINATION**

PGAA, dPGAA, dPGAI, dNR
Combining elemental analysis with NR/NT for heterogeneity-mapping of materials at CER, Budapest

**Neutron Radiography/Tomography (NR/NT)**
- fast: $sec - hours$
- small objects: $in the range of cm’s$
- resolution: $300-400 \mu m$
- sensitivity: $Hydrogen$
- non-destructive: $deep \ penetration (\sim cm)$
- depending on the neutron energy

RAD: fast to thermal; NIPS-NORMA: thermal to cold

**Prompt-Gamma Activation Imaging (PGAI)**
- collimating the neutron beam: $chord$
- + collimating the gamma detection: $isovolume$
- point-wise scanning: $2D/3D \ PGAA$
- resolution reached: $2 - 3 \ mm$
- very time consuming: $> days$

**Radiography/Tomography-driven PGAI**
- visualize and locate the interesting regions first
- prompt-$\gamma$ measurement only where it is needed can save substantial beam time

Neutron methods + positioning = local measurements
Analysis $\rightarrow$ Imaging
Why neutrons (and X-rays) are used for imaging? -> They can give high-resolution information from deep layers of matter.

<table>
<thead>
<tr>
<th>Neutron</th>
<th>Lower energy electromagnetic (THz, IR, vis., UV)</th>
<th>X-ray</th>
<th>Synchrotron</th>
<th>Charged particle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microstructure, phase, texture, strain (tension, torsion), stress</td>
<td>Neutron diffraction (ToF-ND), Bragg edge transmission</td>
<td>Raman</td>
<td>X-ray diffraction (XRD)</td>
<td>SEM, TEM</td>
</tr>
<tr>
<td>Structure (size, orientation, shape) (non-destructive)</td>
<td>Small-angle Neutron Scattering (SANS)</td>
<td></td>
<td>Small-angle X-ray Scattering (SAXS)</td>
<td></td>
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<tr>
<td>Structure (size, orientation, shape) (destructive)</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Morphology</td>
<td>Neutron imaging (NR, NT, NRCl, NRT)</td>
<td>microscopy, laser, THz</td>
<td>X-ray imaging (XR, XT)</td>
<td>IR/vis/UV, soft and hard X-rays</td>
</tr>
<tr>
<td>Composition (non-destructive)</td>
<td>Prompt gamma-ray activation imaging (PGAI), Bragg edge transmission, NRCl, NRT</td>
<td>Raman, FT-IR</td>
<td>X-ray fluorescence (XRF)</td>
<td>X-ray fluorescence, X-ray absorption</td>
</tr>
<tr>
<td>Composition (minimal invasive)</td>
<td>Neutron activation Analysis (NAA)</td>
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<tr>
<td>Composition (destructive)</td>
<td></td>
<td></td>
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<td>SIMS, LA-ICP-MS</td>
</tr>
</tbody>
</table>

| ICP-AES, AAS |
Bimodality, i.e. combination of neutron and X-ray imaging has great advantages
ARCHAEOLOGICAL POTTERY

Examining pottery forming techniques through combined petrographic analysis and neutron tomography

Katalin BAJNOK¹, John GAIT¹, Zoltán KIS¹, Imre SZENTI², Veronika SZILÁGYI¹

¹ Centre for Energy Research, ² University of Szeged
CONTENT REMOVED DUE TO PUBLISHING CONSIDERATIONS
Advantages of NT of archaeological ceramics

- From qualitative results to quantitative analysis:
  bimodal imaging (XT-NT) for discriminating ancient pottery forming techniques by **3D visualization**, applying **statistical analyses** of particle/pore orientation, size distribution and frequency

- Possibility to **compare non-destructive 3D and destructive (thin section) 2D data**
CONTEMPORARY CONCRETE

Porosity and aggregate-distribution of concrete by neutron and X-ray tomography

Zoltán KIS¹, Veronika SZILÁGYI¹, Kyongshoo PARK², Tiana RAZAKAMADIMBY³, Michal GLINICKI³

