Immobilisation of Radionuclides by a Cementitious Backfill

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Summary

- ➔ Prominent role of cement in UK programme
- ➔ Retention of radionuclides by cement
- ➔ Solubility of selected radionuclides in NRVB
  - ➔ Key uncertainties
  - ➔ Effect of organics (legacy reagents, CDP, SP)
- ➔ Diffusion experiments
- ➔ Advection tests
- ➔ Field tests & natural analogues
- ➔ On-going, related & potential future work

Cement and its Role in Geological Disposal

- ➔ Potential uses - grout, containers, *backfill*, structures
- ➔ Readily available, low cost, ease of handling
- ➔ Versatile – design for specific functions (e.g. high density, SRC)
- ➔ Non-hazardous & wealth of experience in construction sector

However:

- ➔ Cementitious barriers are important in UK concept
- ➔ Some countries adopting avoidance/minimisation strategies
- ➔ Backfill requirements (NRVB) are unconventional (high porosity, low strength)
- ➔ Effect of additives (*e.g.* SP) difficult to predict

Demonstrating Chemical Containment

- ➔ Promotes highly alkaline & in some cases reducing matrix
- ➔ Precipitated as discrete phase (oxide, hydroxide etc.)
- ➔ (Co)-ppt or adsorbed on surface of cement minerals
- ➔ Incorporated into hydrated minerals as they (re)crystallise

Last will depend on porosity, maturity & degree of carbonation of backfill

Solubility – Multi-element

		Cs	I	Se	Ni	Eu	Th	U
Oversaturation	NaOH	✓ Steady state	✓ Steady state	✓ Steady state	✓ Steady state	✗ Not steady	✗ Not steady	✓ Steady state
	$Ca(OH)_2$	✓ Steady state	✓ Steady state	✓ Steady state	✓ Steady state	✗ Not steady	✗ Not steady	✓ Steady state
	NRVB	✓ Steady state	✓ Steady state	✓ Steady state	✓ Steady state	✗ Not steady	✗ Not steady	✓ Steady state
	CDP	✓ Steady state	✓ Steady state	✓ Steady state	✓ Steady state	✗ Not steady	✗ Not steady	✓ Steady state
	CDP + $Na_2S_2O_4$	✓ Steady state	✓ Steady state	✓ Steady state	✓ Steady state	✗ Not steady	✗ Not steady	✓ Steady state
	CDP + Fe	✓ Steady state	✓ Steady state	✓ Steady state	✓ Steady state	✗ Not steady	✗ Not steady	✓ Steady state
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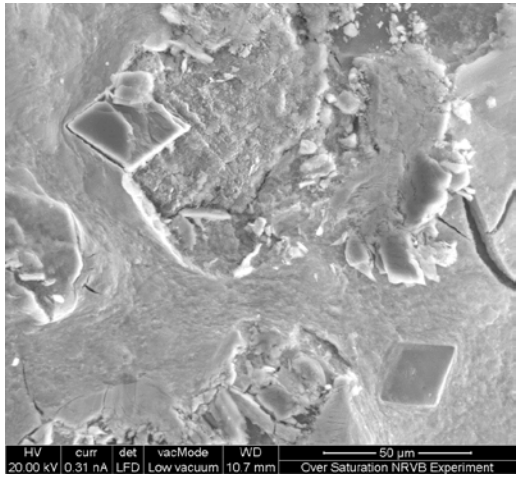
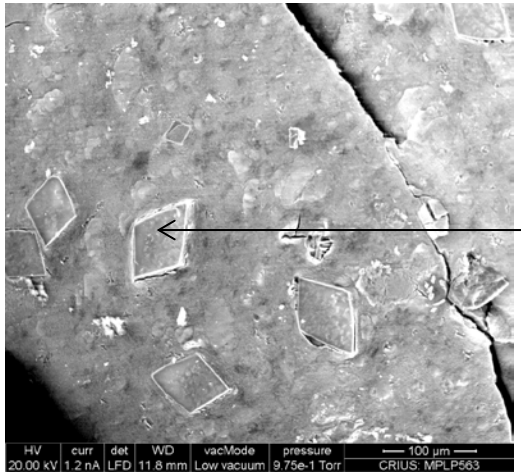
Retention by Precipitation

