Australian Government

Australian Nuclear Science & Technology Organisation

Appraisal of a Cementitious Material for Waste Disposal: Neutron Imaging Studies of Pore Structure and Sorptivity

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ANSTO

NECSA

Aim

To characterise and to evaluate the durability, structural properties and sorptivity of a candidate wasteform for ILW and gain an understanding of the factors that control water movement through the matrix and the resultant degradation process.

Background

- *Australia has a small amount of low and intermediate level radioactive waste from medicine, research and industry.*
- *In addition, ILW from reprocessing of spent fuel will be returned from Dounreay as cement.*
- *In 2004, the Australian Government announced a plan to establish a nuclear waste facility by 2011.*
- *ANSTO has established a project to undertake research relevant to the safety case for the facility.*

Material

- *The samples tested simulated the Materials Testing Reactor (MTR) wasteform (AEA Technology in UK).*
- *Formulation of 9:1 ground granulated blast furnace slag to Ordinary Portland Cement (OPC).*
- *Waste liquor contained detectable amounts of some simulant fission products, although in much lower concentrations than normally encountered in typical MTR cement.*

Methodology

- ***Characterisation* of un-leached and leached cement – bulk solids composition; mineralogy; microstructure**
- ***Durability* testing of cement:**
  - ***previous studies* → long-term non-replacement tests**
  - ***current studies* → replacement tests (ANS 16.1)**
- ***Neutron imaging* (radiography and tomography):**
  - **residual water**
  - **sorptivity (comparison with ASTM gravimetry-based protocol)**
  - **pore size, volume and distribution**

Methodology

Characterisation (before and after leaching)

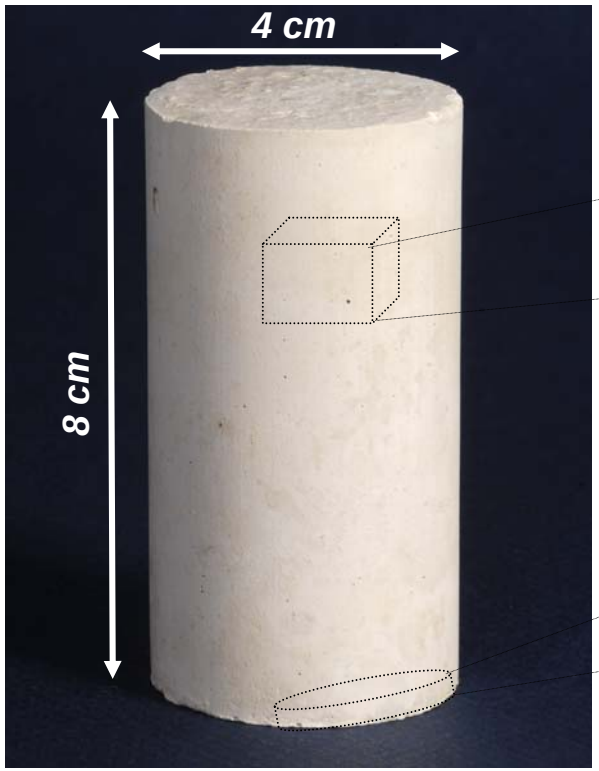
- Mineralogy – XRD
- Bulk solids elemental analysis – XRF
- LOI - TGA
- Microstructural and compositional changes of cement matrix (primary phase for waste encapsulation) - SEM/ EDS

Methodology

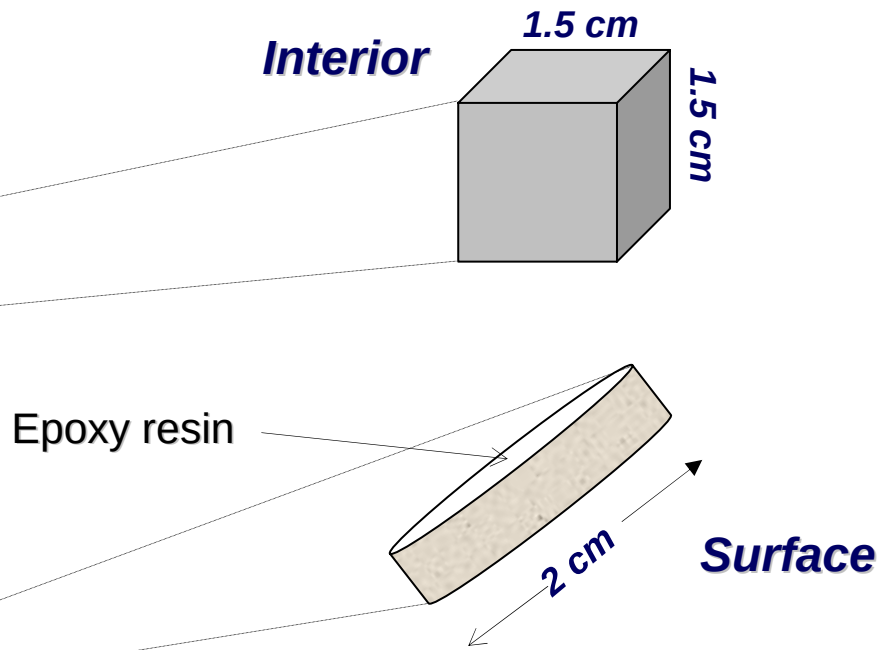
Durability testing

- ***Previous studies*** *- non-replacement in deionised water for 1, 3, 6 mths (40°C) and 92 months (first 12 months at 40°C, thereafter RT); SA/V = 0.03 mm^{-1}; whole specimens*
- ***Current studies*** *– ANS 16.1 - leachate replacement (deionised water at RT) – 2 h to 90 d; SA/V = 0.01mm^{-1} ; sections of interior matrix and surface layer*
- *Leachate analysis – ICP-MS and ICP-AES for Na, Mg, Al, Si, S, K, Ca, Ti, Mn, Fe, Sr, Zr and Ba*

Previous durability studies



Current durability studies (ANS 16.1)



NB: Same SA:V ratio (0.01 mm^{-1}) for interior and surface samples

Methodology

Sorptivity testing

- Samples enclosed in Al tape with only the base exposed, facilitating water transport in one direction only (upwards).
- Base continuously immersed in water - adsorption measured over periods of 1, 2, 4, 6, 9, 12, 16, 20 and 25 minutes (up to a month where possible).
- At the end of each time interval the samples were removed from the water, weighed and then transferred to the Nrad facility to collect 2-D radiographic data and chart water ingress.
- Water contents were computed from the image.
- At the end of the final acquisition period a 3-D tomography was carried out on the specimens to construct macro-pore distributions.

Methodology

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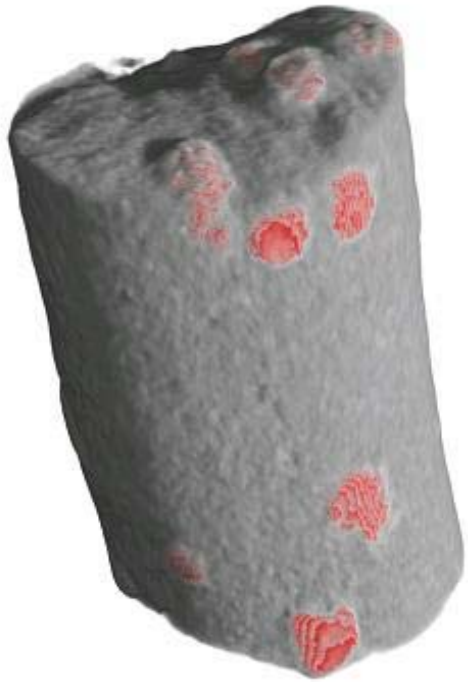
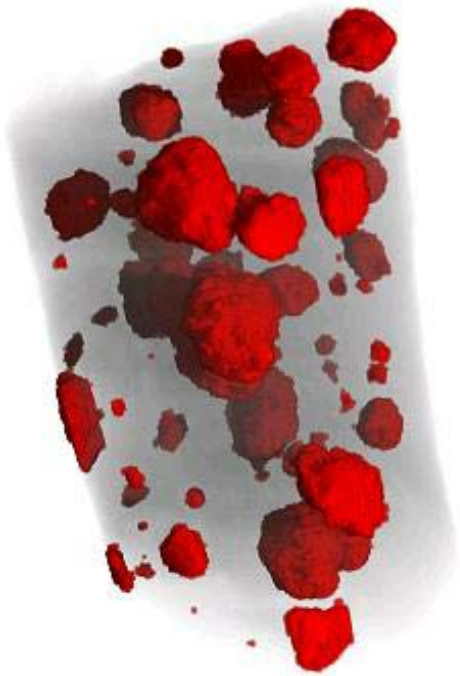
Methodology