¹ Centre for Energy Research, ² Yonsei University, ³ IPPT PAN
The pixel resolutions of the neutron radiographs (sampling frequency) in recent studies (2000-2010ies) were 100, 94, 98, 106 and 30 μm/pixel size, respectively, a significant improvement over those of the previous studies (1980-1990ies) (300 μm/pixel size or more).
Major constituents of concretes

- Binder = Unhydrated clinker and hydrated cement paste of hardened concrete
- Skeleton = Coarse and fine aggregates
- Voids/Pores
- Admixtures

Macro porosity and artificial porosity of concretes can be observed by NT

Properties of the principal types of voids found in hardened concrete

<table>
<thead>
<tr>
<th>Void type</th>
<th>Origin</th>
<th>Size</th>
<th>Morphology</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water voids</td>
<td>Filled with water at time of concrete setting</td>
<td>Typically &gt;3mm</td>
<td>Irregular and elongated shape. Found beneath coarse aggregate particles or reinforcing bars. Internal surface has a granular appearance</td>
</tr>
<tr>
<td>Entrapped</td>
<td>Air entrapped in the concrete during placement and compaction</td>
<td>Mostly &gt;1mm</td>
<td>Typically irregular shape but can also be spherical. Irregular distribution. May increase in size and distribution towards the surface. Internal surface has a glazed lustre</td>
</tr>
<tr>
<td>Entrained</td>
<td>Formed by chemical admixture that is retained on the surfaces of the cement particles during the mixing process</td>
<td>0.01mm to 1mm</td>
<td>Spherical shape and uniformly distributed</td>
</tr>
<tr>
<td>Capillary</td>
<td>Sub-microscopic spaces filled with mix water remain after hydration of cement to form integral part of cement matrix</td>
<td>&gt;0.005mm</td>
<td>Irregular shape</td>
</tr>
</tbody>
</table>
Advantages of Imaging in Concrete Science

- 2D = **static or dynamic radiography** (to follow e.g. moisture propagation)
- 3D = **tomography** (spatial distribution and spatial dimensions of constituents, raw data for modelling)
- **Bimodality** = linked evaluation of neutron and X-ray attenuation images
- Resolution
- Sensitivity for chemical composition (≠ phase differentiation)
- Adaptation of 2D conventions to the 3D data set
Bimodal imaging – concrete

TS = thin section

NT, XT
Qualitative evaluation - Basis of segmentation

Two independent knowledges:

- Map of Linear attenuation coefficients, $\Sigma(x,y,z)$ (which is the result of the tomographic imaging and visualized in the grey scale values)
- Petrography of the phases (aggregates)
Bimodal imaging – concrete

AGGREGATE quality (limited)

Complex grain:
Fe-px + feldspar

FeO-OH

Fe-oxide rich rock fragment

PPL

XPL

Block 3

NT

XT

18
Clearly observable

*In NT image:*
AGGREGATES, PASTE DIFFERENCES

NT: colour segmented image = ‘detailed constituent distribution’
Clearly observable

In XT images:
MACRO-PORES, some AGGREGATES

XT: colour segmented image = ‘constituent distribution’
Qualitative evaluation - segmentation

**NT for** AGGREGATES, PASTE DIFFERENCES

**XT for** PORES, some AGGREGATES

**Combination of NT and XT for** PORE distribution, AGGREGATE distribution, PORO-GRANULOMETRY, AGGREGATE quality (limited)

Kim et al. 2021
Quantitative evaluation
Calculations on the basis of imaging techniques

**Combination of NT and XT:**
AGGREGATE distribution, GRANULOMETRY
MACRO-PORE distribution
Block 1
Calculated macro-porosity: 0.19%
Largest void: 0.65 mm³
on the basis of XT

Block 1
Calculated aggregate content: 26.66%
Largest aggregate: 3.94 mm³
on the basis of NT
## Quantitative evaluation

