QUANTIFICATION OF PORE STRUCTURE CHARACTERISTICS FOR DETERIORATED MORTAR DUE TO CALCIUM LEACHING BY SYNCHROTRON MICROTOMOGRAPHY

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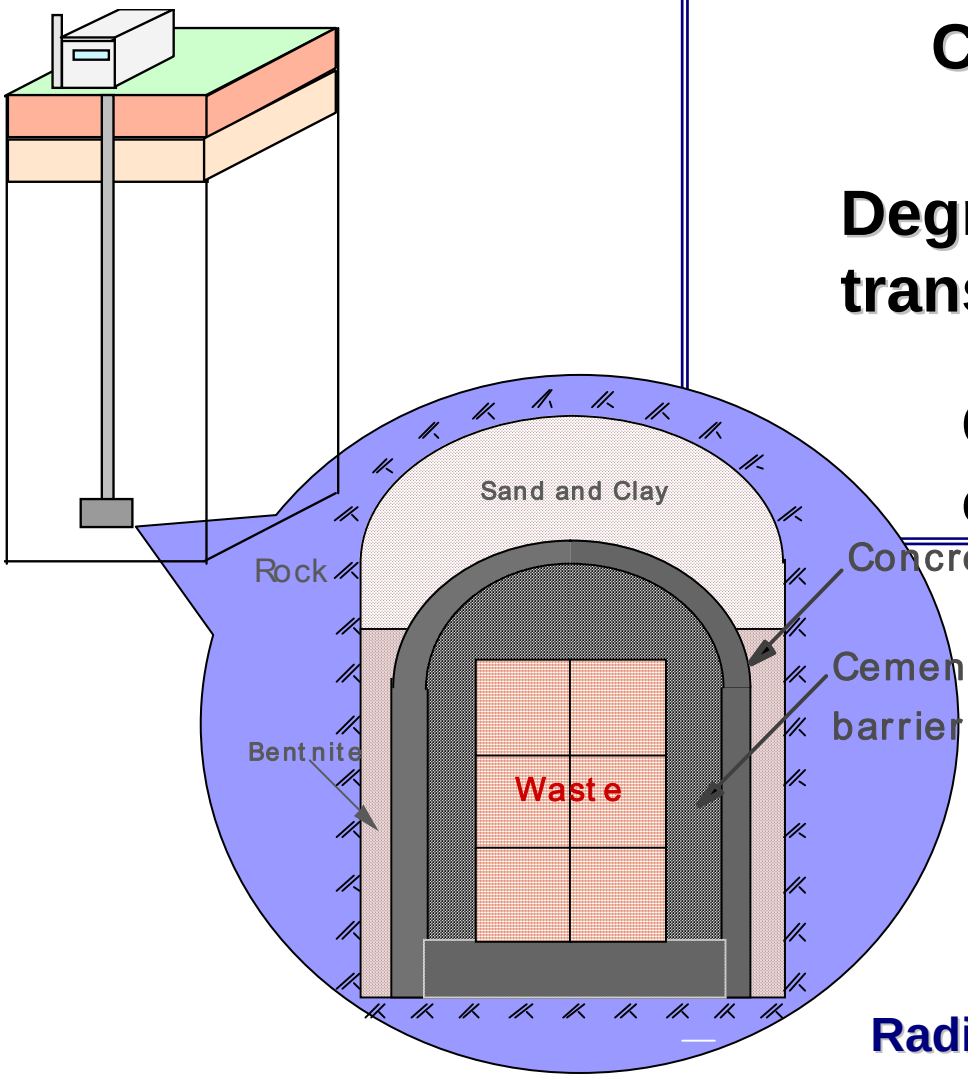
Material Degradation in Long Term Service



Calcium leaching

⇩

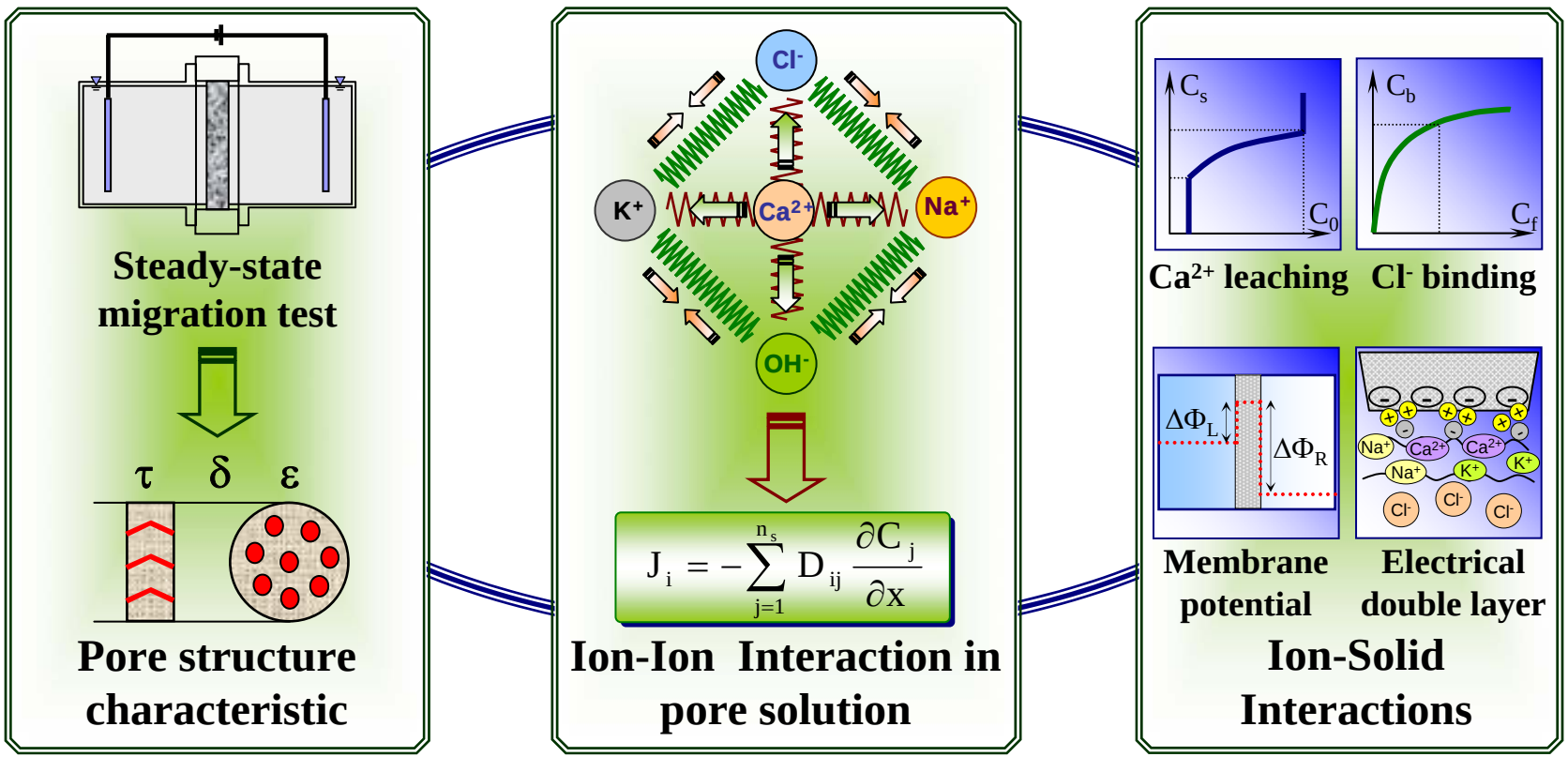
Degrading mechanical and transport properties

⇩

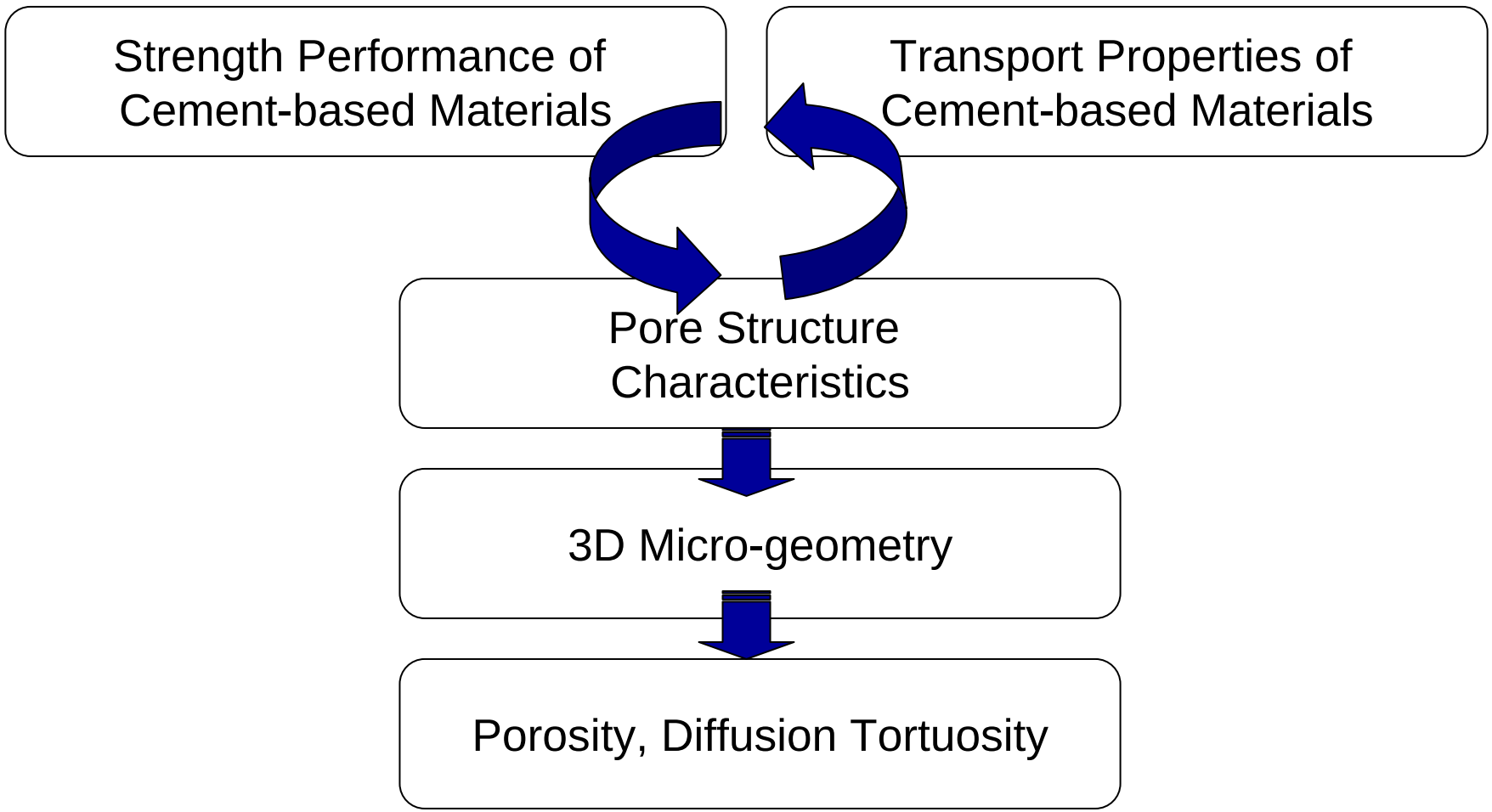
Change of pore structure characteristics

Radioactive Waste Repository

Development for calculation model of ion transport in hydrated cement system (SiTraM in 2003)



Significance of pore structure characteristics for material properties



Pore Structure Characteristics of Cement-based Materials estimated from 3D Micro-geometry using Synchrotron Microtomography

- Methodology: **Synchrotron microtomography**
  Random Walk Simulation
- Application to **deteriorated mortars** and **cement pastes**
- **Accelerated electrical tests** for calcium leaching

Synchrotron Microtomography

Bentz et al 2000, Helfen et al. 2005, Lu et al. 2006, Burlion et al. 2006, Koster 2006, Gallucci et al. 2007

SPring-8 (Japan)

- Same principle as medical CT scan
  - Creates X-ray image of ‘slice’ through object that can make 3D volume
  - But higher-energy, more focused Synchrotron-based X-rays (higher spatial resolution)
  - X-ray source is tunable, X-ray radiation is monochromatic, and X-ray beam is flat
- Applications

  Geology, Anthropology, Biology, Medicine, Engineering

- Advantage and Disadvantage

3D micro-geometry technique

X-ray imaging of specimen

SPring-8

3D reconstruction of image

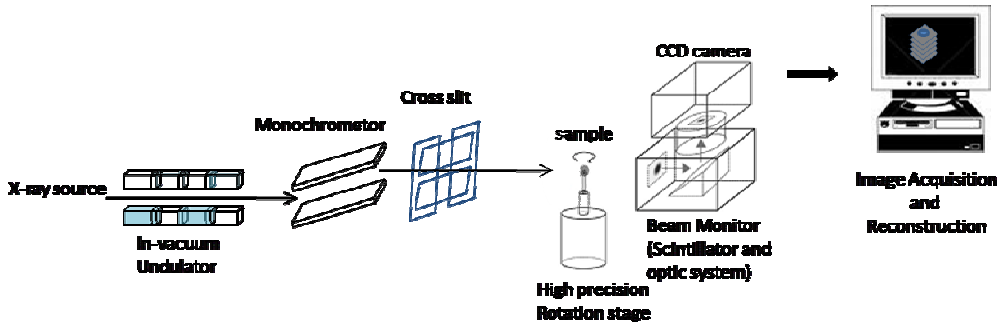
Pixel size = 0.5 micron

3D Image processing

Extraction of 3D pore space

Mathematica program
(Nakashima et al.2007)

Quantification of tortuosity based on random walk simulation (RWS)



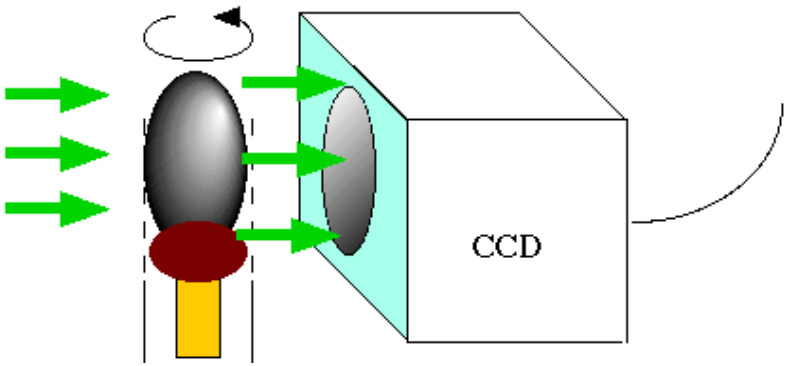
SLICE (Nakano et al., 2007)