Neutron Imaging

- *Penetrating; complementary to X-ray and gamma radiography.*
- *Require strong, stationary, n sources for good beam collimation and for a high spatial resolution ⇒ reactor or accelerator based.*
- *For Ntom, require fixed beam line, stationary detector, and rotating turntable for sample.*
- *Advantage over X-rays is their high interaction probability with H and lower attenuation in several heavy elements.*

SANDSTONE FROM LIVERINGA GROUP





Neutron Tomograph

Red is high neutron attenuation
Red indicates very high H conc.

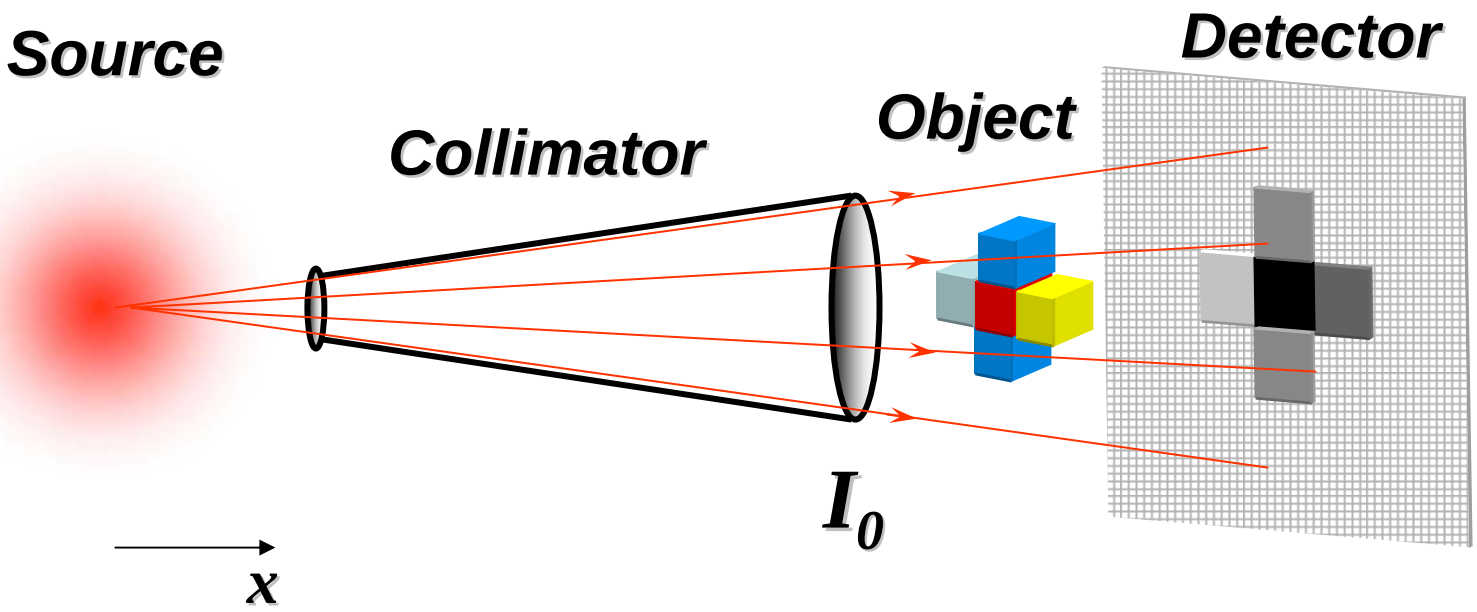
Image has had low attenuation regions subtracted

X-ray Tomography

Left: Tomograph of core surface
Right: 3D perspective with low X-ray attenuating material subtracted
Red indicates zones of high density

NOTE: X-RAY IMAGE SHOULD REPRESENT THE OPPOSITE TO NEUTRON IMAGE.
THUS: Neutron "sees" hydrocarbon; X-ray "sees" matrix