### Numerical data set

<table>
<thead>
<tr>
<th>Probability</th>
<th>Radius (mm)</th>
<th>Diameter (mm)</th>
<th>Center x,y,z (mm)</th>
<th>Volume (mm³)</th>
<th>Voxel Surface (mm²)</th>
<th>Classification</th>
<th>Gap (mm)</th>
<th>Compactness</th>
<th>Sphericity</th>
<th>Position x,y,z (mm)</th>
<th>Projected size x,y,z (mm)</th>
<th>PCA deviation 1,2,3 (mm)</th>
<th>PCA max. dev. ratio (%)</th>
<th>PCA min. dev. ratio (%)</th>
<th>Grey value (min, max, mean, dev)</th>
<th>Label</th>
<th>Thickness (min, max, mean)</th>
<th>Relative diameter</th>
<th>Cut surface (mm²)</th>
<th>Edge distance (in/outside, min, max)</th>
<th>Projected area (3 planes)</th>
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</table>
Quantitative analysis – Aggregate size distribution

Grain size distribution

Frequency

0 50 100 150 200 250 300

Diameter (mm)

0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.1 1.2 1.3 1.4 1.5 1.6 1.7 1.8 1.9 2 2.1 2.2 2.3 2.4 2.5 2.6 2.7 2.8 2.9 3 3.1 3.2 3.3 3.4 3.5 3.6 3.7 3.8 3.9 4

Passing fraction (%)

0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1

Diameter (mm)

0.1 1 10
Discriptor measurements on a single aggregate grain

**Three principal dimensions** (projected sizes in an axis-aligned minimum bounding-box)

- $a = 1.76 \text{ mm}$
- $b = 1.35 \text{ mm}$
- $c = 1.21 \text{ mm}$

**Two aspect ratios**

- Elongation index $EL = \frac{b}{a} = 0.77$
- Flatness index $FL = \frac{c}{b} = 0.90$

**Radius of the circumscribed sphere**

- $R = 0.95 \text{ mm}$

**Radius of the inscribed sphere**

- $r = 0.45 \text{ mm}$

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**Bimodal imaging – concrete**

**Shape analysis on the aggregate population in the concrete**

![Diagrams showing shape analysis](image)

- Inscribed sphere
- Circumscribed sphere

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**Graphs showing sphericity and aspect ratios**

- Sphericity vs. Particle diameter
- Elongation index $EL = \frac{b}{a}$ vs. Flatness index $FL = \frac{c}{b}$

---

**2/3**

- $FL = \frac{c}{b}$
- $EL = \frac{b}{a}$

---

**Legend**

- Finer but more spherical
- Coarser but more elongated
Characterization of the pore and air voids system in concrete by quantitative description of pore size and connectivity.

Three meaningful parameters of the air-void system: (1) the **total content** of voids, (2) the air-void **size distribution**, (3) the **void-to-void proximity** (i.e., spacing factor, the distribution of the distance between the air voids).

Wawrzeńczyk and Kozak 2015
Converting data into mesh

Exporting mesh data to .stl format and visualization in other programs (e.g. GOM)
Von Mises stress field using the concrete microstructure obtained from combined X-ray and neutron CT

Principal strain field using the concrete microstructure obtained from combined X-ray and neutron CT
Advantages of bimodal NT-XT of concretes

1) Visualization of concrete constituents
2) Differentiation of constituents by grey value-based segmentation
3) Calculation of macro-porosity and aggregate distribution
4) Raw data for modelling
BUILDING STONES

Neutron-based dynamic chemical characterization and imaging of porous media
Why to investigate historical building materials?

- Complexity of heritage buildings + demand for diagnostics + non-destructive techniques (NDT) → numerical and/or physical modelling (especially structural modelling) to investigate the behaviour of the real building → physical preservation
- Models must implement mechanical properties → empirical data or laboratory measurements are needed
- Historic building materials (traditional solid hand-made bricks, lime mortars, natural stones) are composite materials (POROUS and BRITTLE, which may encounter cracking and disruption). Their physical properties depend on: (1) Properties of components; (2) Bond pattern; (3) Effect of working conditions through time (loading, water content and migration, environmental conditions, thermal and freeze-thaw cycles, weathering, ...)
ION-MIGRATION IN BUILDING STONES