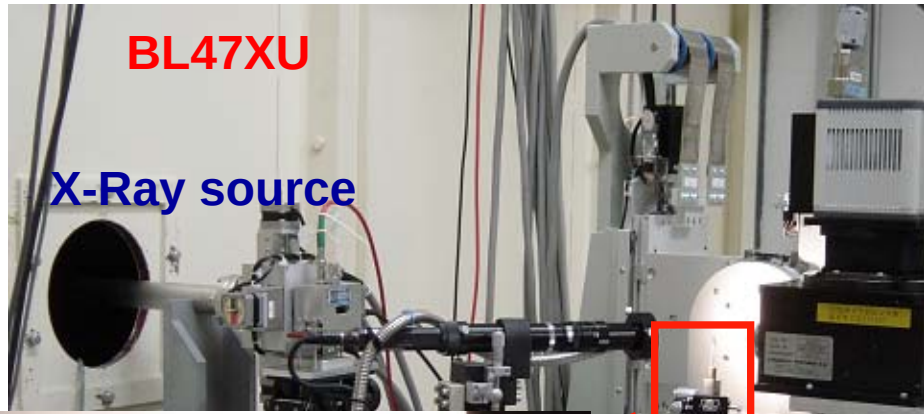
Pore segmentation

Pore cluster multiple labeling

Visualization and quantification of porosity

X-ray Scanning of Specimen

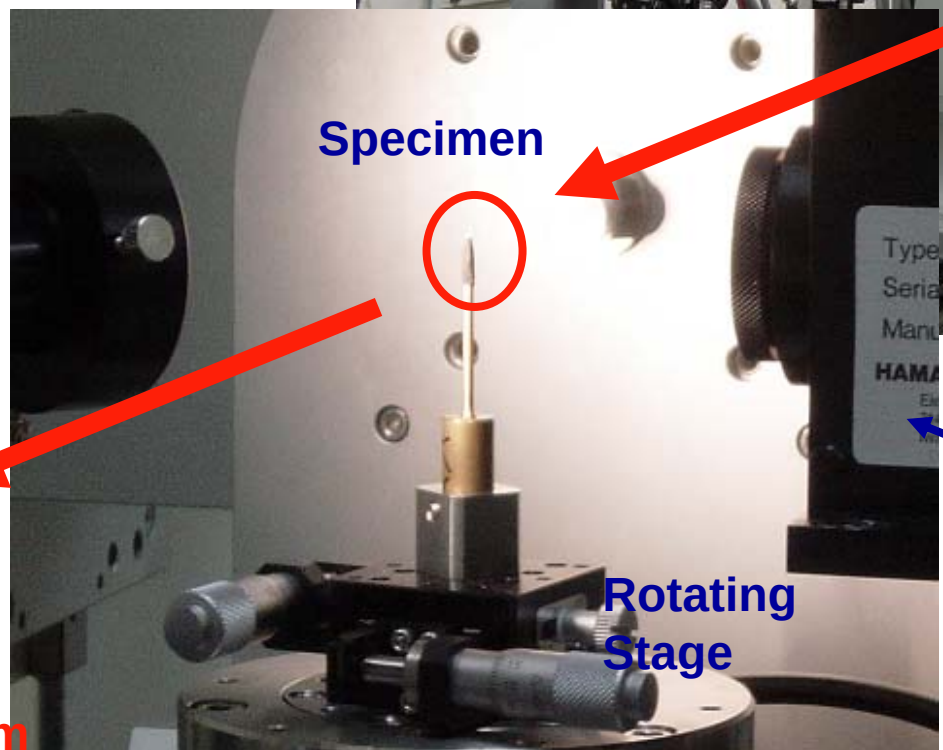


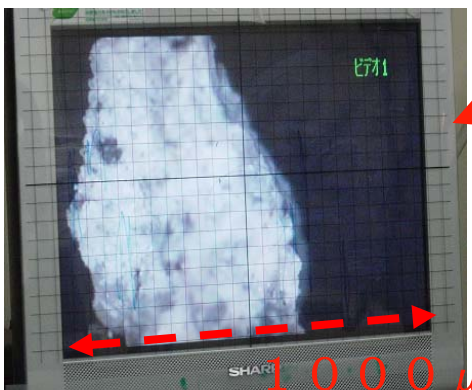


Beam energy: 15 kev

2000x1300 px CCD

1500 projections
(180^0 rotation)

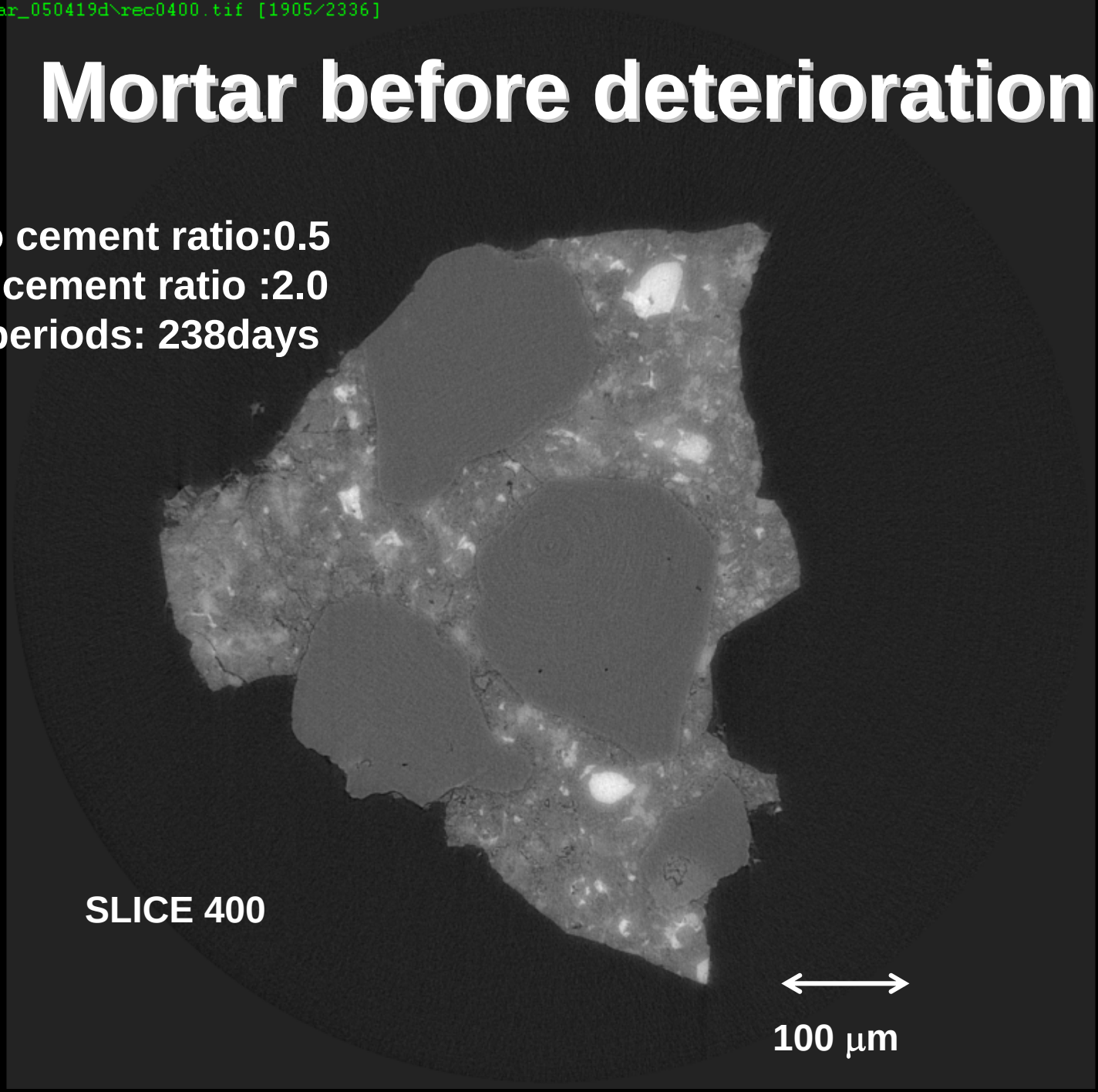




S:\recons\nmortar_050419d\rec0400.tif [1905/2336]

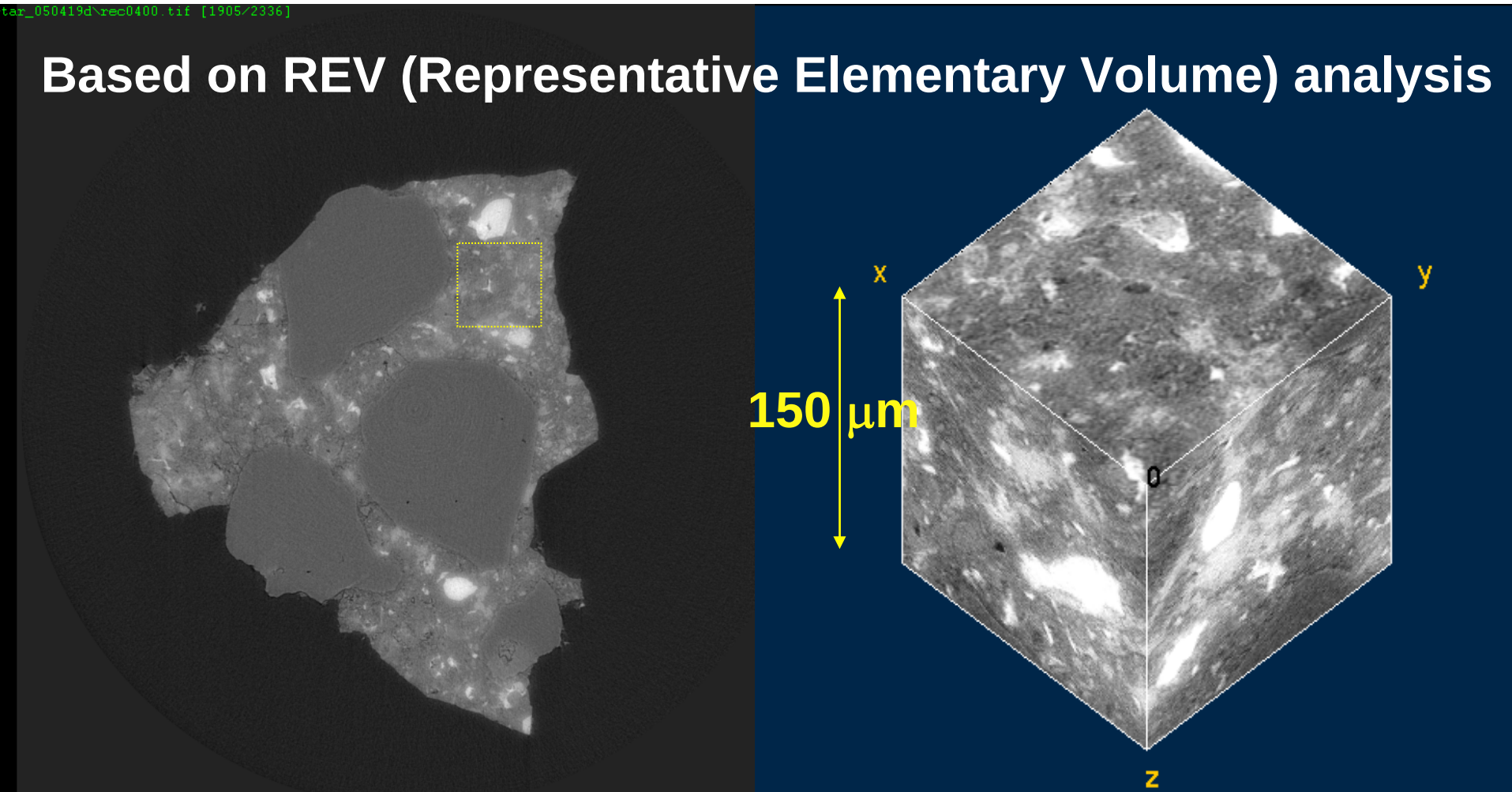
Mortar before deterioration

Water to cement ratio:0.5
Sand to cement ratio :2.0
Curing periods: 238days

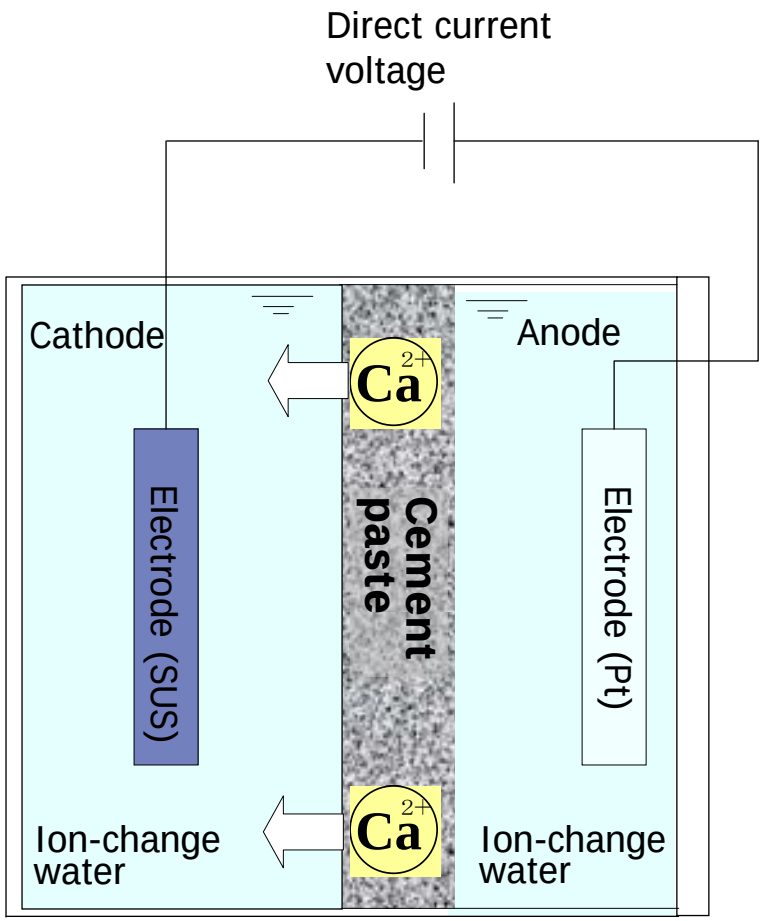


Extraction of 3D image (VOI)