Principle of Conventional Radiography

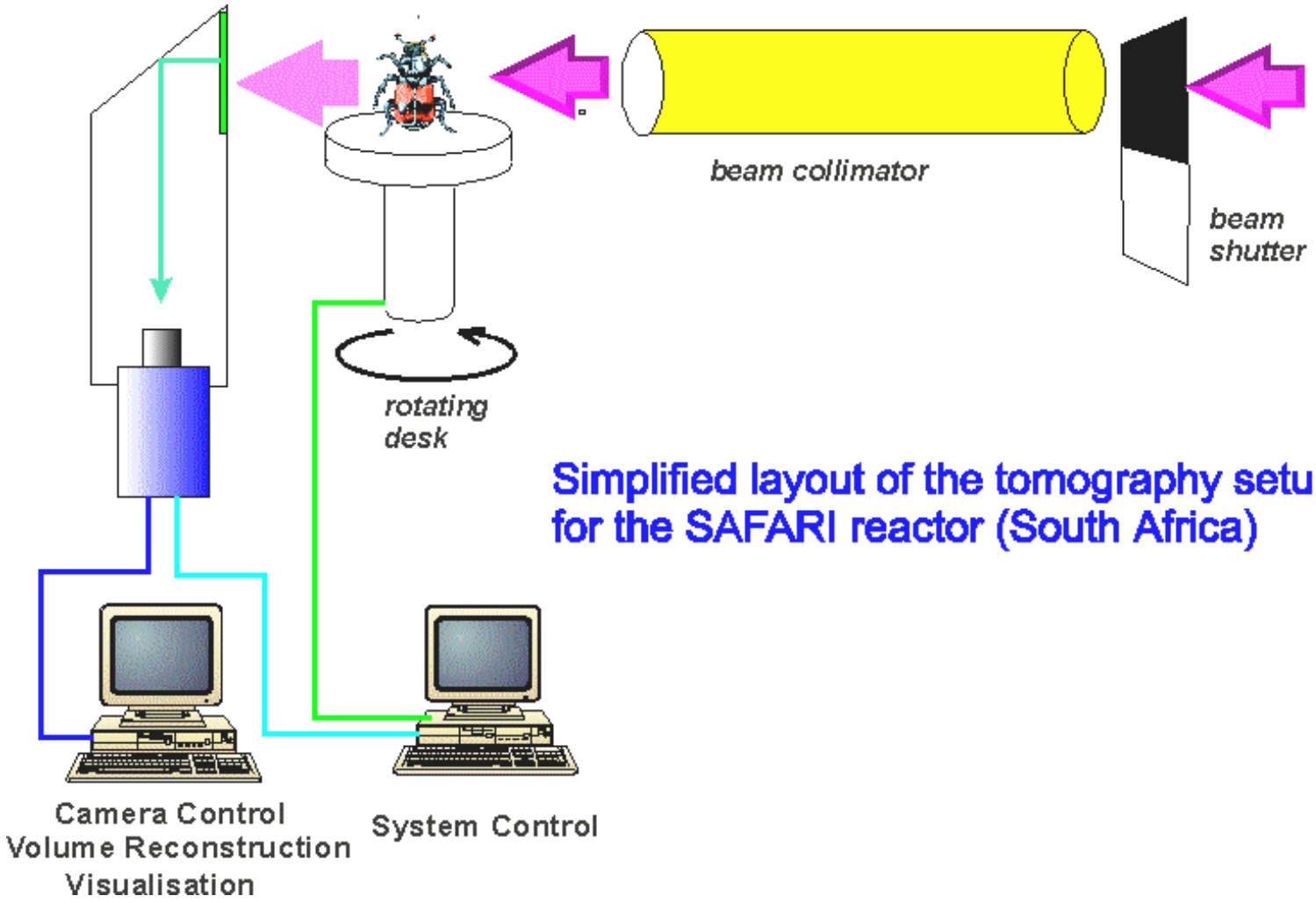


$$\sim I_0 e^{-\int \Sigma(x)dx}$$

x – propagation direction

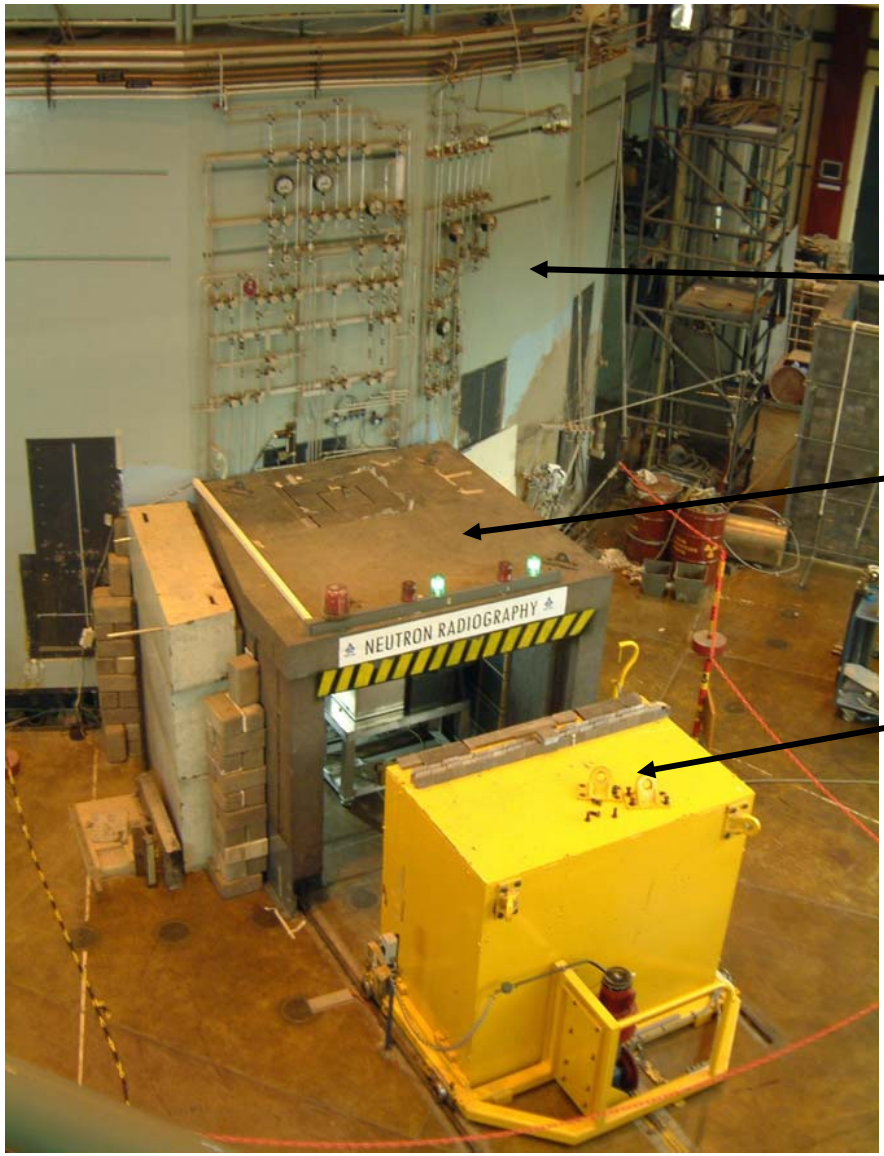
I_0 – primary beam

$\Sigma(x)$ – attenuation coefficient



Simplified layout of the tomography setup for the SAFARI reactor (South Africa)

Beam line 2 : Neutron Radiography



SAFARI-1 reactor wall

Shielding

Beam stop/ door

Methodology

Application of Nrad/ Ntom

- *Neutrons - transmit thick layers of material samples such as cements/ concretes.*
- *Can neutron radiography be used to interpret sorptivity in cement?*
- *How do the data compare with the traditional ASTM procedure?*
- *Where can neutron radiography and tomography be applied that offer advantages over other cement characterisation techniques?*
  - » *Water loss determination*
  - » *Pore distribution*
  - » *Sorptivity determination*

Results

XRF - average bulk solids elemental concentrations (wt%) of whole, interior and surface (on pressed powders)

Element	Na	Mg	Al	Si	S	K	Ca	Ti	Fe	Sr
Whole	4.0	2.4	5.1	9.9	0.6	0.3	22.1	0.3	0.4	0.04
Interior	3.6	2.5	5.1	10.0	0.6	0.3	22.2	0.3	0.4	0.04
Surface	5.6	2.3	5.1	9.6	0.3	0.4	20.3	0.3	0.4	0.04

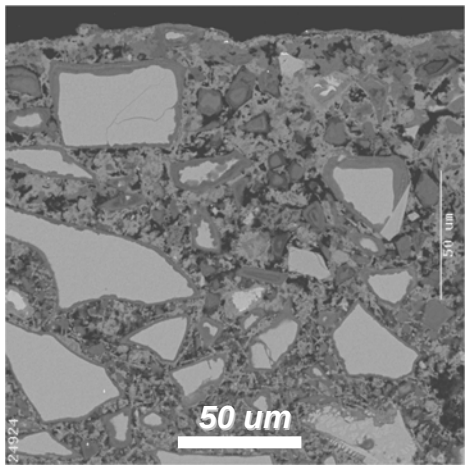
Unleached

After 92 months

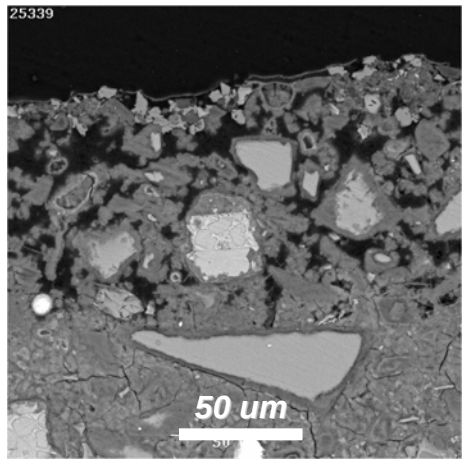
NB: These samples used in the neutron imaging and sorptivity studies