Neutron tomography of water/pore distribution and studying the propagation of water and salt ions in porous construction materials by PGAI

Zoltán KIS\textsuperscript{1}, Francesca SCIARETTA\textsuperscript{2}, László SZENTMIKLÓSI\textsuperscript{1}

\textsuperscript{1}Centre for Energy Research, \textsuperscript{2}University of Venice
The effects of WATER and SALT IONS can:

1. induce chemical modifications and mechanical stress which cause material disruption and facilitate other types of decay
2. affect the strength and elastic modulus of porous brittle materials even if no damage is visible

Non-destructive or Micro-destructive diagnostic techniques allow to detect (or to infer) the presence of water and salts inside the structural members of a building

... but such test alone give only QUALITATIVE information!
Why neutron-based techniques?

QUANTITATIVE assessment

To prove sound relationships between water/salt presence and properties’ variation

To clarify water and salts’ migration processes inside porous construction materials

- Measured concentration-profile of water and salts inside a porous material
- Available data on the material properties in presence of certain concentrations of water and salts
- Material quality assurance

Establishing a multidisciplinary NDT:
by the joint application of NR/NT- and PGAI-based investigations
to usual property assessment techniques
The investigation at NIPS-NORMA facility

All samples were dried in a lab oven till constant weight (80°C for 19h) before the tests.

**NT in dry and saturated condition**
Negligible lateral evaporation (<1h test time)

**Water infiltration → dNR**
MilliQ water 18.2 MΩ/cm
Constant water level
Lateral evaporation prevented (hours- to day-long test time)

**PGAI (NR-driven)**
NaCl solution (50.24 g NaCl, 210 ml H₂O)
the salt solution has resemblance to sea water

Vial + tube + reservoir system in the sample chamber, to keep the water level constant (communicating-vessels)

*NR image of a stone:*
Darker areas = already-wet part. The neutron irradiated area was always between the yellow lines: V(ert)×H(oriz) = 2 × 43 mm²
Porosity of the investigated stone types (by NT)

a, Vicenza calcareous rock (V)
b, Trachite volcanic rock (T)
c, Istria limestone (I)
d, Carrara marble (C)

a-b, Bulky reservoirs, interconnections of pores
c, Conduction channels, effective transport of the rather low water content
d, Very low porosity
NR & PGAI - Temporal behavior of Cl and H concentration

- Cl/H concentration ratio set to a level, which gave approximately the same count rates at the 1163 keV doublet peak of Cl and at the 2223 keV peak of H.

- Time dependence of their normalized count rate: same pattern for both Cl and H, but Cl (salt solution) is transported slower due to its higher density and viscosity compared to water.

Pan-Galactic Accelerator Initiative (PGAI) results: time dependence of Cl and H count rates.
Advantages of dynamic PGAA of imbibition

• Establishment of a **multidisciplinary procedure to characterize** (relation of qualitative to quantitative information) porous historic **construction materials**.

• To understand the **effect** of the presence and propagation of water and salt ions content **on these properties**.

• The results reveal the **accurate water intrusion patterns**, the evaluation of the **water content** in unsaturated conditions, the **movement of water and salt** contents inside the stone samples.

• Future: to **compare with in situ** measured mechanical properties
Dynamic NR of water uptake in hardened cement slabs

Experiment series studying the uptake of water in hardened cement slabs (irradiated with gamma radiation for different time spans).

Water uptake of hardened cement slab, Sample Ni
DESALINATION OF BUILDING STONES

Understanding of salt transport mechanism between a salt laden substrate and a building material by dynamic PGAA – a pilot study

Zoltán KIS¹, Judit ZÖLDFÖLDI², Boglárka MARÓTI¹

¹ Centre for Energy Research, ² University of Stuttgart
Deterioriation due to salts → desalination

Degradation of building materials = soluble salts are considered as one of the most common causes; they can damage the fabric of porous materials and lead to powdering of the surface, sometimes causing substantial loss.