300 x 300 pixels in 2D → **300 x 300 x 300 pixels (VOI)**



Accelerated Electrical Method



Schematic diagram for accelerated electrical test

Acceleration test underway using Acrylic cell

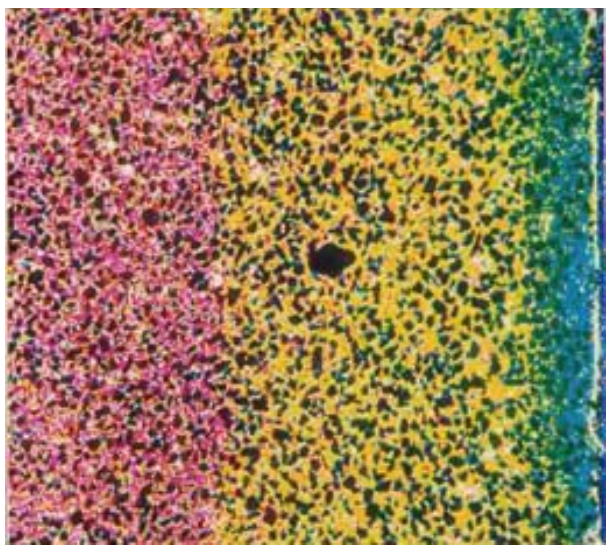
Distribution of CaO/SiO_2 ratio in cement hydrate (obtained by EPMA)

According to Saito et al. ACI Materials J. 1999

Diffusion test

After 2,000days

Inner side — Surface



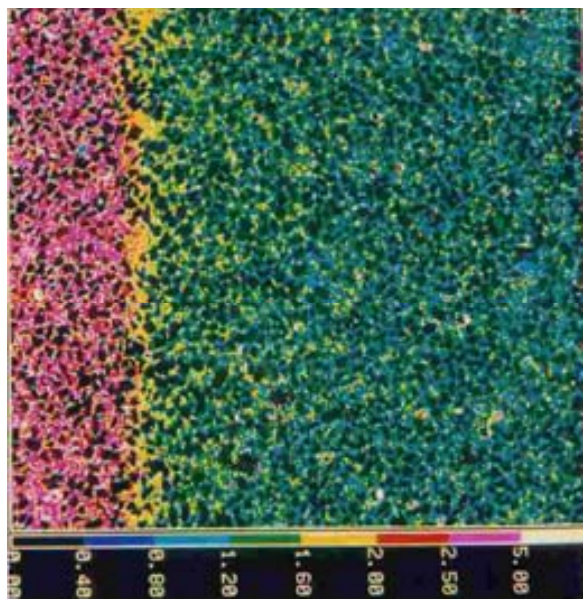
2mm

8mm

Acceleration test

After 2months under 5 V/cm

Inner side — Cathode side



6mm

Specimens under investigation

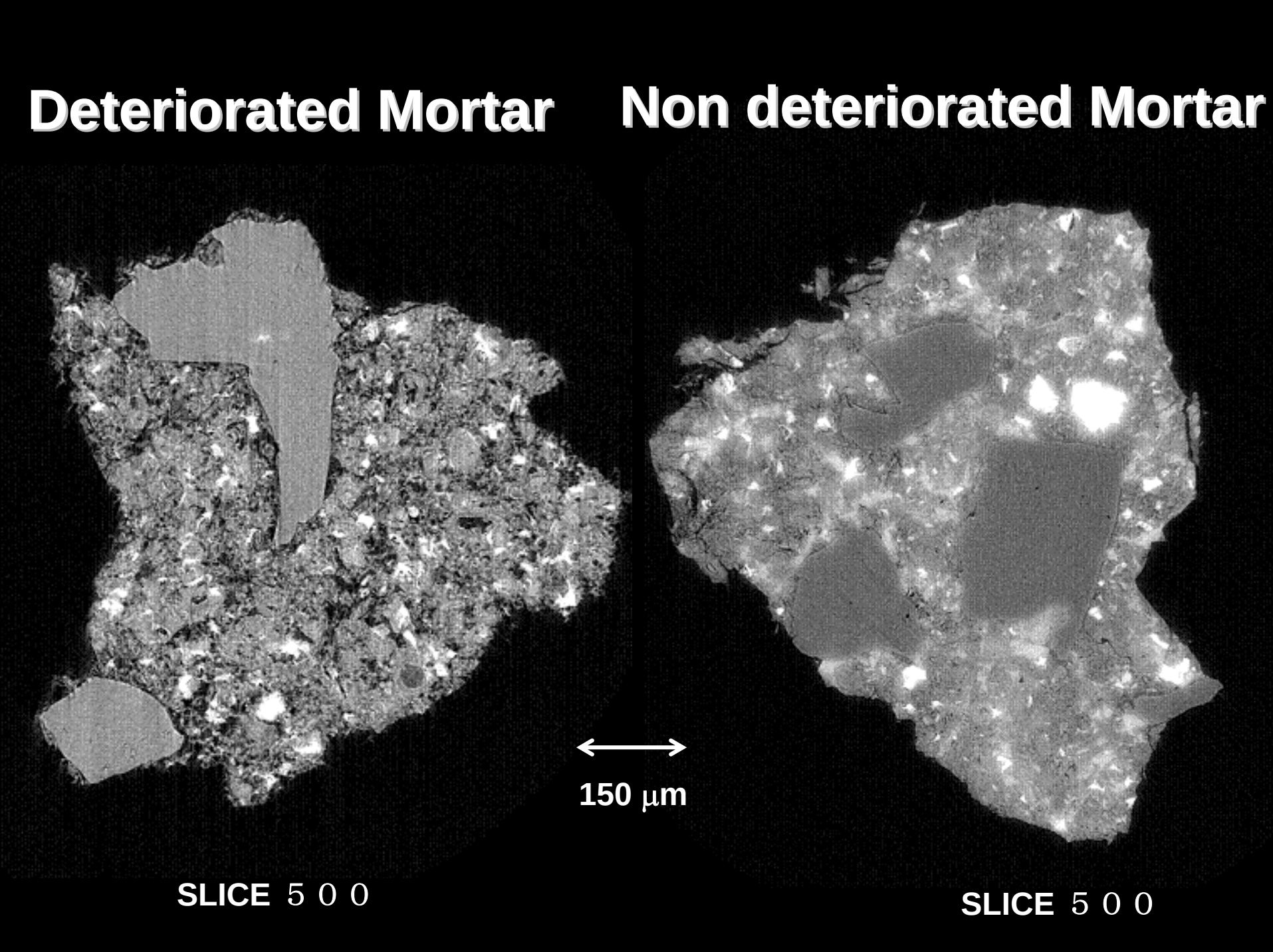
	W/C	Cement	Sand	Chemical admixture
Mortar	0.5	OPC	Sieved under 210μm (S/C:2.0)	Super-plasticizer
Cement paste	0.5	OPC	Non	Viscosity agent (cellulose-ether type)

OPC: Ordinary Portland Cement JIS R5210

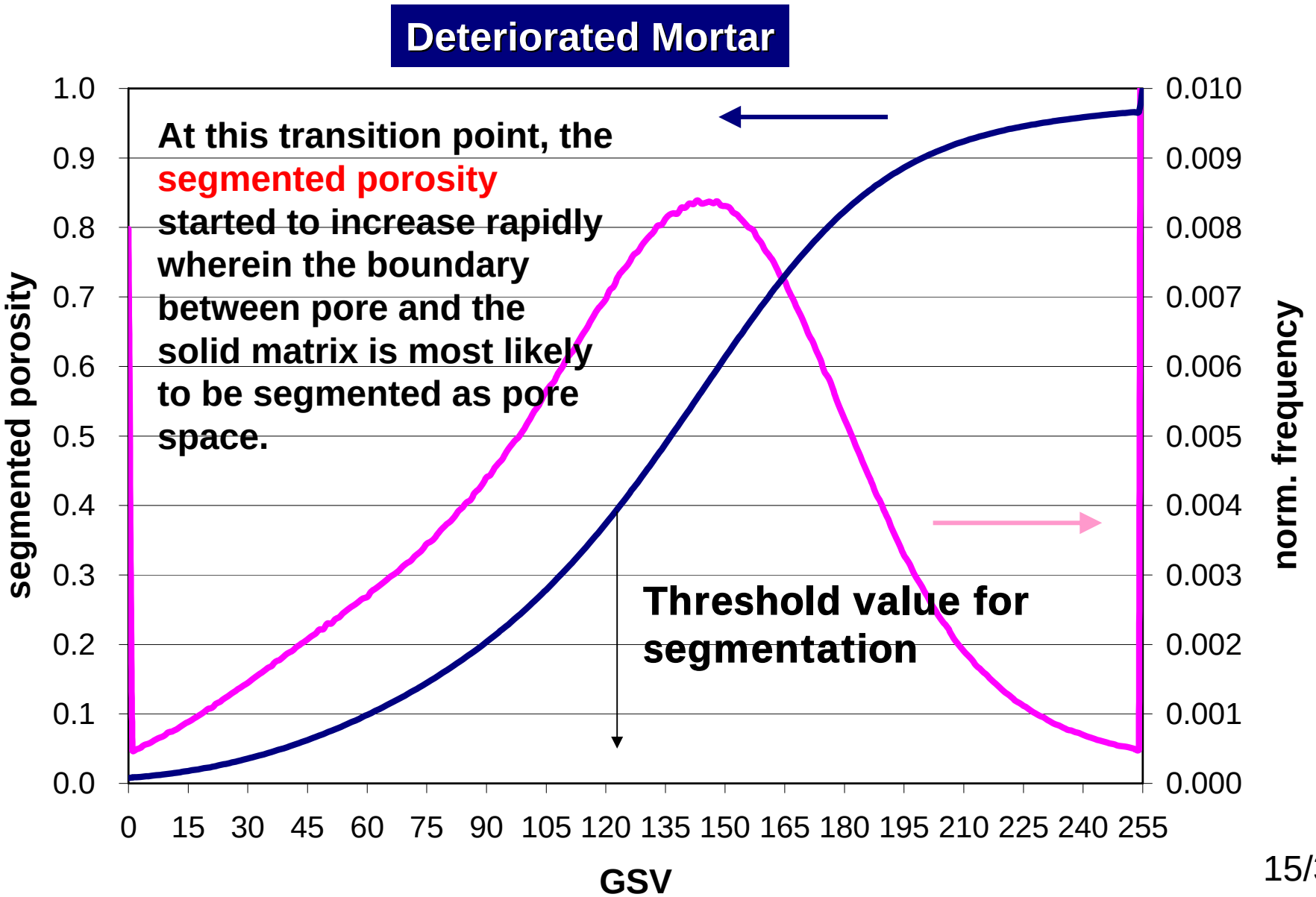
Non-deteriorated mortar: 30 weeks in curing

Deteriorated mortar: 20weeks in curing followed by acceleration test for 13weeks

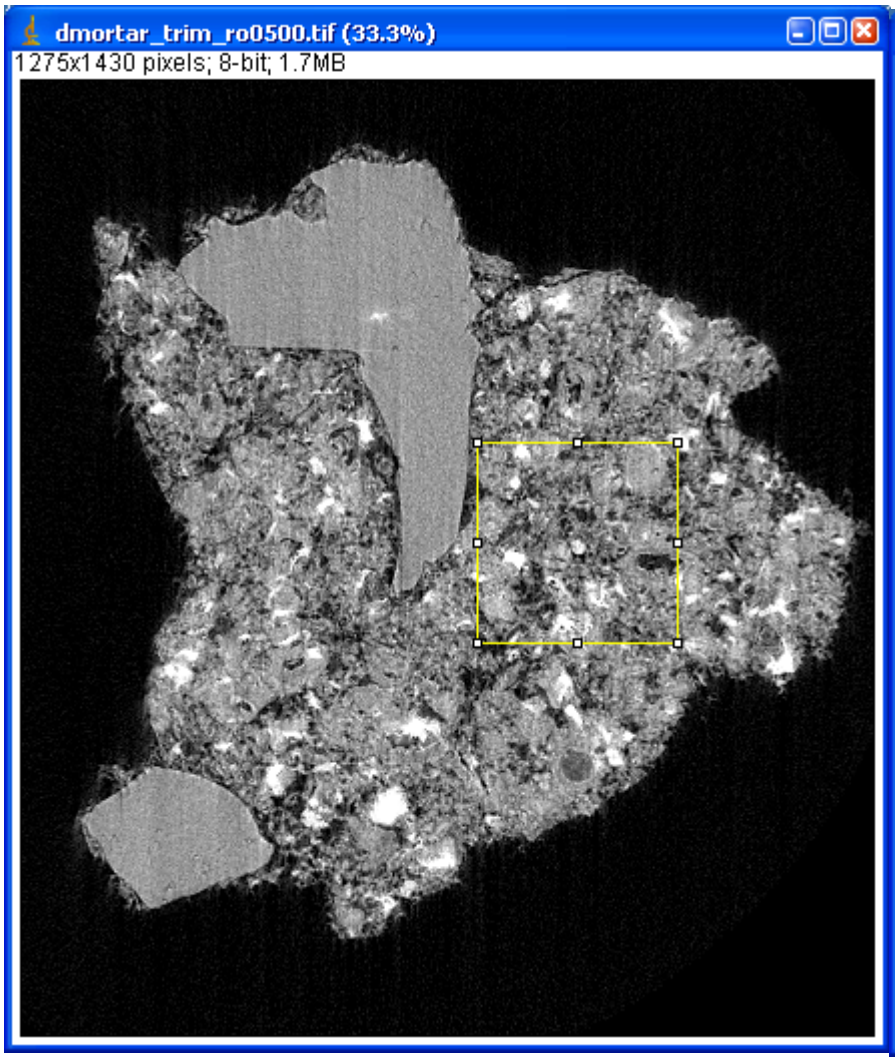
Cement paste: 20weeks in curing followed by acceleration test for13weeks