SEM/ EDS

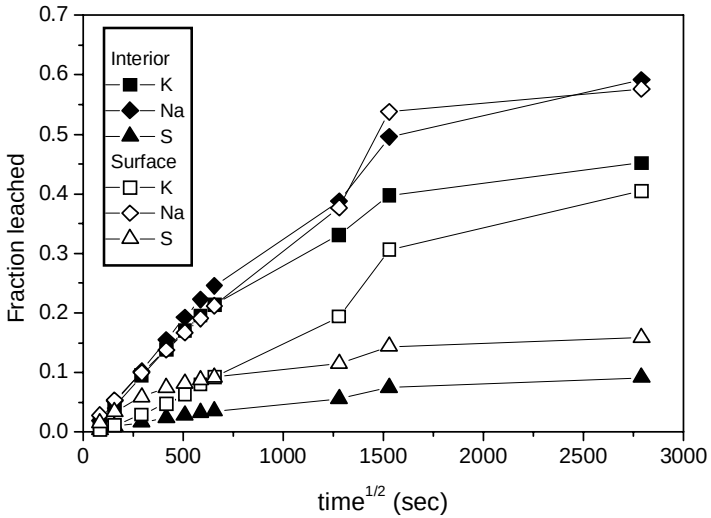
Unleached

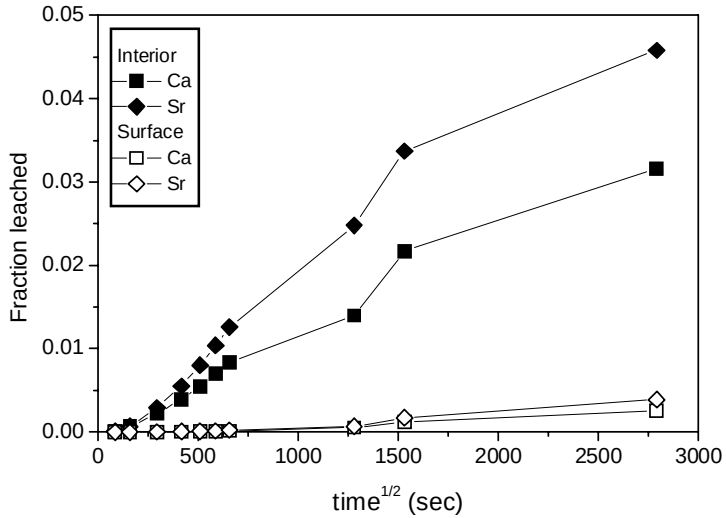


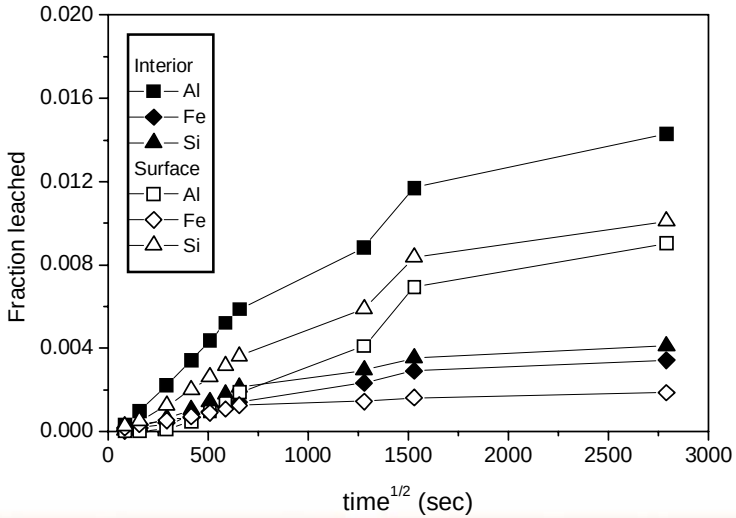
Leached for 92 months

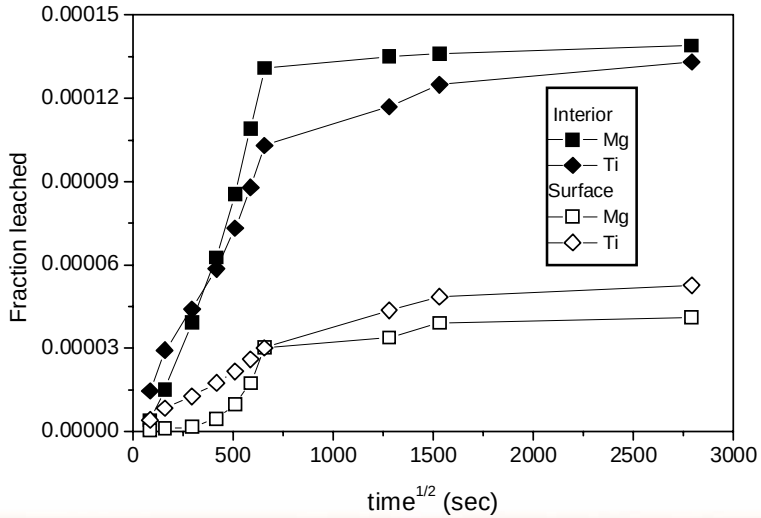


Leach results – current studies (replacement leachate)









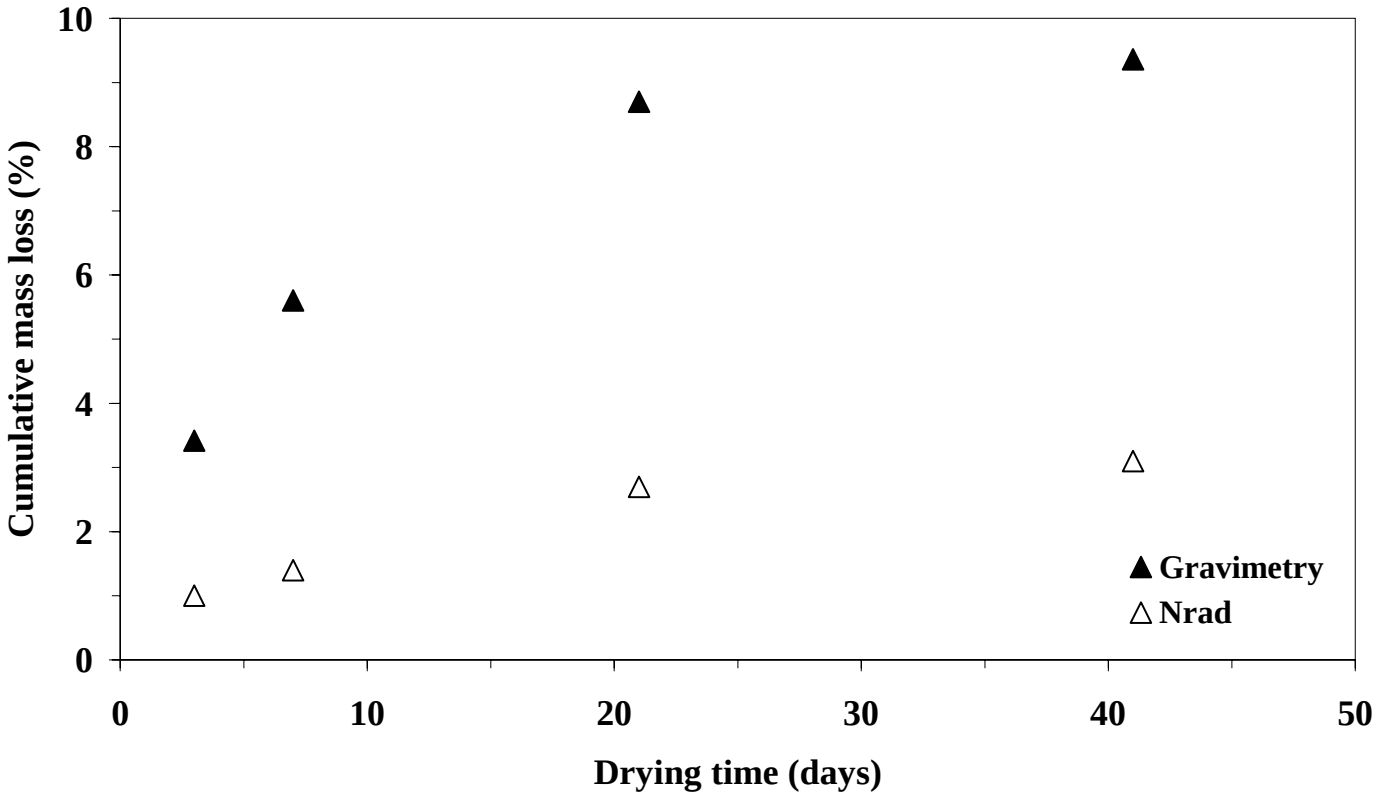
Summary of durability tests

- *Fractional releases of K, Na, S and Fe similar for interior and surface samples over total 90 day leach period.*
- *Al, Mg and Ti within a factor of 3 higher, and Si within a factor of 3 lower, from the interior samples.*
- *Ca and Sr - factor of 12 lower from the surface samples than from the interior.*
- *Materials in the surface samples that bind Ca and Sr not present in the interior sample?*
- *Investigated further by Nrad in attempt to determine any structural or water transmission differences between surface layer and underlying matrix.*

