Imaging and elemental analysis of porous materials at the BNC

Zoltán Kis, László Szentmiklósi, Boglárka Maróti, Veronika Szilágyi

Nuclear Analysis and Radiography Department
Format of the lecture

• Introduction
• Instrumentation
• Case studies:
  – Imaging of static systems
  – Dynamic imaging of processes
  – Elemental analysis for quantification
• Conclusions
Porous media

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)
Investigation possibilities of porous media at BNC

(1) the distribution of static constituents (spatial composition, porosity, etc.) → IMAGING

Neutron Imaging: NR, NT
X-ray Imaging: XR, XT

(2) the propagation rate (time dynamics) of a certain agent (moisture, chemicals) → DYNAMIC AND POSITION SENSITIVE COMPOSITION DETERMINATION

PGAA, dPGAA, dPGAI, dNR
RAD and NIPS–NORMA @ BNC

Budapest

RAD

NIPS - NORMA

BNC

13th Central European Training School on Neutron Techniques
5-10th May 2019
Combining elemental analysis with NR/NT for heterogeneity-mapping of materials at MTA EK, Budapest

- **Neutron Radiography/Tomography (NR/NT)**
  - fast: \( \text{sec} – \text{hours} \)
  - small objects: \( \text{in the range of cm’s} \)

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

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

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13\textsuperscript{th} Central European Training School on Neutron Techniques
5-10\textsuperscript{th} May 2019
Imaging possibilities with neutrons

– Why do we like neutrons?
  • Non-destructive testing of structure, elemental composition, mineral and metal phases
  • Different sensitivity according to their energy
  • No charge → Deep penetration (~cm, energy dependent)

– Neutron methods
  • NR/NT (2D/3D morphology) : Neutron radiography/tomography
  • PGAA (0D elemental analysis) → PGAI: Prompt-gamma activation imaging (3D)
  • ND (2D phase structure) → NDT : Neutron diffraction tomography (3D)
  • NRCA (0D elemental analysis) → NRCI: Neutron Resonance Capture Imaging (3D)
  • NRT (Neutron Resonant Transmission) (native 2D; 3D)

– Neutron methods + positioning = local measurements
  Analysis → Imaging
Positioning neutron 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>Microstructure, phase, texture, strain (tension, torsion), stress</th>
<th>Neutron diffraction (ToF-ND), Bragg edge transmission</th>
<th>Raman</th>
<th>X-ray diffraction (XRD)</th>
<th>X-ray diffraction (XRD)</th>
<th>SEM, TEM</th>
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<tbody>
<tr>
<td>Structure (size, orientation, shape) (non-destructive)</td>
<td>Small-angle Neutron Scattering (SANS)</td>
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<td>SEM, TEM</td>
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<tr>
<td>Structure (size, orientation, shape) (destructive)</td>
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<td>Morphology</td>
<td>Neutron imaging (NR, NT, NRCI, NRT)</td>
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<tr>
<td>Composition (non-destructive)</td>
<td>Prompt gamma-ray activation imaging (PGAI), Bragg edge transmission, NRCI, NRT</td>
<td>Raman, FT-IR</td>
<td>X-ray fluorescence (XRF)</td>
<td>X-ray fluorescence, X-ray absorption</td>
<td>PIXE, PIGE, RBS</td>
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<tr>
<td>Composition (minimal invasive)</td>
<td>Neutron activation Analysis (NAA)</td>
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<tr>
<td>Composition (destructive)</td>
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<td>Lower energy electromagnetic (THz, IR, vis., UV)</td>
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<td>X-ray</td>
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<td>Synchrotron</td>
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<td>Charged particle</td>
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</tbody>
</table>

Power of neutrons

1. Neutron: Lower energy electromagnetic (THz, IR, vis., UV)
2. X-ray: X-ray diffraction (XRD)
3. Synchrotron: X-ray diffraction (XRD)
4. Charged particle: SEM, TEM

Composition (non-destructive)

- Prompt gamma-ray activation imaging (PGAI), Bragg edge transmission, NRCI, NRT
- Neutron activation Analysis (NAA)
- ICP-AES, AAS

Composition (minimal invasive)

- Neutron activation Analysis (NAA)
- SIMS, LA-ICP-MS

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Comparison: X-ray vs. neutron tomography

Fig. 1. Some 3D tools for 3D imaging in materials: non-destructive character and approximate spatial resolution.
Neutron and bimodal (neutron and X-ray) imaging of porous media

ARCHAEOLOGICAL POTTERY
Examining pottery forming techniques through combined petrographic analysis and neutron tomography

Katalin BAJNOK, John GAIT, Zoltán KIS, Imre SZENTI, Veronika SZILÁGYI

1 MTA Wigner Research Centre for Physics, 2 Eötvös Loránd University, Budapest, 3 Fitch Laboratory, British School at Athens, 4 MTA Centre for Energy Research, 5 University of Szeged
What can be seen in a ceramic by neutrons and X-rays?