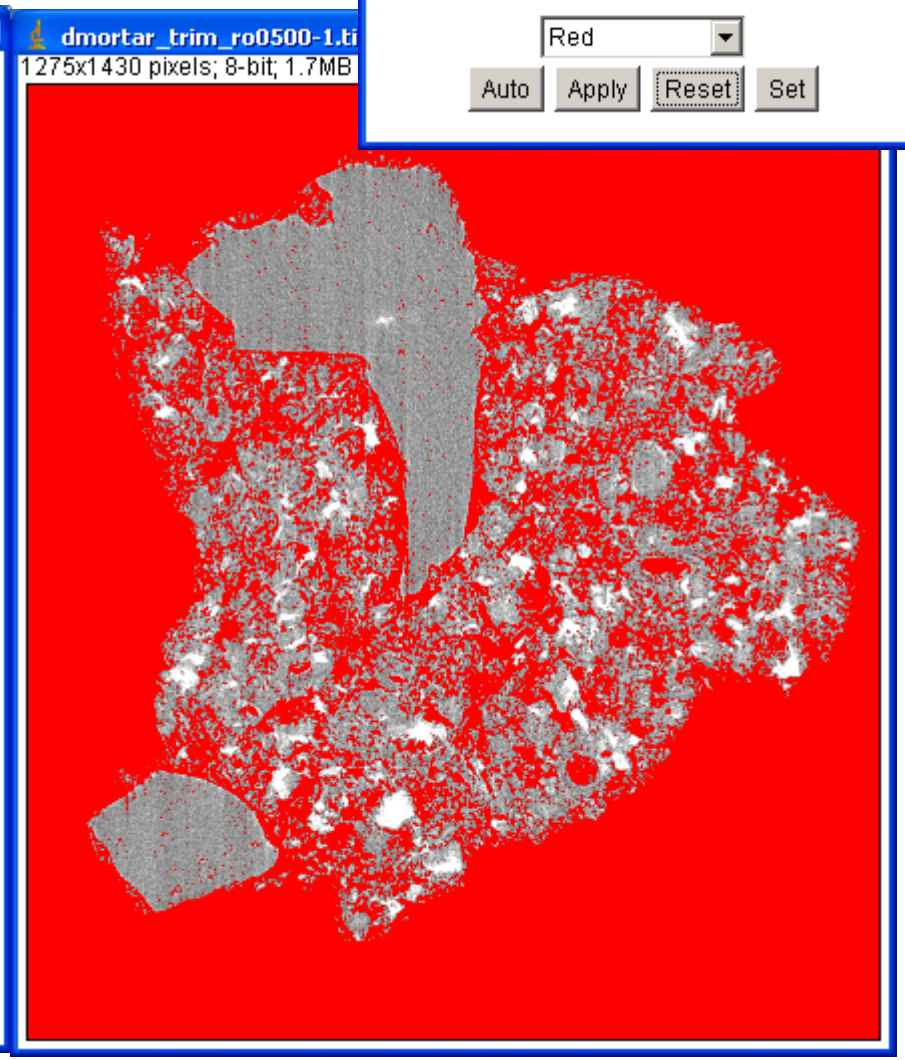

Deteriorated Mortar
Non deteriorated Mortar
150 μm
SLICE 5 0 0
SLICE 5 0 0

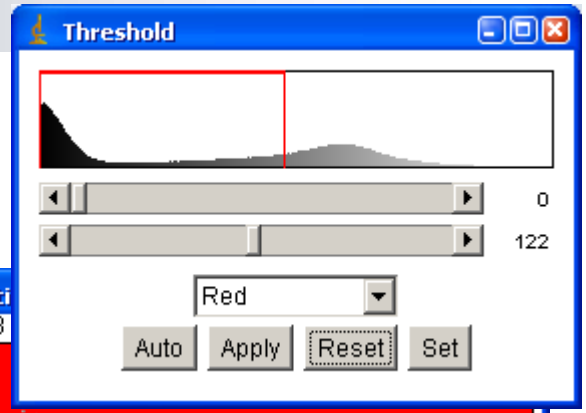
Porosity-Threshold dependency curve of VOI



Deteriorated Mortar (D.M.)

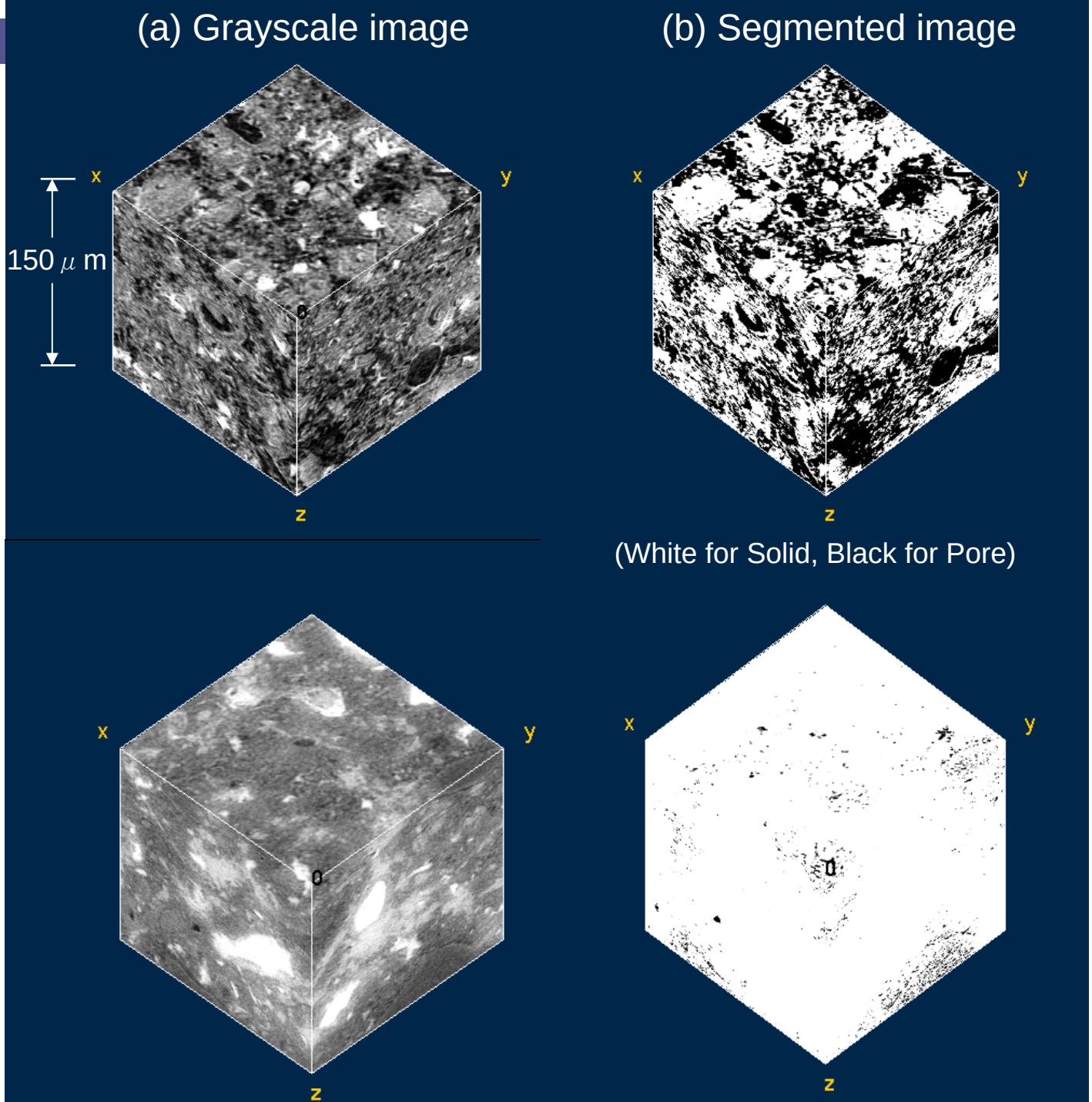




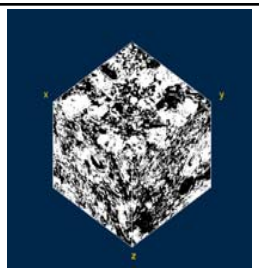
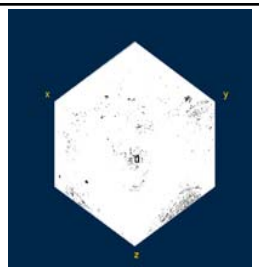


D. M.

Non D. M.


(a) Grayscale image
(b) Segmented image
x
y
z
150 μ m
(White for Solid, Black for Pore)

Quantification of porosity

	Segmented porosity, ε_t	Connectivity γ	Effective porosity, ε_e
	0.39	0.98	0.38
	0.04	0.51	0.02

$$\varepsilon_t = \frac{\text{Total pore voxels}}{\text{Total voxels}} \qquad \varepsilon_e = \varepsilon_t \times \gamma$$

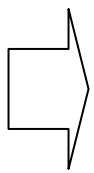
$$\gamma = \frac{\text{No. of voxels of the largest percolating pore}}{\text{Total pore voxels}}$$

Pore Cluster Multiple Labeling

Hoshen-Kopelman Algorithm

Binary Image Matrix (Pore GSV = 0)

0	0	255	255	255	0	255	255	255	255
0	0	255	255	255	0	255	255	255	255
255	255	255	255	0	0	0	255	255	255
255	255	255	0	0	0	0	0	255	255
0	0	0	0	255	255	255	0	255	255
255	0	0	0	255	0	255	0	0	255
255	255	0	0	255	255	255	0	0	255
255	255	0	0	0	0	0	0	0	255
0	255	255	255	255	255	255	255	0	0
255	0	255	255	255	255	255	255	255	0



Labeled pore clusters

2	2	0	0	0	1	0	0	0	0
2	2	0	0	0	1	0	0	0	0
0	0	0	0	1	1	1	0	0	0
0	0	0	1	1	1	1	1	0	0
1	1	1	1	0	0	0	1	0	0
0	1	1	1	0	5	0	1	1	0
0	0	1	1	0	0	0	1	1	0
0	0	1	1	1	1	1	1	1	0
3	0	0	0	0	0	0	0	1	1
0	4	0	0	0	0	0	0	0	1

Diffusion Tortuosity and Random Walk

Time-dependent diffusion coefficient of random Brownian motion of molecules → To probe the geometry of porous media

MSD → $$\left\langle r^2 \right\rangle = \left\langle \left[r'(t) - r'(0) \right]^2 \right\rangle = 2dD(t)t$$

For 3D random walk (d =3)

Diffusion Tortuosity $$\tau = \frac{D_0}{D(t)}$$

Free space (porosity = 100 %)

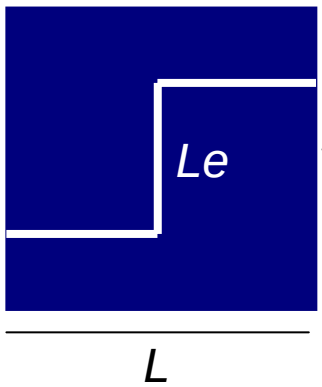
$$D_0 = \frac{1}{6}\frac{\left\langle r^2 \right\rangle}{t}$$

Pore space (restricted diffusion)

$$D(t) = \frac{1}{6}\frac{d\left\langle r^2 \right\rangle}{dt}$$

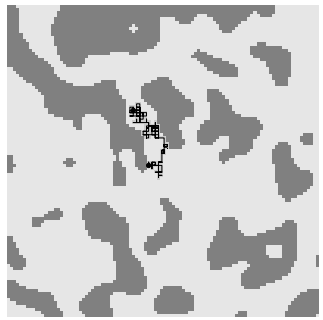
Definition of tortuosity

Pore structural model: Capillary model



$$Tortuosity = \frac{Le}{L}$$

Pore space : Diffusion tortuosity

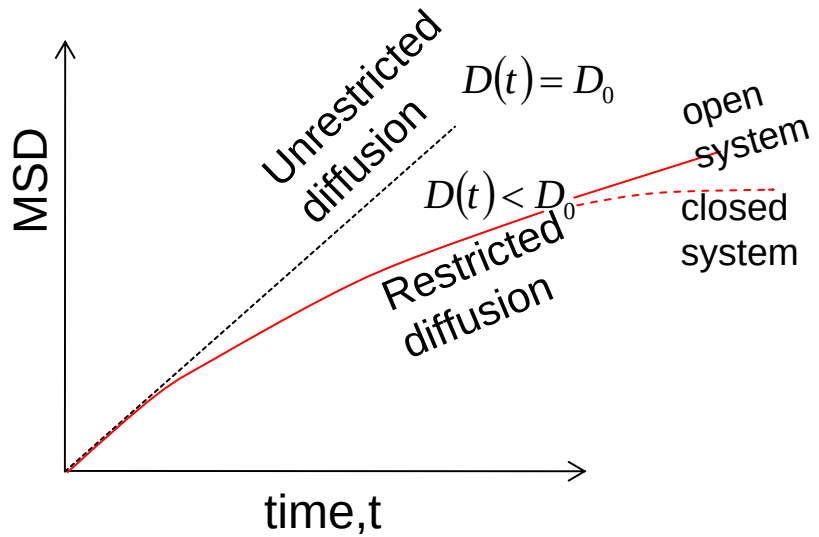


$$Tortuosity = \frac{D_o}{D_\infty}$$

Unidimensional:
percolating in the x-direction

$$\tau_f \geq 1$$

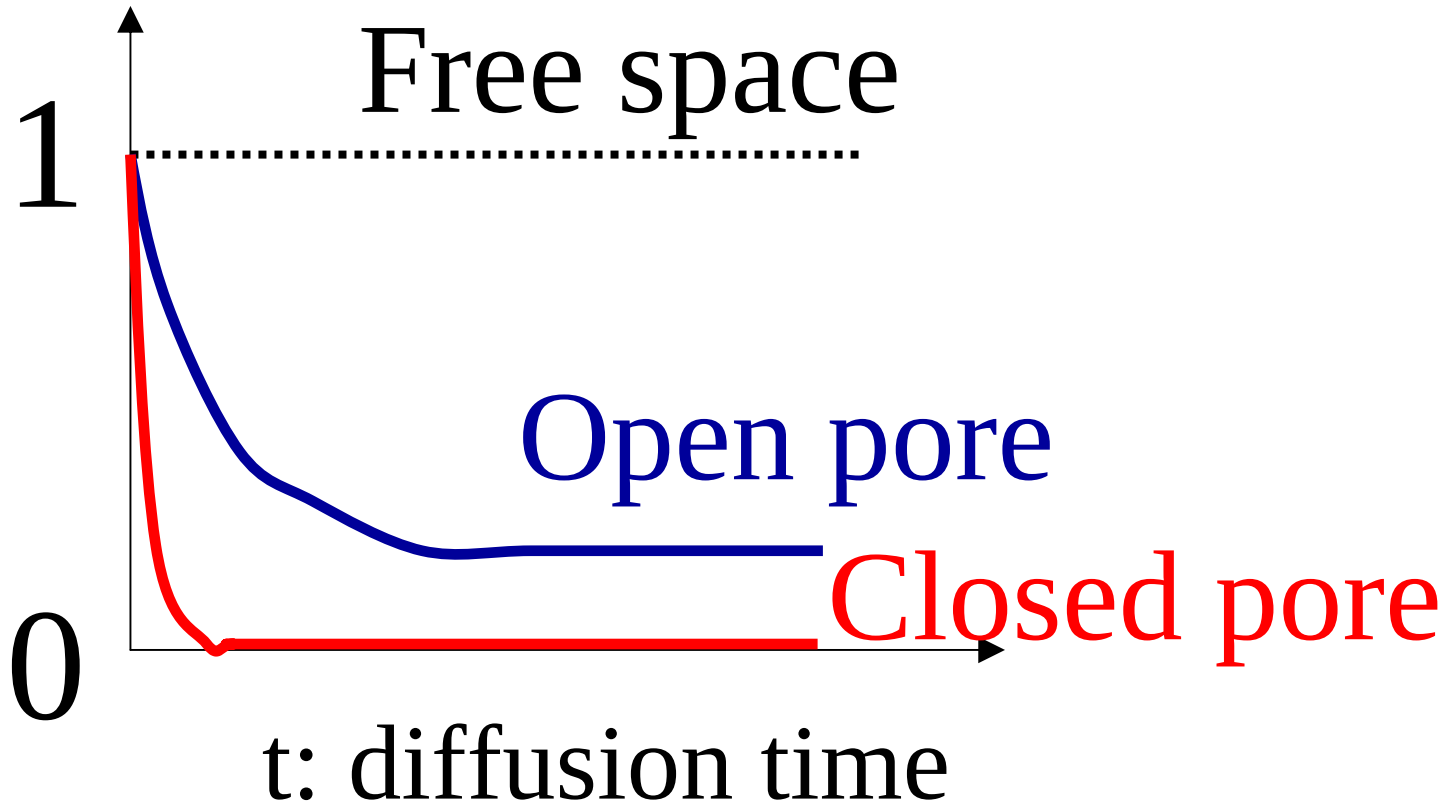
$$\tau_f = \left(\frac{Le}{L}\right)^2$$