Results - Neutron imaging

- **Residual water determination**
- **Sorptivity:**
  - » **Gravimetry (ASTM C1585-04)**
  - » **Nrad**
  - » **Comparison with OPC**
- **2D imaging (Nrad):**
  - » **Water front progression**
- **3D imaging (Ntom):**
  - » **Macro-pore distribution**
  - » **Constructed tomograms**

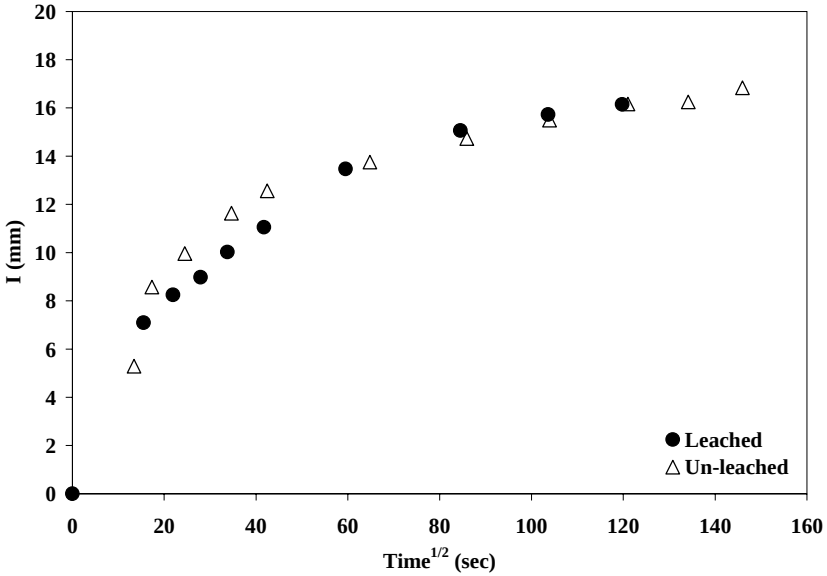
Residual water determinations



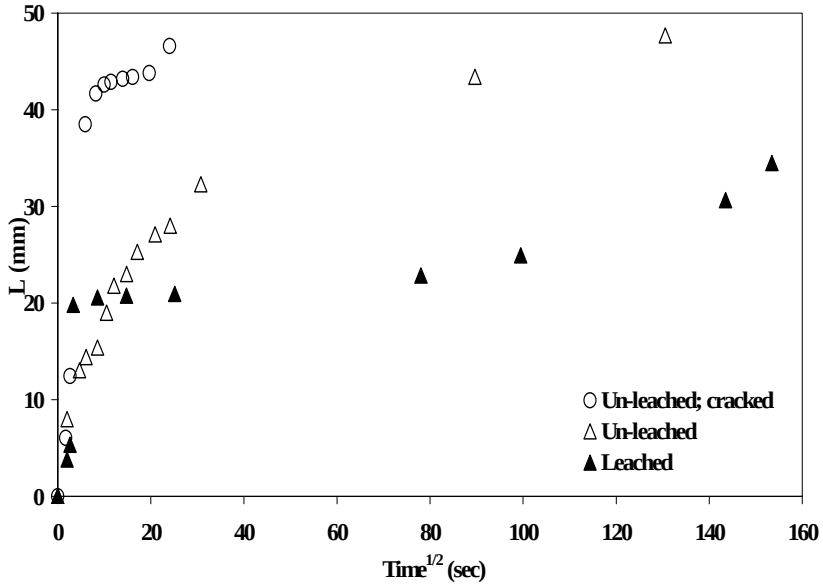
- *Un-leached cement as determined by gravimetry and Nrad*
- *Specimens dried at 50℃ to constant weight*
- *Difference between gravimetry and Nrad due to multiple neutron scattering effect by water (Hassanein et al – correction factor 2 to 2.5)*

Sorptivity – Gravimetry (ASTM) and Nrad

Gravimetry



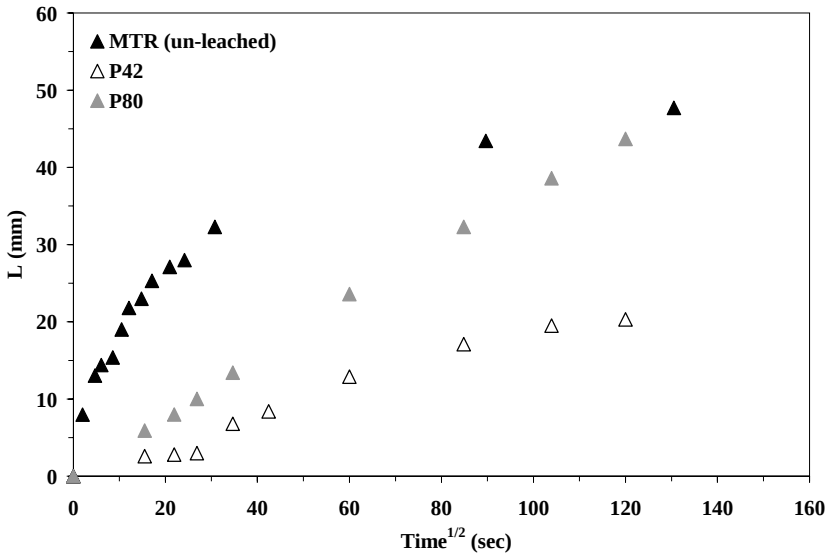
Nrad



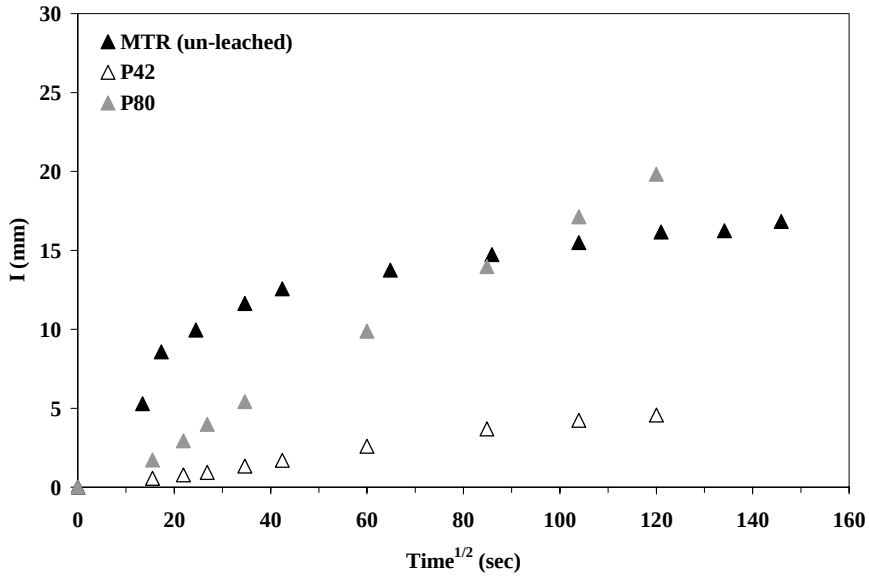
- I and L labels to distinguish between derived values obtained directly (ASTM procedure) and those calculated from a pixel intensity using Nrad.
- Nrad a factor >3 for the *un-leached* cement than gravimetric calculated value, and a factor >2 for the *leached* cement than gravimetric measurement.
- Gravimetric determinations of water movement appear to underestimate the true value.