GOAL = to totally remove salts

Desalination = the process to remove salts (their respective ions) from the pore system of porous materials (e.g. natural stone: sandstone, limestone, tuff, etc., brick or terracotta, renders/plasters, or wall paintings). Treatments can be carried out in situ, or in a workshop for movable objects. Many desalination agents/techniques → unsatisfactory results

Better understanding of the desalination process is needed to support the conservator with clear guidelines for choosing a suitable desalination material and method.
CONTENT REMOVED DUE TO PUBLISHING CONSIDERATIONS
Advantages of dynamic PGAA in desalination study

• The moisture and salt distribution in the substrate and in the poultice products applied could be measured by means of dPGAA

• The chemical composition of the whole prism could be recorded, not only the composition of the surface.

• Future: to prove, by further polutice receipts, that size and arrangement of grains are important parameters to formulate poultices, (while workability, adhesion, consistency and shrinkage are crucial properties in determining the actual possibility of using a poultice in practice).

• Based on the velocity of water front propagation, the so-called sorptivity of the sample can be calculated during the image processing with simple calculations.
NANOCOATINGS ON BUILDING STONES

Neutron radiography of nanostructured coatings on stone surface

Vincenza CRUPI 1, Francesco D’AMICO 2, Barbara FAZIO 1, Zoltán KIS 3, Mauro F. LA RUSSA 4, Domenico MAJOLINO 1, Barbara ROSSI 2, Michela RICCA 4, Silvestro A. RUFFOLO 4, Valentina VENUTI 1

1 Università degli Studi di Messina, 2 Elettra – Sincrotrone Trieste, 3 MTA Centre for Energy Research, 4 Università della Calabria, Arcavacata di Rende
Biological degradation of stone surfaces

Conservation “philosophy”

- In the **early stages of cleaning** of an area affected by biological degradation, a fundamental operation is represented by the **removal of biological patinas**
- The removal of biological patinas requires the **use of biocides** (organic compounds in aqueous or organic solvent)
- The removal of biological patinas does **not ensure an inhibiting effect** over time
- Titanium Dioxide, that can **assure an inhibition effect** can produce benefits: economically, less cleaning interventions over time for the removal of biological patina; environmentally, linked to reduced use of biocides and solvents

>> **COATINGS WITH TiO$_2$ NANOPARTICLES**
Photo-catalytic effect of TiO$_2$

UV light < 390 nm

Self cleaning effect and biocidal effect occurs on titania surface

Larger surface area – Higher efficacy

Unresolved issues

• Behaviour of the nanostructured coatings with variable amount of nanoparticles, optimal amount of nanoparticles (beside aesthetical effect)

• Long-term behaviour of nanocoatings
**Application on stone materials**

**Modica stone:**

- Limestone
- white-cream coloured
- Porosity around 27%.
- Packstone Dunham (1962)

Further information have to be gained on the influence of the treatment on water sorption properties by dNR.
RAD @ BNC – Wetting of samples

Dynamic neutron radiography of wet stone materials

Graph showing water uptake vs. TiO$_2$ concentration.

Images of stone samples with different treatments and water uptake over time.
Advantages of dNR in nanocoating investigations

- Contact angle: The hydrophobicity of treated surface increases as the amount of TiO$_2$ increases, however this effect disappears along time. Over about 20 g/m$^2$, there is not any advantage to increase the amount of TiO$_2$ nanoparticles in term of photocatalytic effect.

- Raman: The amount of TiO$_2$ needed for a total coverage is 24 g/m$^2$

- dNR: Agreement with photocatalysis and Raman (ca. 20 g/m$^2$ TiO$_2$) + the penetration depth is detectable
Conclusions

• Neutrons are adequate to measure properties of porous materials
• Neutrons are sensitive to Hydrogen, i.e. water
• Neutrons can do non-destructive characterization, i.e. the sample is available for further studies
• In situ experiments can reveal time dynamics of the processes
• Practical application in cultural heritage, conservation science, as well as present-day technical problems


Gait, J., Bajnok, K., Kis, Z. 2017 Examining pottery forming techniques through combined petrographic analysis and neutron tomography. NINMACH Conference, Poster.

Centre for Energy Research

Thank you for your attention