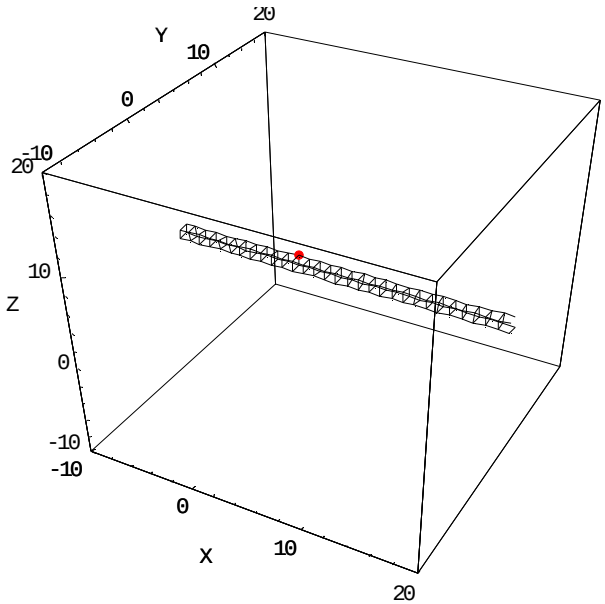
Mean square displacement vs time

Time-Dependent Diffusion Tortuosity

$$\frac{1}{\tau} = \frac{D(t)}{D_0}$$

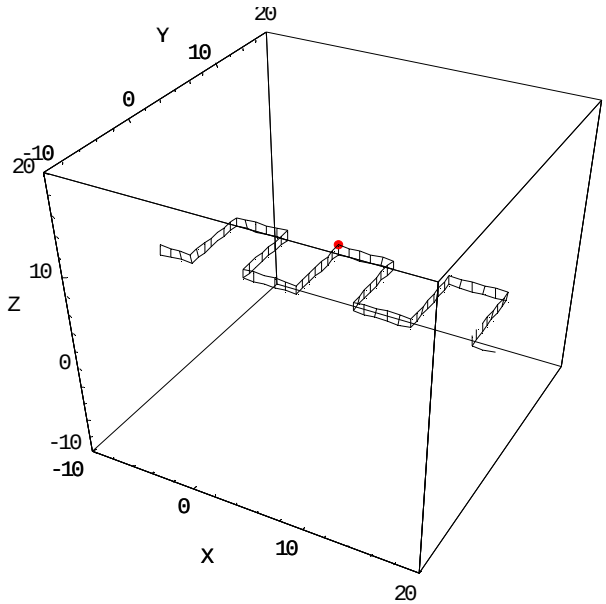


Diffusion tortuosity based on RWS in simple capillary model



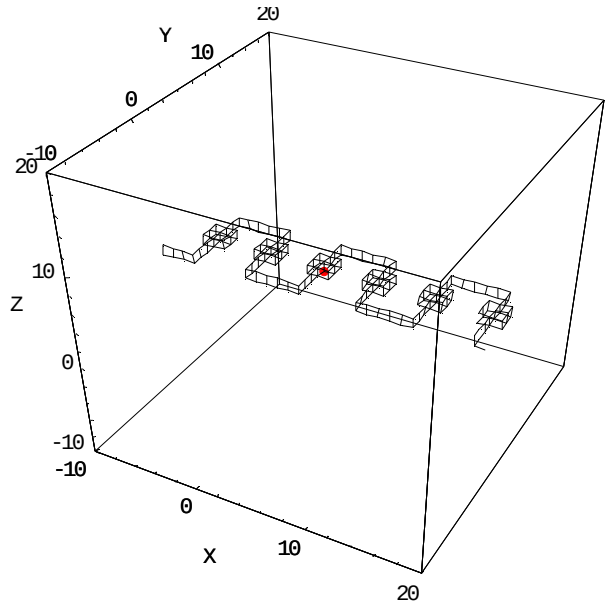
$$\tau = 1.00$$

$$\left(\frac{Le}{L}\right) = 1$$



$$\tau = (2.40)^2$$

$$\left(\frac{Le}{L}\right) = 2.40$$

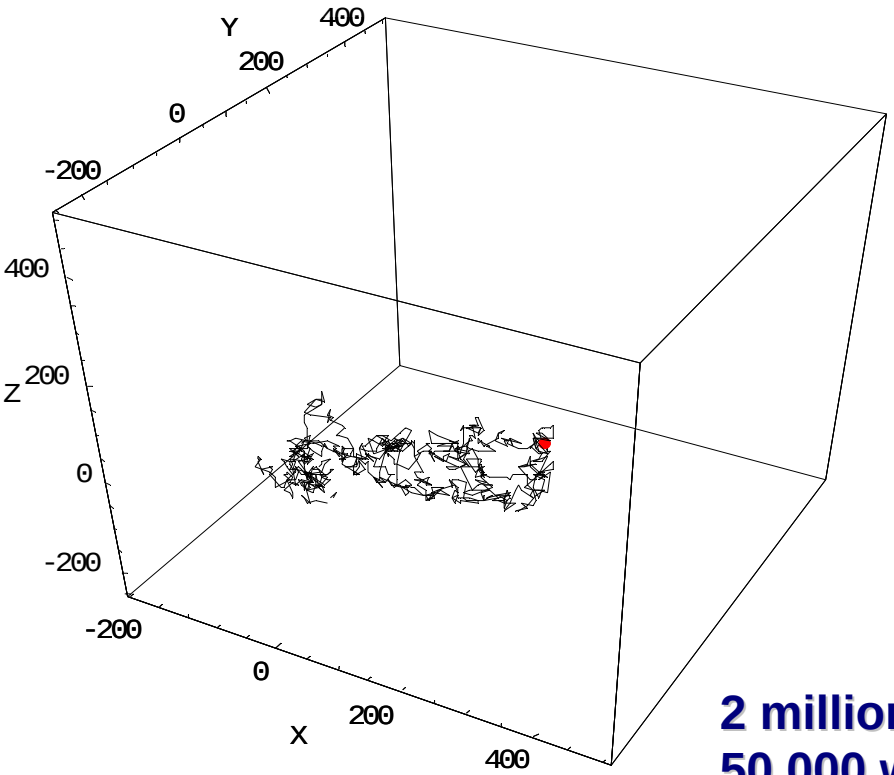


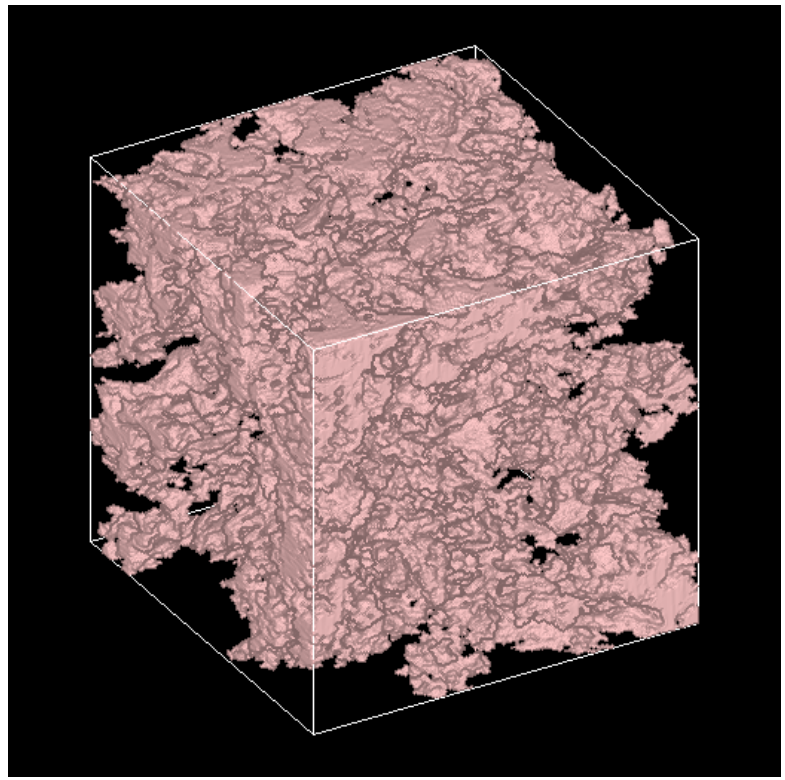
$$\tau = (2.78)^2$$

$$\left(\frac{Le}{L}\right) = ?$$

Deteriorated Mortar

A sample trajectory of a random walker in 3D pore space of DM



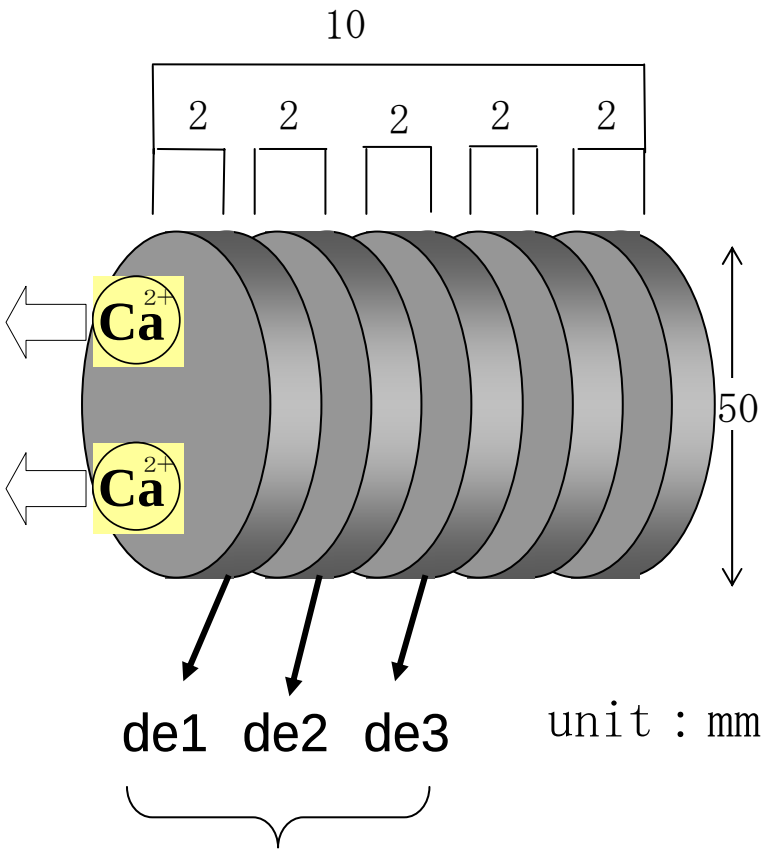


Percolating pore=0.38
(98% of Porosity)