Sorptivity – MTR and OPC (Nrad vs Gravimetry)

Nrad

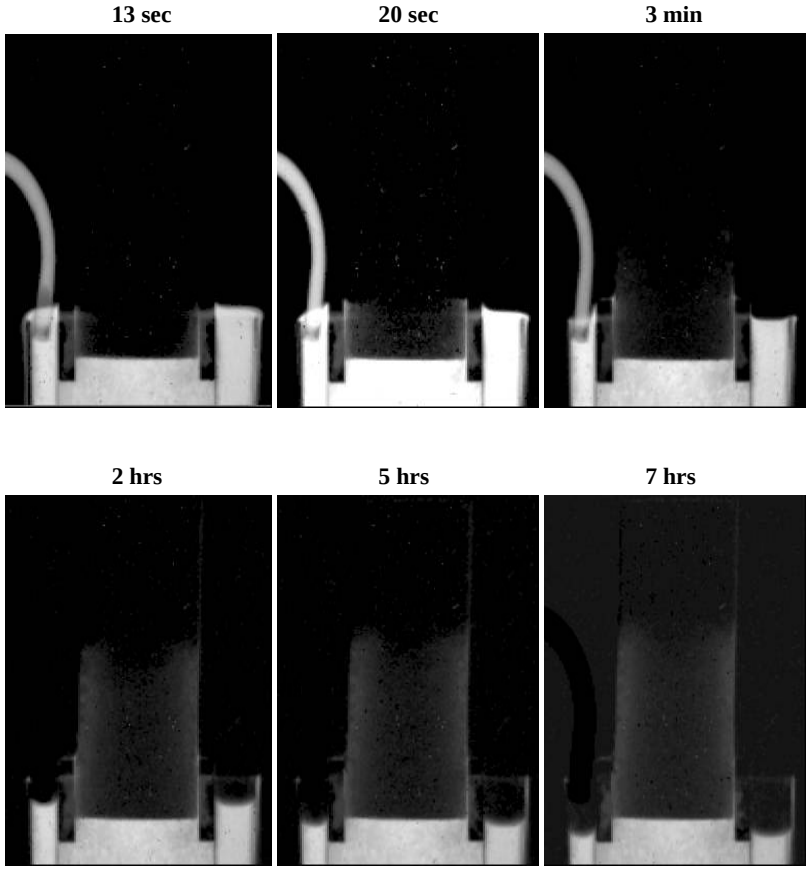


Gravimetry

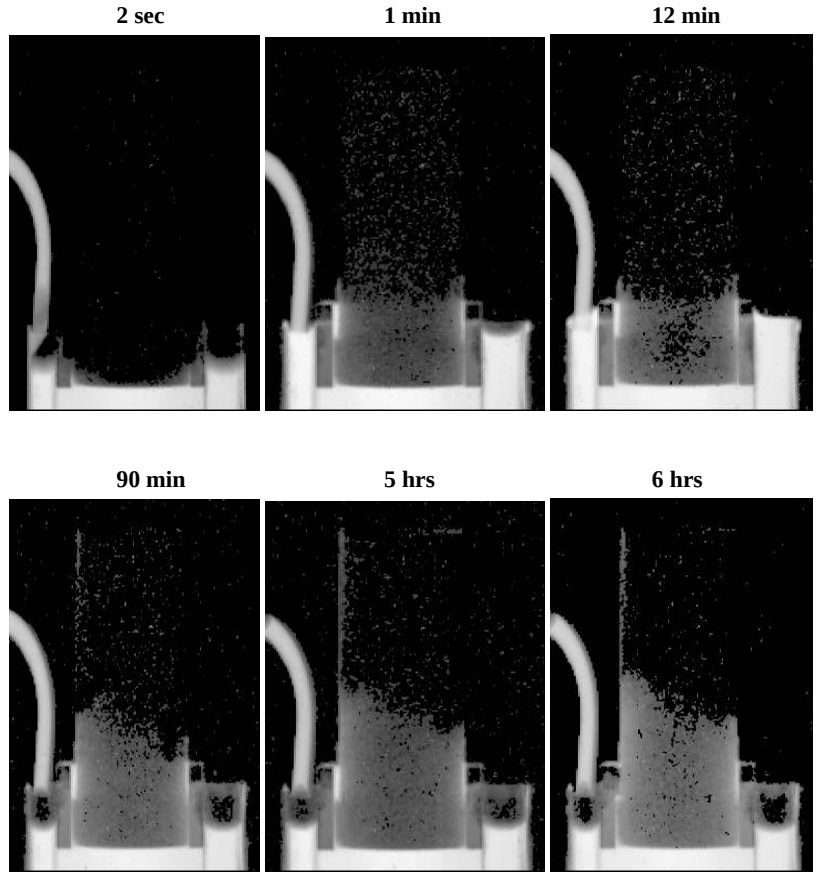


- MTR cement has a higher rate of sorptivity than both the OPC samples, although is similar to the OPC with a w/c of 0.8 after about 4 hours.
- Short-term sorptivity rate higher for MTR.
- Gravimetric values typically lower ⇒ NRad measures actual position and ASTM method calculates the value of water movement.

Water front movement (Nrad)



Un-leached



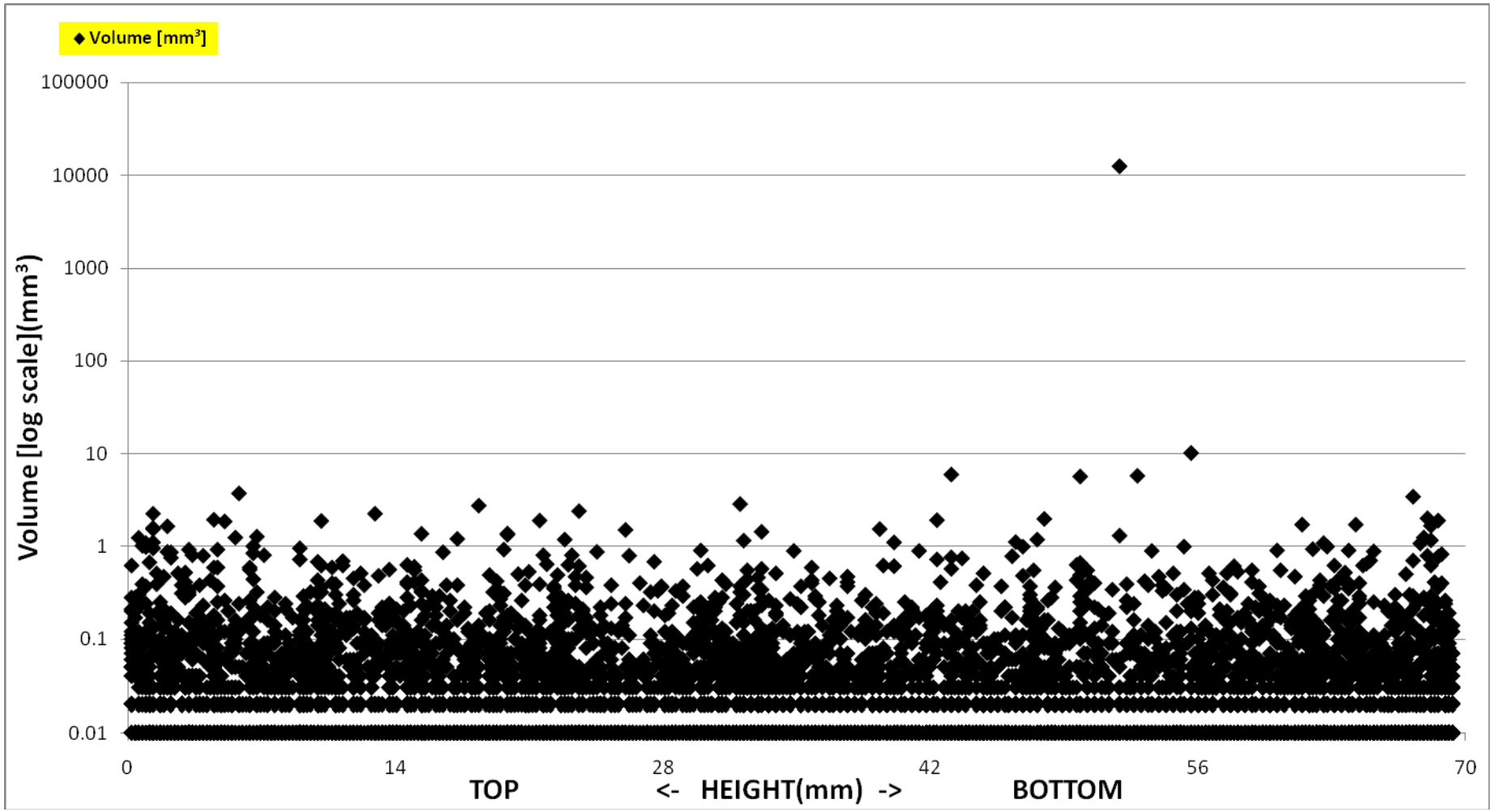
Leached (92 months)