- **Neutron tomography:** hydrogen content (organic materials)
- **X-ray tomography:** more dense material (higher atomic number)

**Neutron images**

Original ceramic sherds and a contemporary complementary material (gypsum) for the lacking parts

**X-ray images**

Pore structure

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Case study

Lower Nubia
Late Neolithic – Early Bronze Age (BC 3400-1600)
Pottery forming techniques

**COILING**

Fibres aligned parallel to walls and rim plane

*Arkell 1939*

**PERCUSSION**

Fibres aligned parallel to walls, and unaligned to rim plane

*Arkell 1939*
Comparison: archaeological vs. experimental

- 6 archaeological Nubian pottery
  (4 A-Group & 2 C-Group)
- 6 experimental replicas
  (3 coil-built & 3 percussion-built)

Neutron tomography @ BNC
Orientation determination in the spherical coordinate system:

Polar angle ($\theta$) vs. azimuthal angle ($\phi$)
Advantages of NT of archaeological ceramics

1. NT for discriminating ancient pottery forming techniques by 3D visualization

2. From **qualitative** results (3D imaging) $\rightarrow$ to **quantitative** (statistical) analysis

3. Instead of thin sections, whole sherds/complete vessels can be analysed non-destructively
Neutron and bimodal (neutron and X-ray) imaging of porous media

CONTEMPORARY CONCRETE

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

Zoltán KIS\textsuperscript{1}, Veronika SZILÁGYI\textsuperscript{1}, Petr STEMBERK\textsuperscript{2}, Michal GLINICKI\textsuperscript{3}

\textsuperscript{1}MTA Centre for Energy Research, \textsuperscript{2}Technical University of Prague, \textsuperscript{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).
Concrete constituents

Major constituents of concretes:
• Binder = Unhydrated clinker and hydrated cement paste of hardened concrete
• Skeleton = Coarse and fine aggregates
• Voids/Pores
• Admixtures
Concrete constituents – Pores

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 voids</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 voids</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 voids</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>
Bimodal imaging of Czech concrete blocks
Clearly observable

_In NT image:_
AGGREGATES, PASTE DIFFERENCES

_In XT images:_
MACRO-PORES, some AGGREGATES

_Comboination of NT and XT:_
PORE distribution,
AGGREGATE distribution,
GRANULOMETRY, POROMETRY,
AGGREGATE quality (limited)
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)
Quantitative evaluation

Calculations on the basis of imaging techniques

**Combination of NT and XT:**
AGGREGATE distribution, GRANULOMETRY

MACRO-PORE distribution
Quantitative evaluation

Block 1
Calculated macro-porosity: 0.19%
Largest void: 0.65 mm³
on the basis of XT
Quantitative evaluation

Block 1
Calculated aggregate content: 26.66%
Largest aggregate: 3.94 mm³
on the basis of NT
Quantitative evaluation – Raw data for modelling

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</th>
<th>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>
</tr>
</thead>
<tbody>
<tr>
<td>1 Power of neutrons</td>
<td>2 PM vs. Imaging</td>
<td>3 PM vs. Dynamic PGAA/PGAI/NR</td>
<td>13th Central European Training School on Neutron Techniques 5-10th May 2019</td>
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</table>
Quantitative analysis – Aggregate size distribution

Grain size distribution

Frequency

Passing fraction (%)

Diameter (mm)

Diameter (mm)

Power of neutrons
PM vs. Imaging
PM vs. Dynamic PGAA/PGAI/NR

1 Power of neutrons
2 PM vs. Imaging
3 PM vs. Dynamic PGAA/PGAI/NR

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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 \( \text{EL} = \frac{b}{a} = 0.77 \)
- Flatness index \( \text{FL} = \frac{c}{b} = 0.90 \)

Radius of the circumscribed sphere
- \( R = 0.95 \text{ mm} \)

Radius of the inscribed sphere
- \( r = 0.45 \text{ mm} \)
Shape analysis on the aggregate population in the concrete

- Power of neutrons
- PM vs. Imaging
- PM vs. Dynamic PGAA/PGAI/NR

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Quantitative evaluation – Raw data for modelling

Converting data into mesh

1 Power of neutrons
2 PM vs. Imaging
3 PM vs. Dynamic PGAA/PGAI/NR
Quanitative evaluation – Raw data for modelling

Exporting mesh data to .stl format and visualization in other programs (e.g. GOM)
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
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, ...)

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Venice 2008

Venice 2018
Neutron-based dynamic chemical characterization and imaging of porous media

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 KIS¹, Francesca SCIARETTA², László SZENTMIKLÓSI¹

¹ MTA Centre for Energy Research, ² University of Venice
Damage of building stones

• 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?

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

Joint application of NR/NT and PGAI to clarify – in a quantitative approach – 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 combination 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 → NR**
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)
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

• Part of an experiment series studying the propagation of water and salt ions (NaCl solution) in porous medium

• Stones @ NIPS-NORMA: The water capillary system and a photo of a stone taken before the imbibition experiment showing its Al wrapping and the Al holder

• NR image of a stone (darker areas = already-wet part). The neutron irradiated area was always between the yellow lines: \( V(\text{ert}) \times H(\text{oriz}) = 2 \times 43 \text{ mm}^2 \)
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

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.
Neutron-based dynamic chemical characterization and imaging of porous media

**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 TiO₂ 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)
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
Dynamic neutron radiography of wet stone materials

RAD @ BNC – Wetting of samples
Measurements have been made at 0, 42, 66 hours of wetting
Neutron radiographic imaging: Results

### 1. Power of neutrons

- **U**: 3 cm
- **B**: treatment
- **2.5**:

### 2. PM vs. Imaging

- **0h**, **42h**, **66h**

### 3. PM vs. Dynamic PGAA/PGAI/NR

- **10 g/m²**
- **10**, **20**, **40**

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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
Acknowledgements
THANK YOU FOR YOUR ATTENTION!

Sources of results:
Kis, Z., Sciaretta, F., Szentmiklósi, L. Water uptake experiments of historic construction materials from Venice by neutron imaging and PGAI methods. Materials and Structures 50:159.
Gait, J., Bajnok, K., Kis, Z. Examining pottery forming techniques through combined petrographic analysis and neutron tomography. NINMACH Conference, Poster.