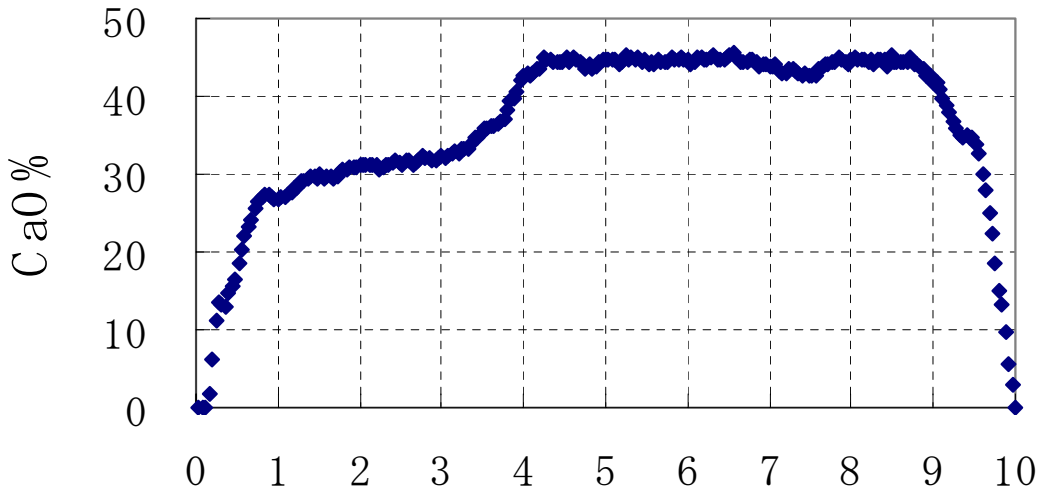
2 million time steps
50,000 walkers

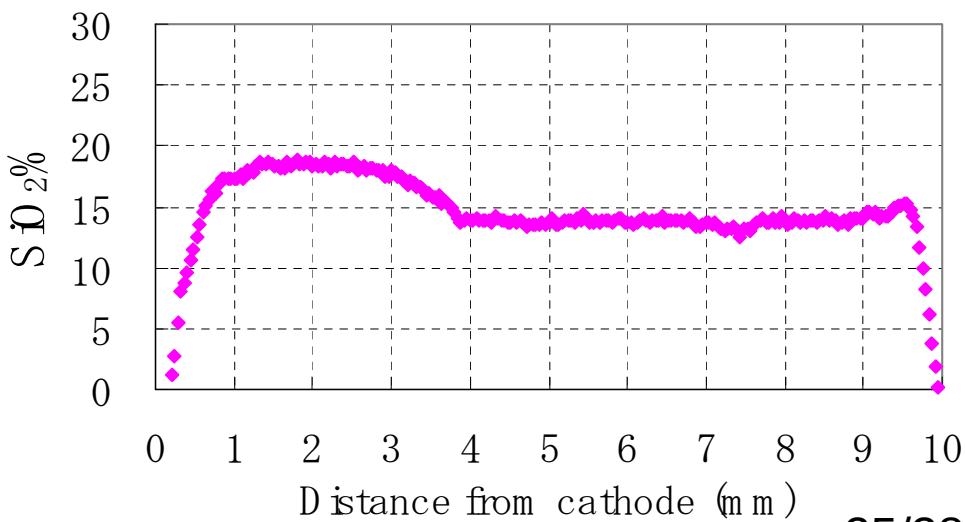
Diffusion tortuosity: 4

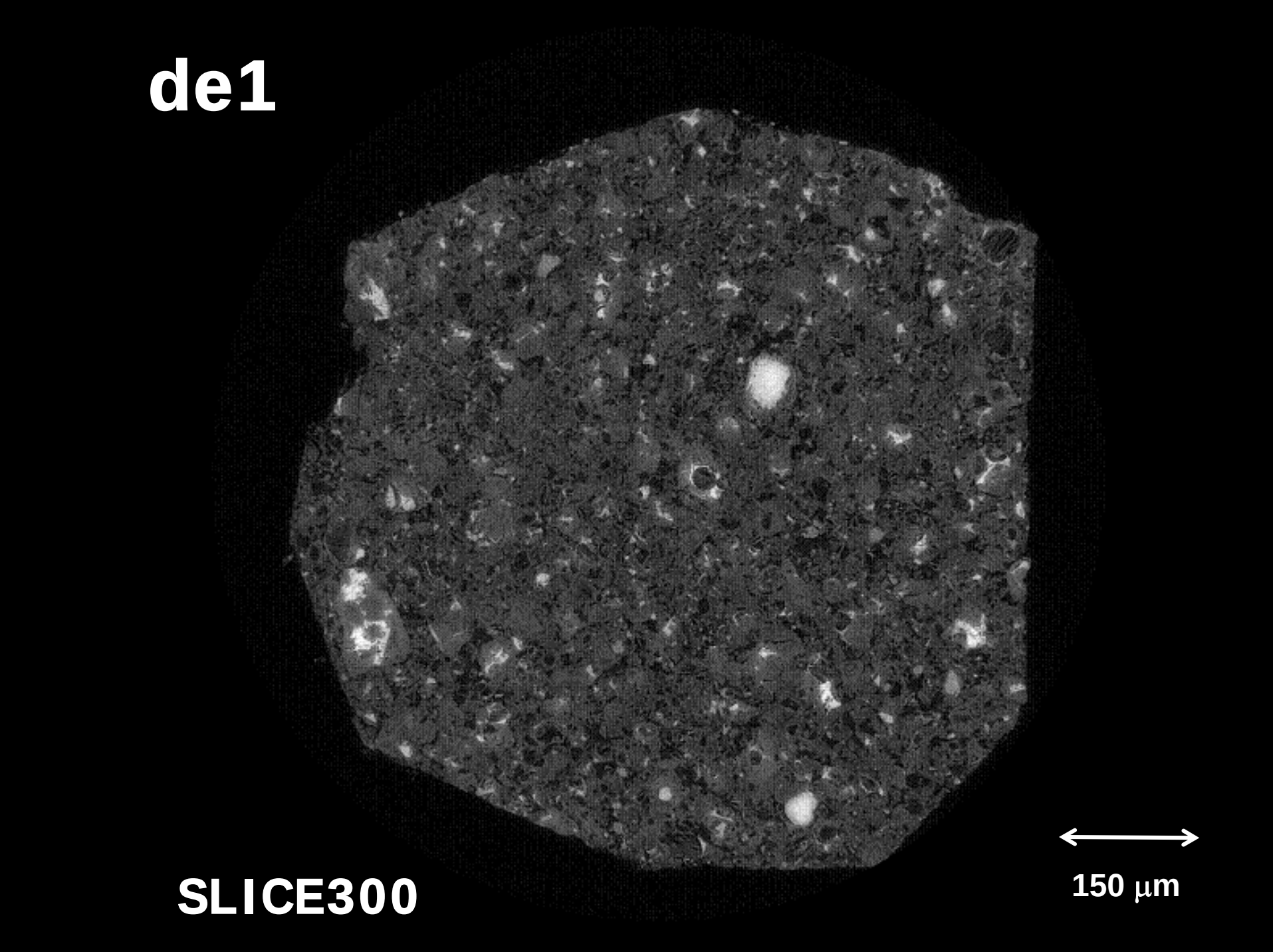
Cement paste: Profiles for Ca and Si

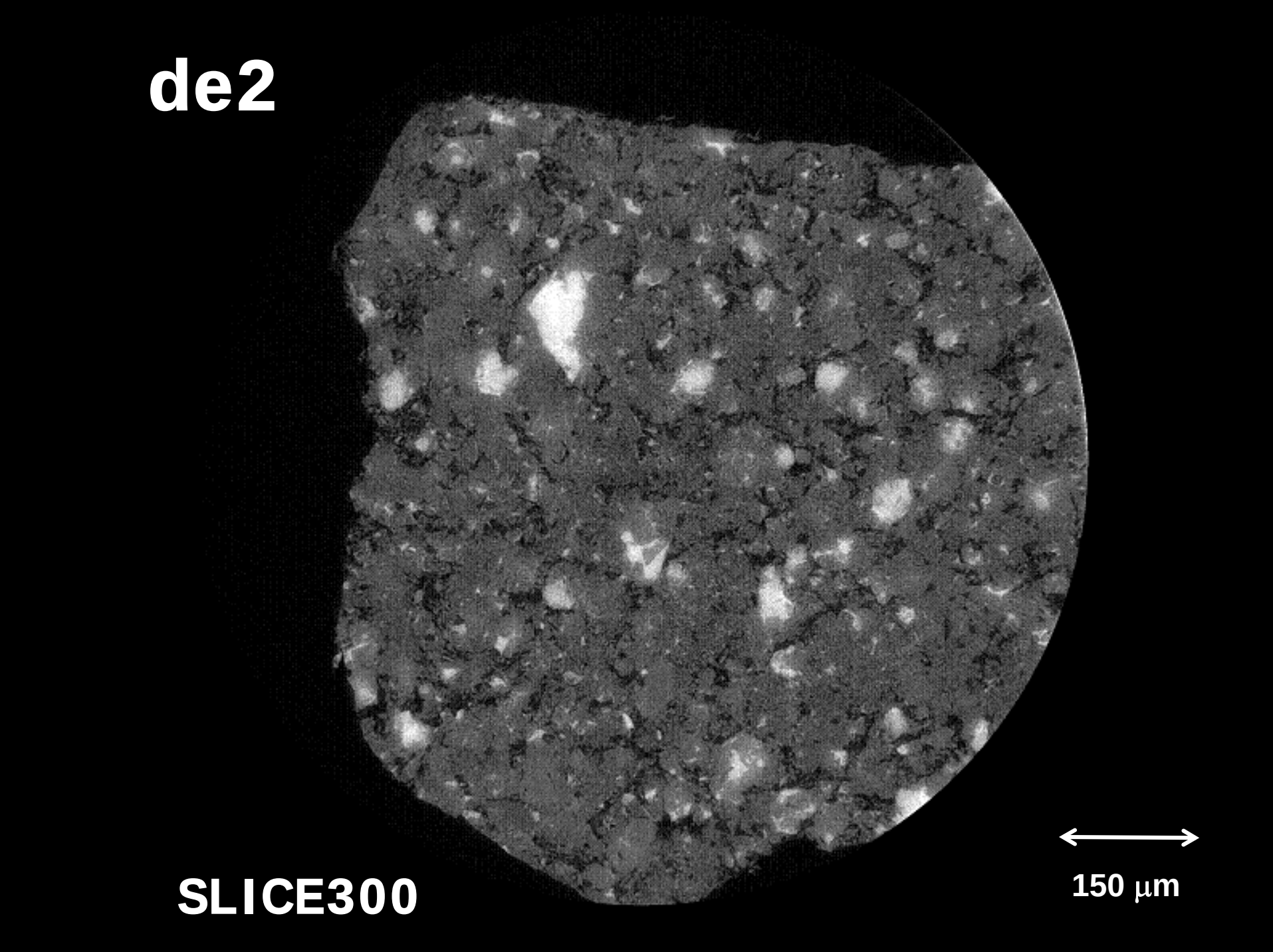


Sliced samples for X ray CT

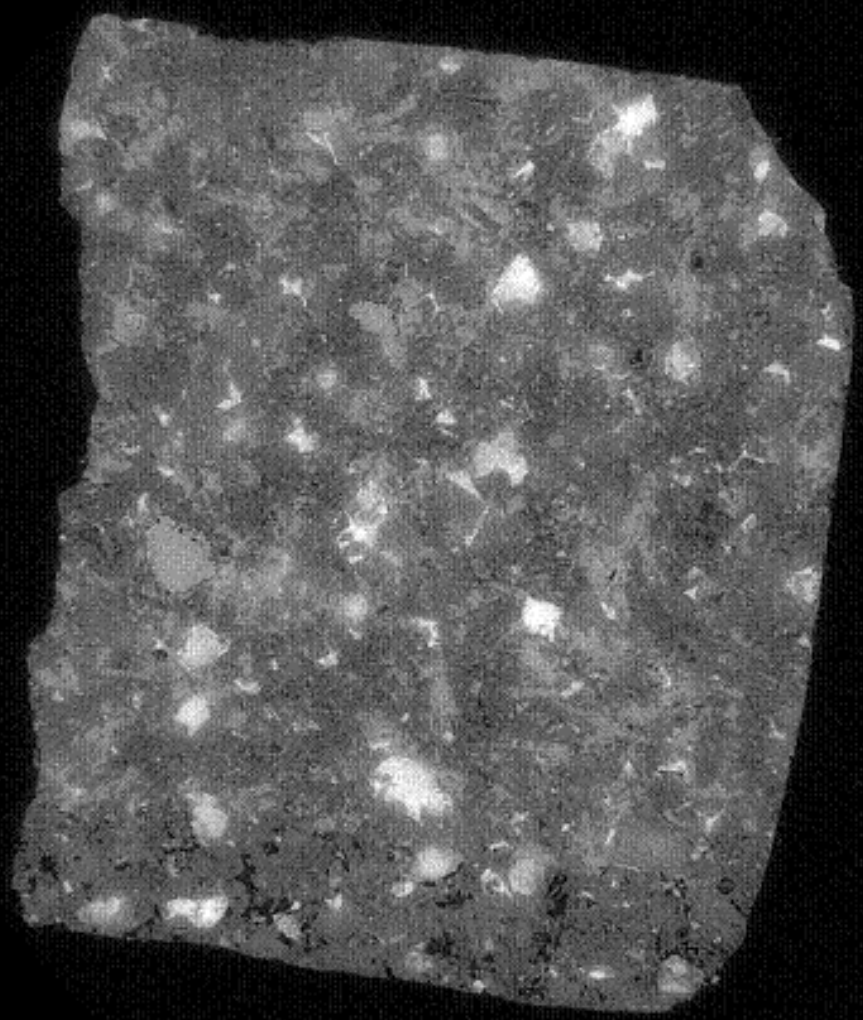





de1
SLICE300
150 μm

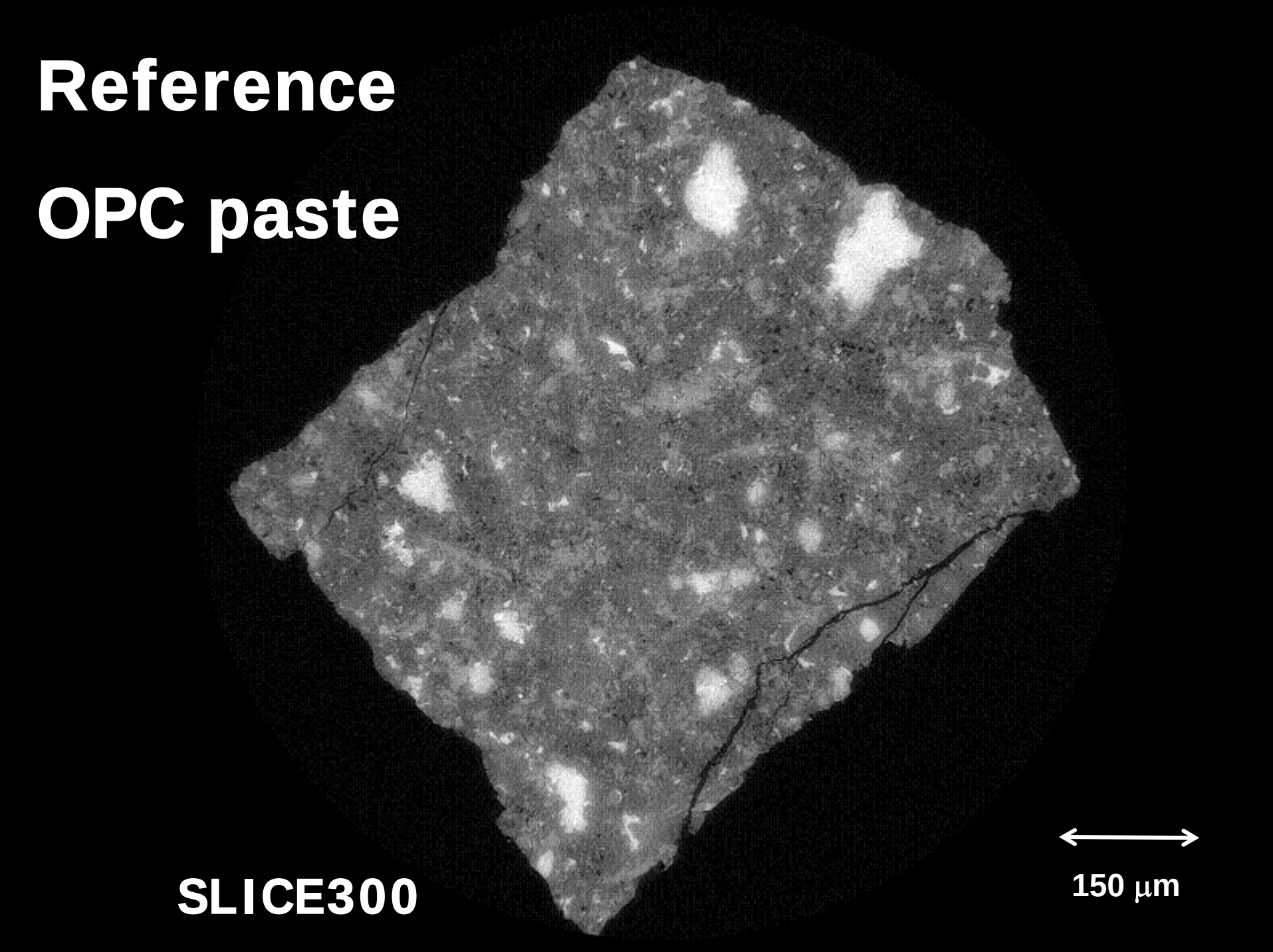

de2
SLICE300
150 μm

de3



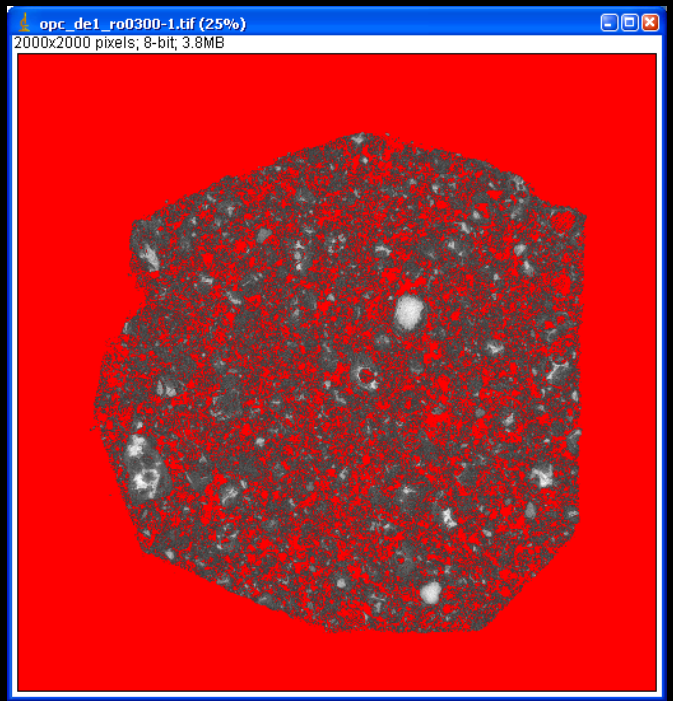
SLICE300

150 μm

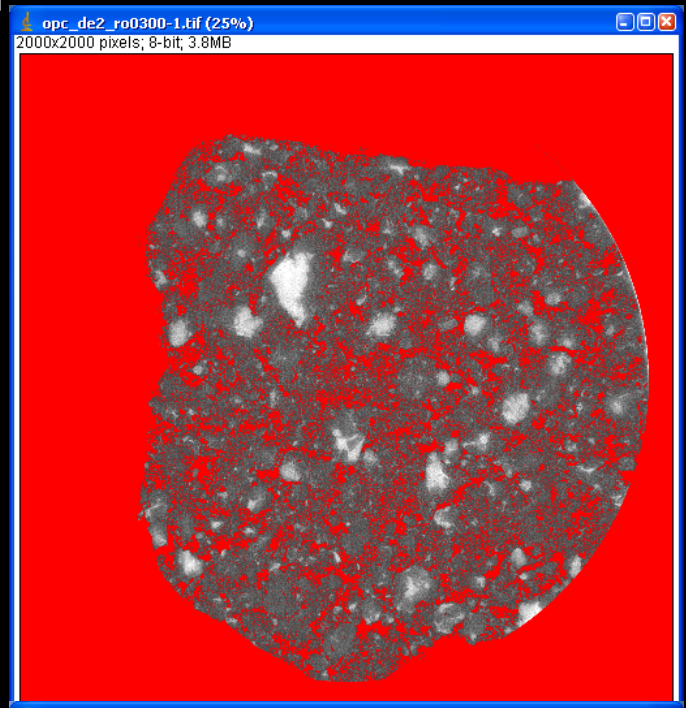

Reference
OPC paste
SLICE300
150 μm

Segmented pores

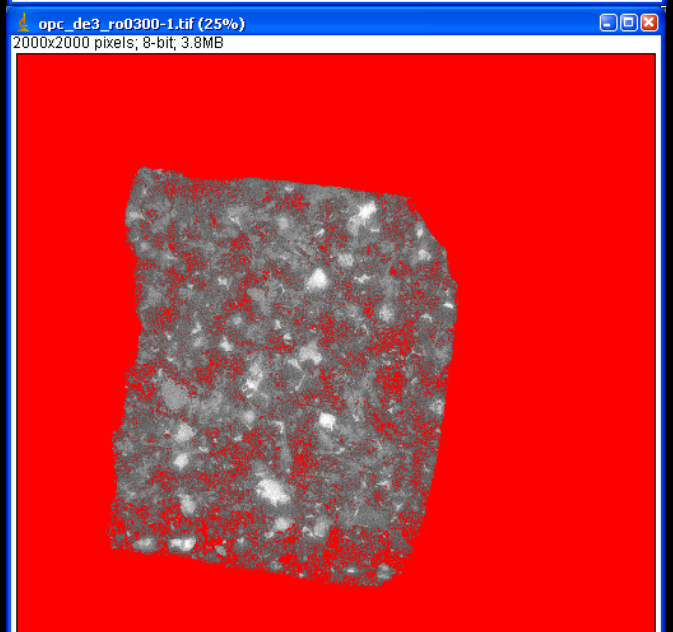
de1



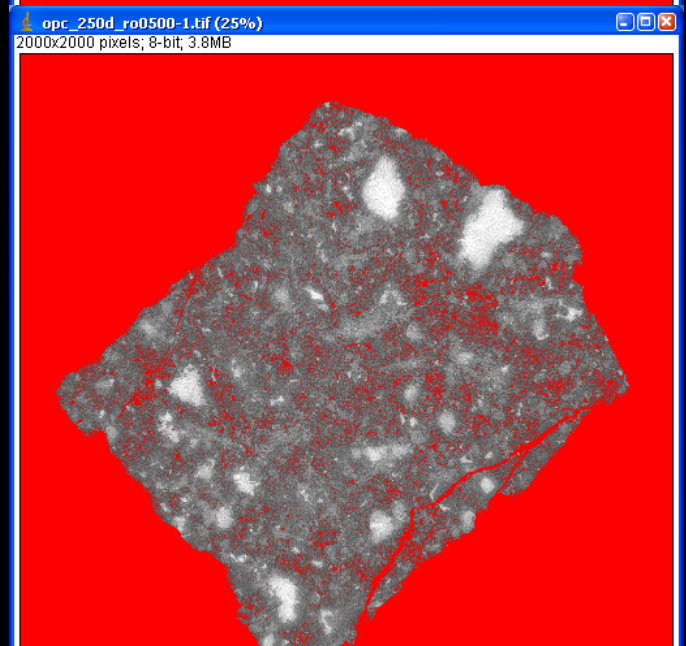
de2



de3

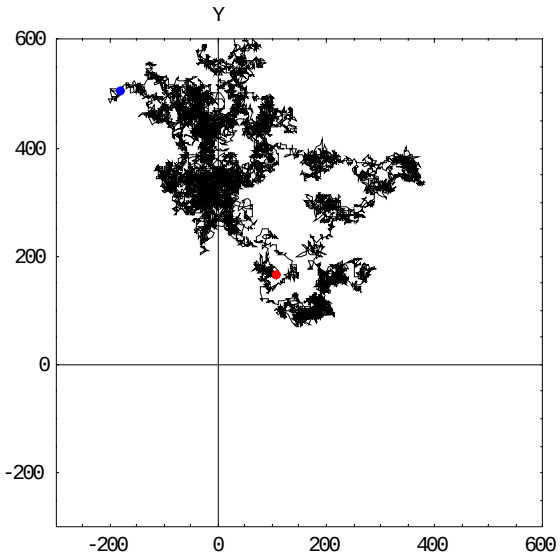


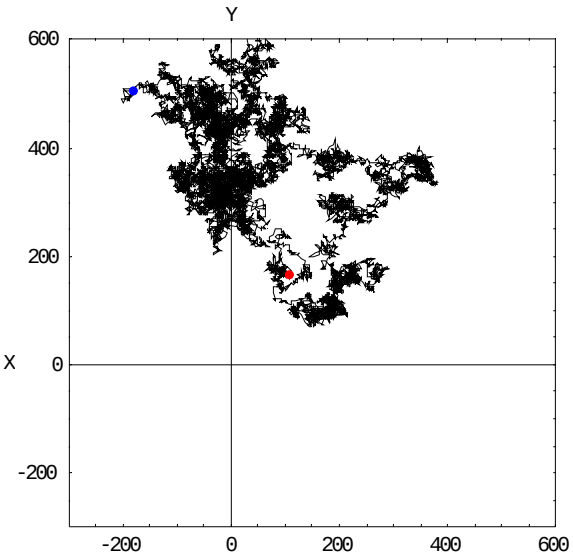
OPC

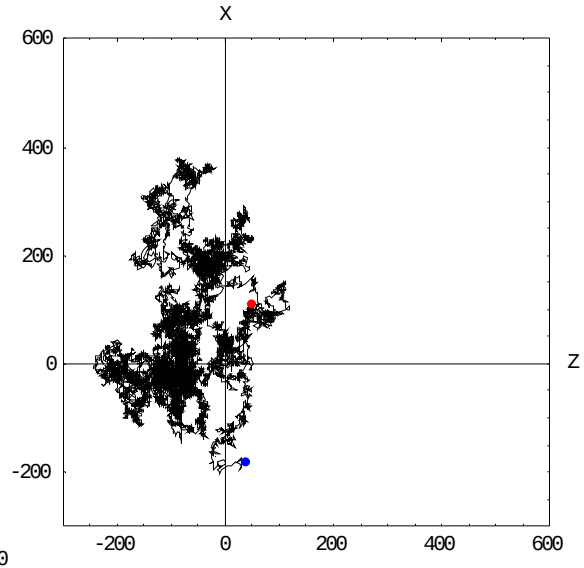


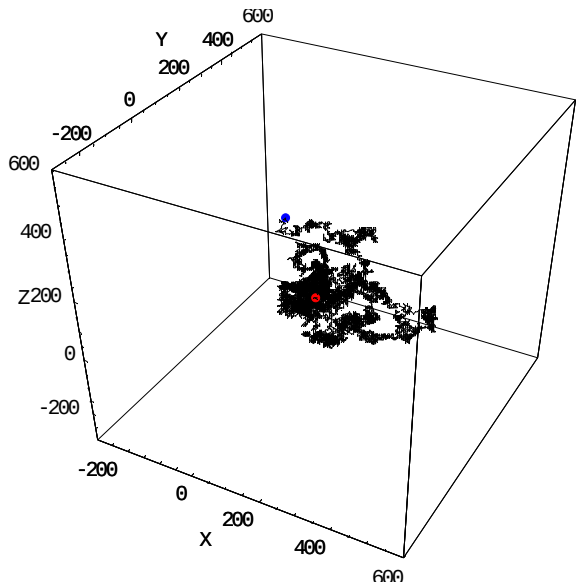
RWS de1

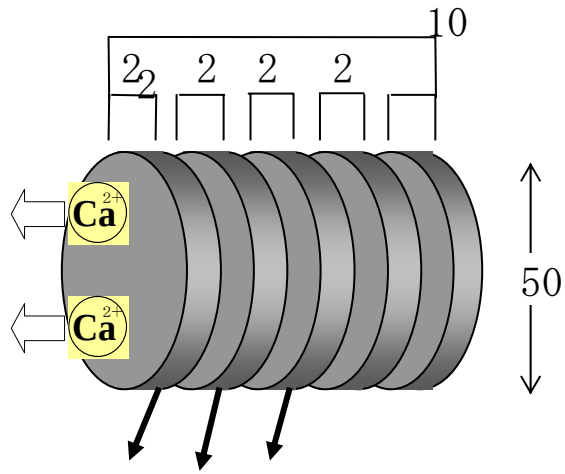