Water front movement (Nrad) - Summary

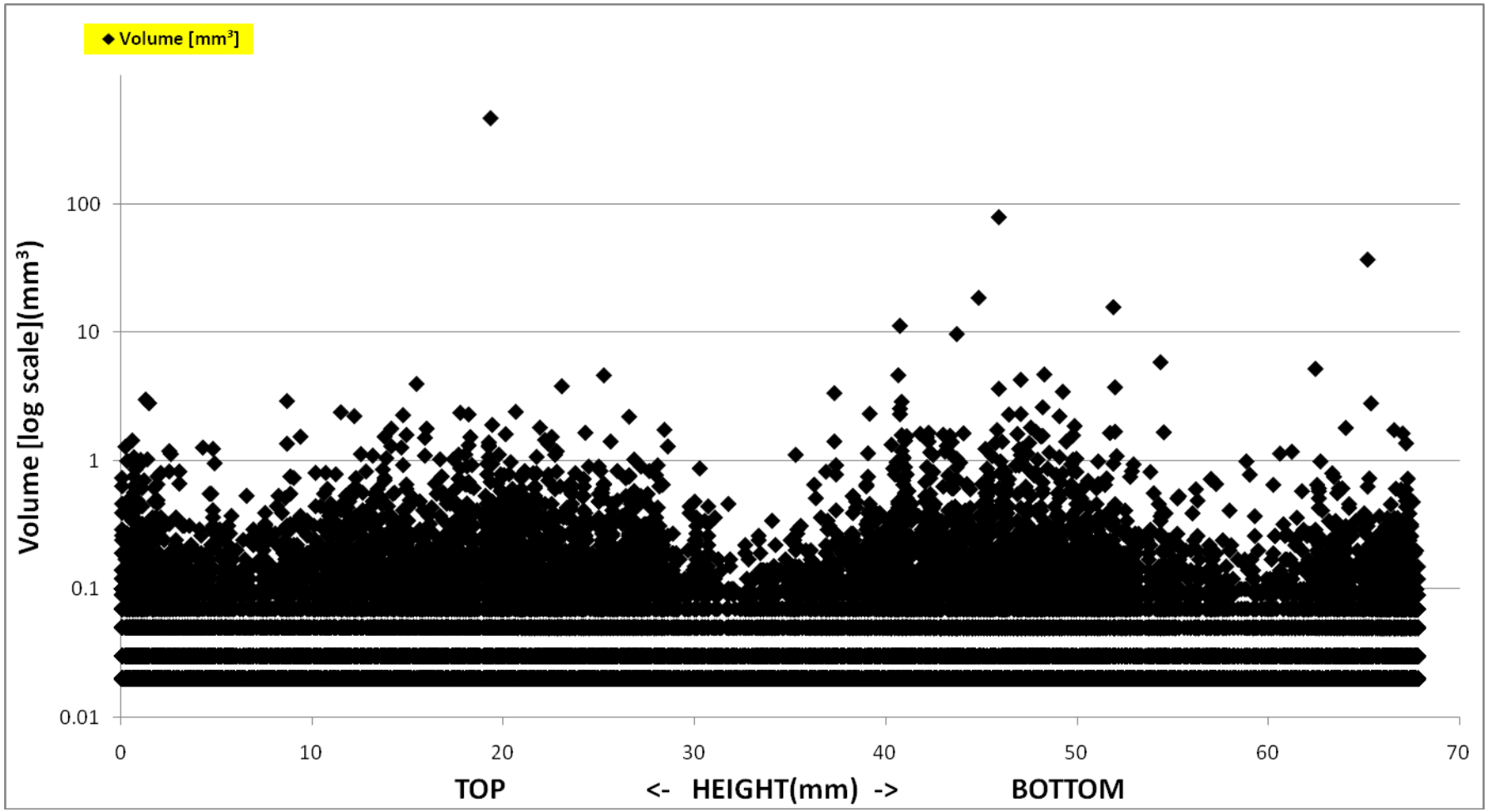
- *Analyses of the un-leached and leached cement verify the sorptivity calculations ⇒ un-leached cement visually has a greater sorptivity rate than leached sample.*
- *Nrad results could not highlight any significant differences in the rate of water movement between the surface layer and the interior of the sample.*
- *Resolving any differential in sorptivity between the thin surface layer and the underlying matrix difficult due to the fine scale (<1 mm) and the relatively rapid water movement through the cement.*

3D Imaging – Neutron Tomography

Macro-pore volume distribution as a function of depth within the un-leached cement sample



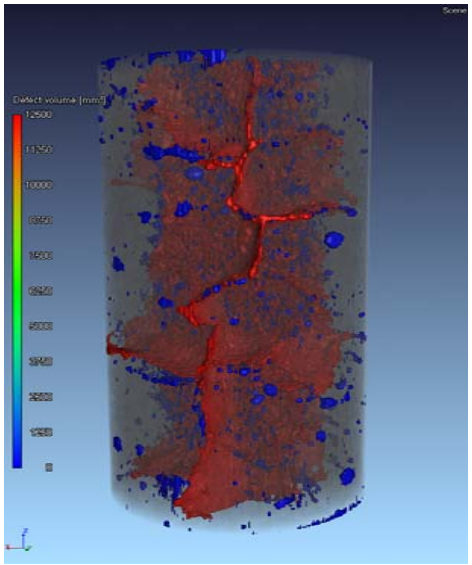
Macro-pore volume distribution as a function of depth within the leached cement sample