2 million time steps
50,000 walkers







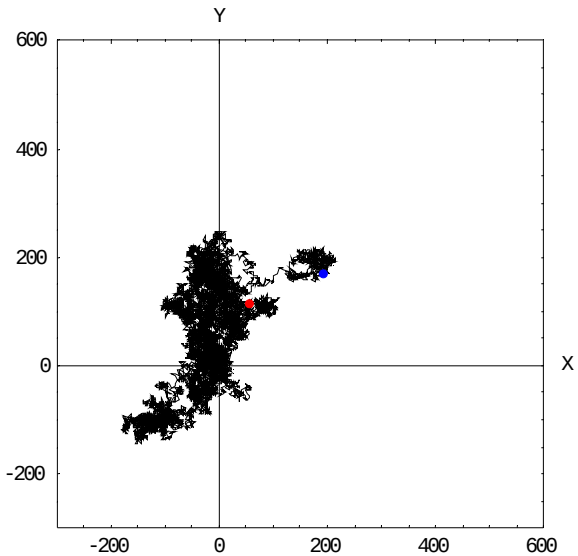


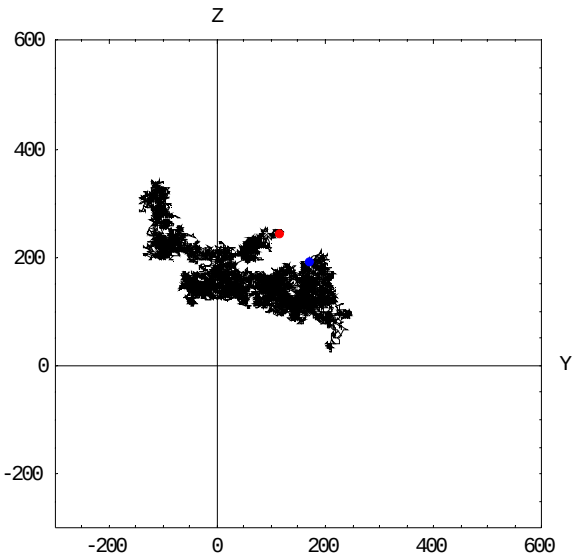


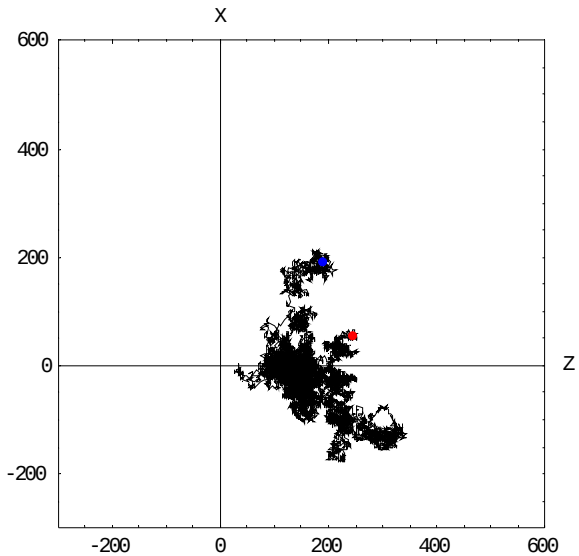
de1 de2 de3 unit : mm

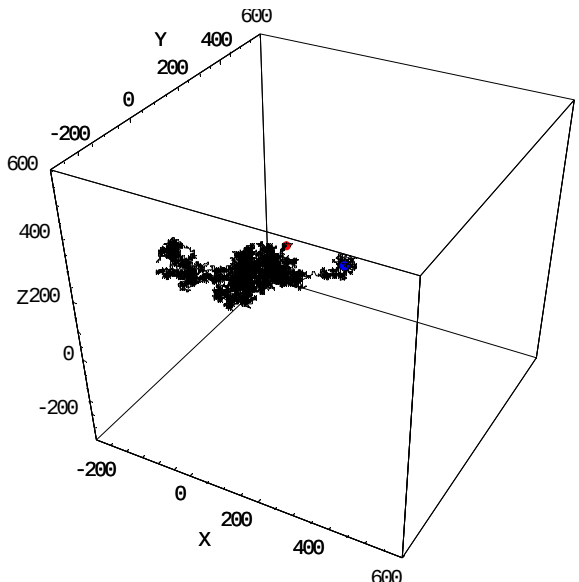
RWS de2

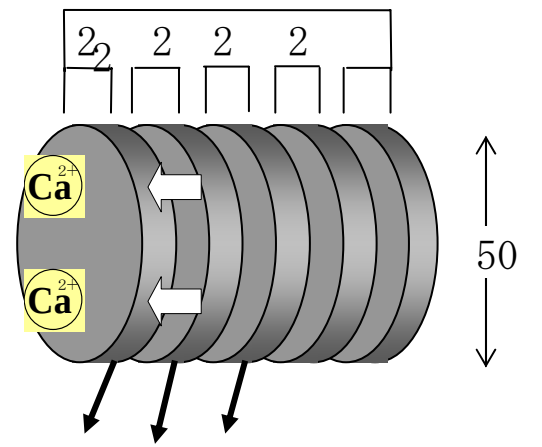
2 million time steps
50,000 walkers





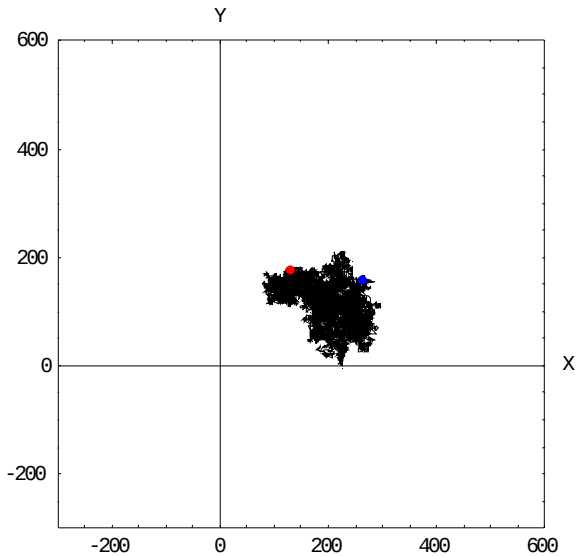


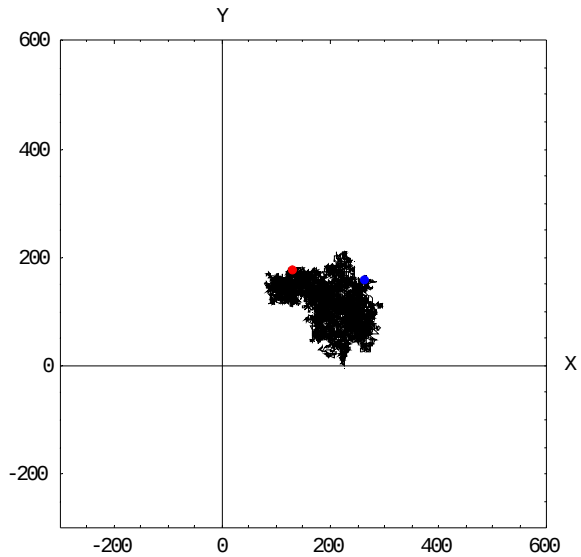


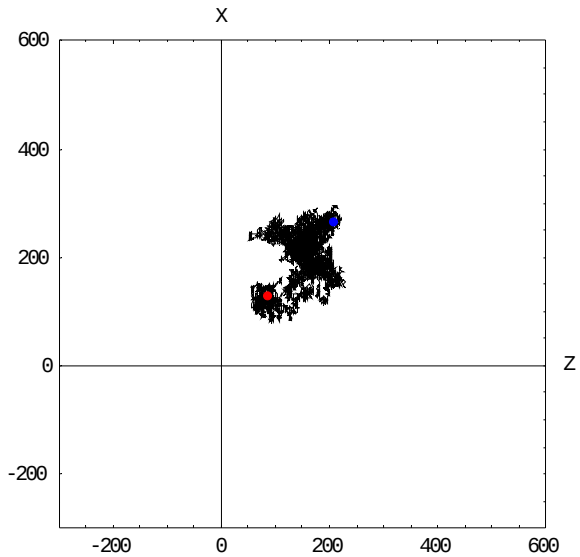


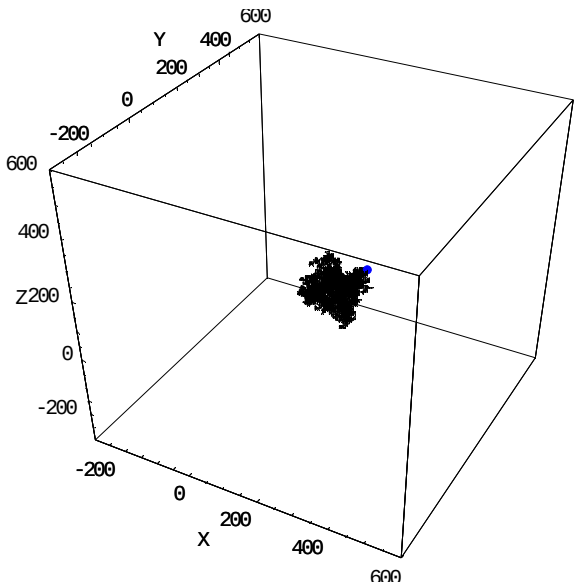
RWS de3

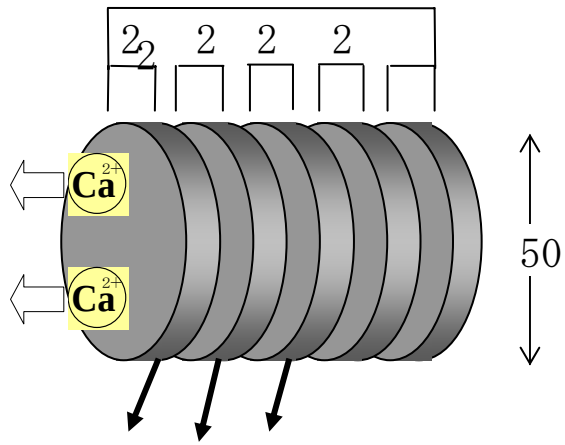
2 million time steps
50,000 walkers



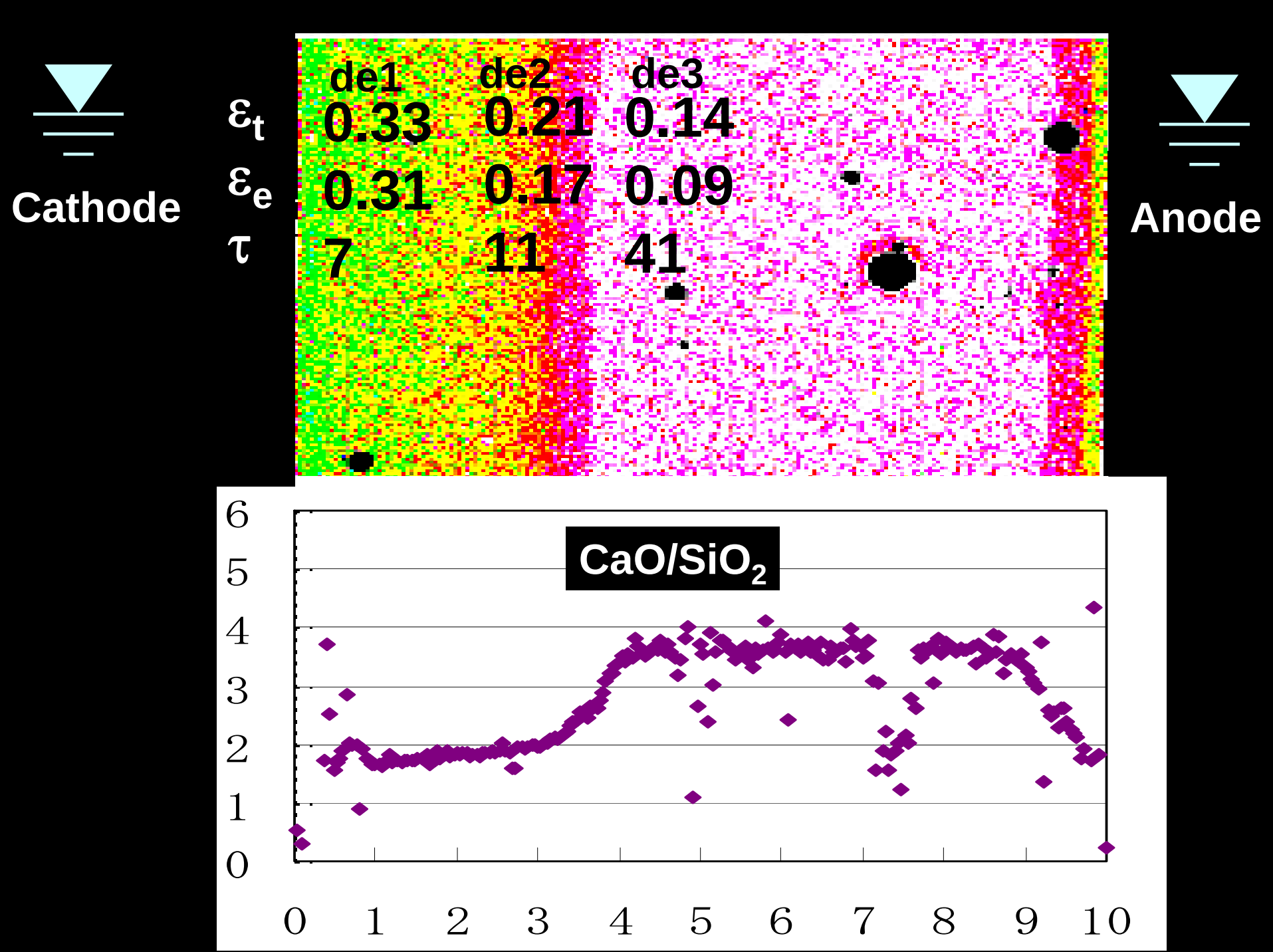


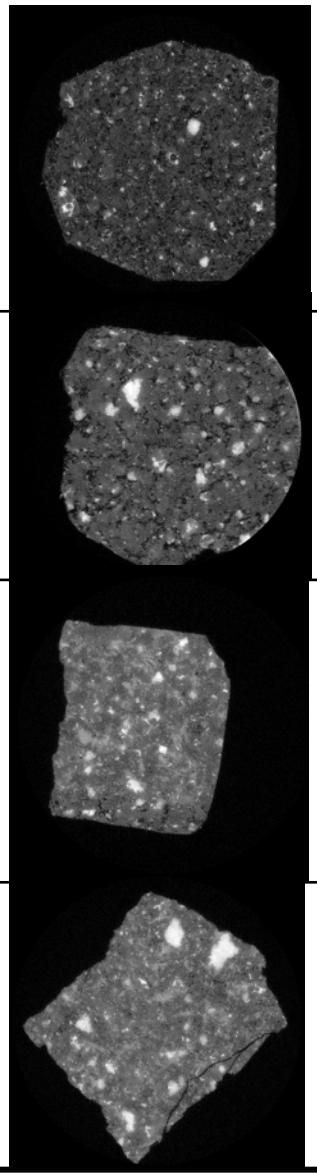






de1 de2 de3 unit : mm


Cathode
Anode
de1
de2
de3
ε_t
0.33
0.21
0.14
ε_e
0.31
0.17
0.09
τ
7
11
41
CaO/SiO2
0
1
2
3
4
5
6
0
1
2
3
4
5
6
7
8
9
10

	Segmented porosity, ε_t	Effective porosity, ε_e	Diffusion tortuosity, τ
	0.33	0.31	7
	0.21	0.17	11
	0.14	0.09	41
	0.09	0.02	n/a

Conclusions 1/2

(1) The Synchrotron Microtomography technique can provide better understanding of the microstructure change in deteriorated mortar and cement paste.

(2)The segmented porosity of the deteriorated mortar was increased by approximately ten times of that of non-deteriorated one. Especially the effective porosity was increased by approximately twenty times. The diffusion tortuosity was 4 for deteriorated mortar.

Conclusions 2/2

(3) For cement pastes as the CaO/SiO_2 ratio was reduced from 3.6 to 1.8 the effective porosity was increased from 0.14 to 0.33 while the diffusion tortuosity was reduced from 41 to 7.

(4) Potential applications to predict transport properties such as diffusivity and permeability are being considered.

Thank you for listening.

Acknowledgments

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