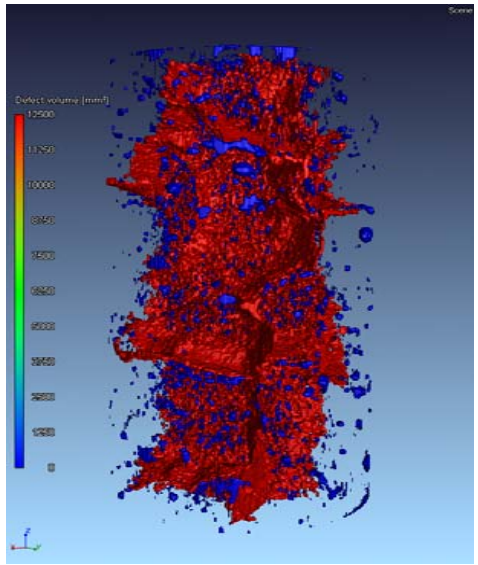


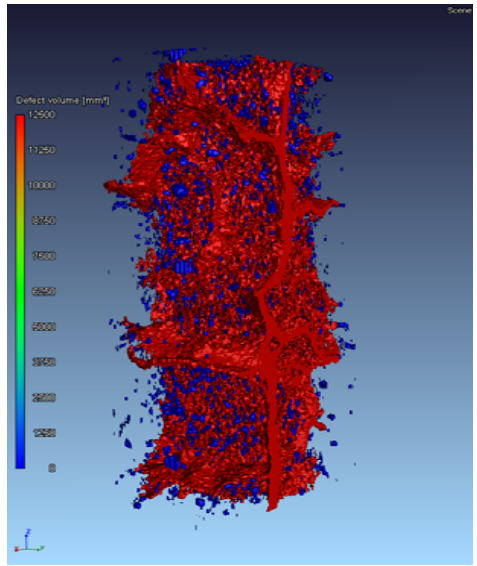
3D Macro-pore analysis - Summary

- *Macro-pore size distribution in both the un-leached and leached cement samples between 0.01 and 1 mm^3.*
- *Un-leached sample - 88% of pores have a volume < 0.1 mm^3, whilst for the leached sample 95% of the pores have a volume < 0.1 mm^3.*
- *The leached cement has a higher density of smaller pores throughout its entire length.*
- *Macro-pore distribution is reasonably even in both samples showing that matrix segregation not significant.*
- *Ntom - useful information on the position and density of the pores showing that they may contribute to water transmission.*

Neutron Tomograms – Un-leached and Leached Cement

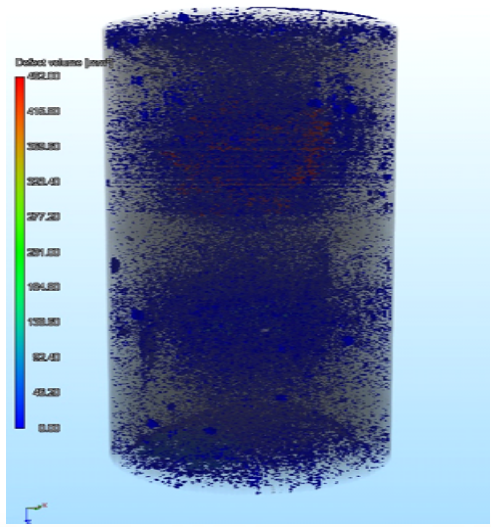


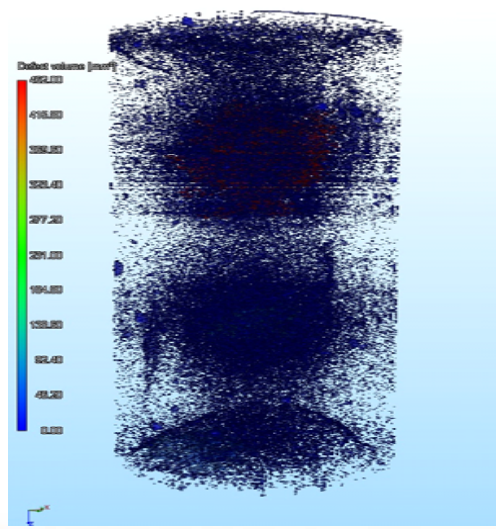




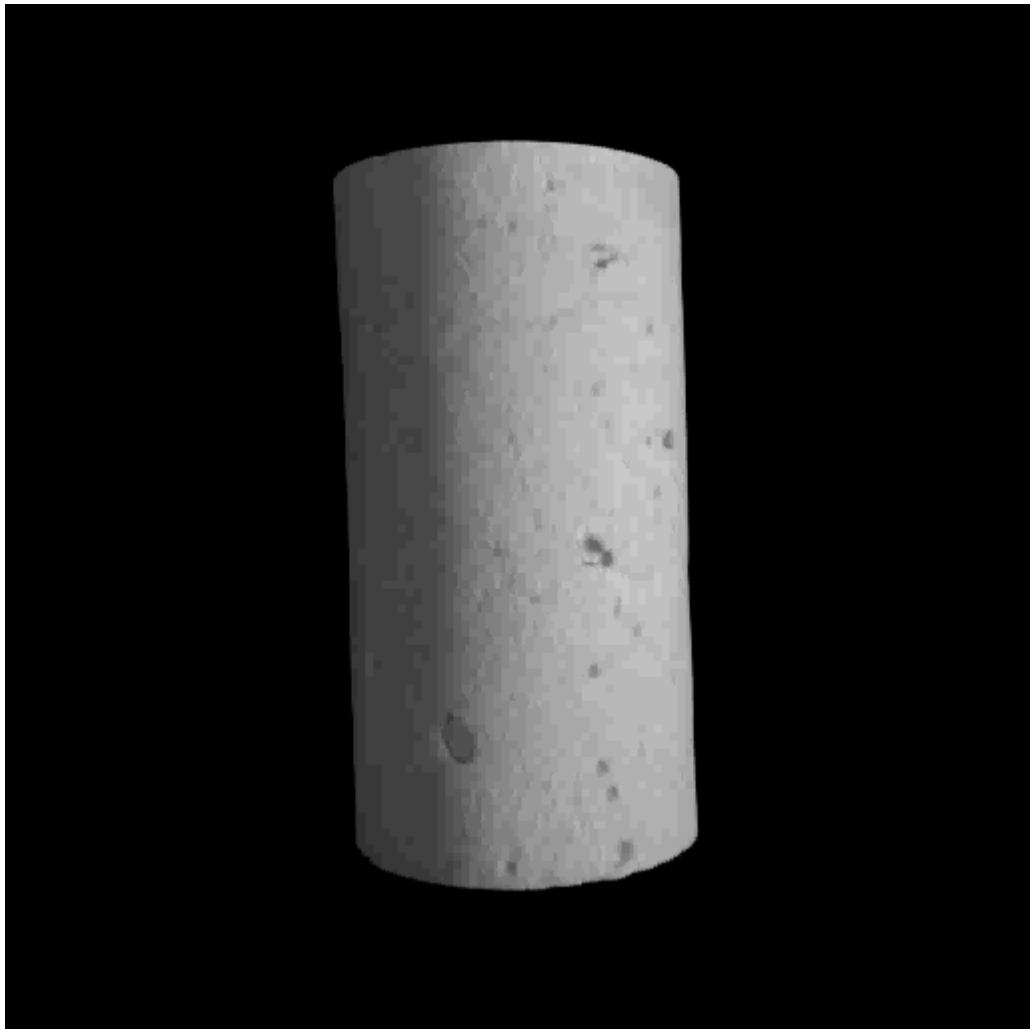
Un-leached **cement which (as tested for sorptivity with water using Nrad)**

Leached **cement which (as tested for sorptivity with water using Nrad)**





Neutron Tomography – pore structure



3D Neutron Tomography - Summary

- *Provides detailed reconstruction of the pore and crack microstructure in the sample.*
- *Visualisations correlate well with the respective sorptivity rates for the un-leached and leached cements.*
- *Apparent greater void volume and connectivity of the pores and cracks in the un-leached sample reflected in its higher sorptivity rate.*

Conclusions

- ***Different rates of leaching Ca and Sr from the surface layer and the bulk interior of the wasteform controlled by undetermined binding mechanism.***
- ***Correlate sorptivity rates determined by Nrad with pore size and connectivity, and crack density, exhibited by Ntom analysis.***
- ***Water penetration rate compared to those on other cement types e.g. OPC.***
- ***Advantage of visualising and measuring, non-destructively, material distribution within macroscopic samples and to describe their inherent processes.***
- ***Useful in tracking movement of water through the cements due to the strongly attenuating properties of hydrogen.***