- ➔ Insoluble hydroxides (Co, Ni, Cd)
- ➔ LDH, hydrotalcite-like (Co, Ni + anions)
- ➔ Insoluble Ca metallates (e.g. $CaUO_4$); however most are rel. soluble



Oversat. / NRVB / Year 1



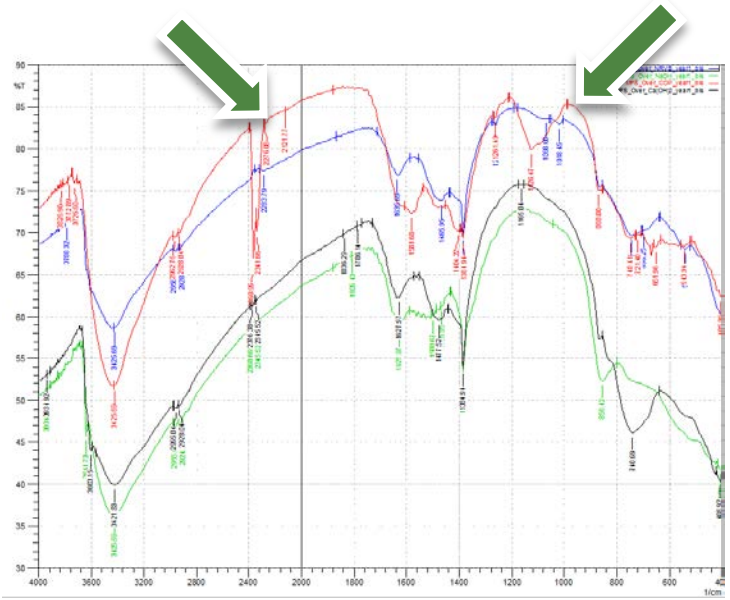
$CaSeO_3$

Oversat. / $Ca(OH)_2$ / Year 2

Incorporation in Aft & Afm Phases

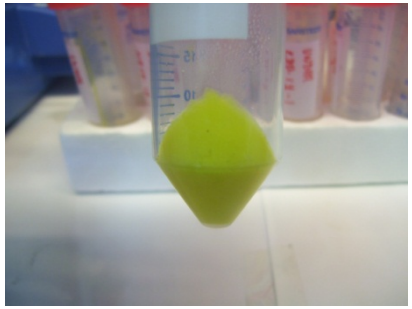
- ➔ Both cations & anions incorporated
- ➔ Trivalent cations form ettringite-type phases $Ca_6[M(III)(OH)_6.12H_20](SO_4)_3.2H_2O$
- ➔ Tetravalent cations form thaumasite-type phases $Ca_6[M(IV)2(OH)_{6.}12H_2O](SO_4)_2(CO_3)_2$

- Solids formed in $Ca(OH)_2$ and NRVB show very similar spectra
- Solids formed in CDP show distinctive FTIR pattern

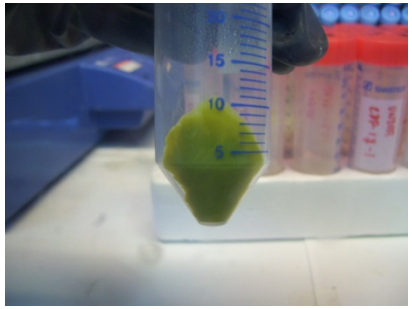


Solid Phase Characterisation

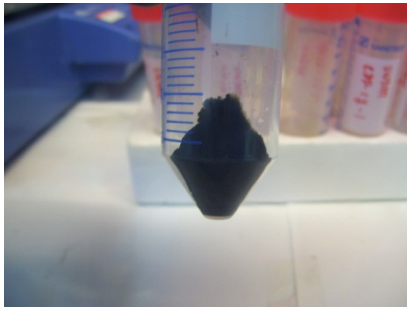
Sampling of solids Year 1 & 2



Precipitate in NaOH



Precipitate in CDP



Precipitate in CDP + $Na_2S_2O_4$

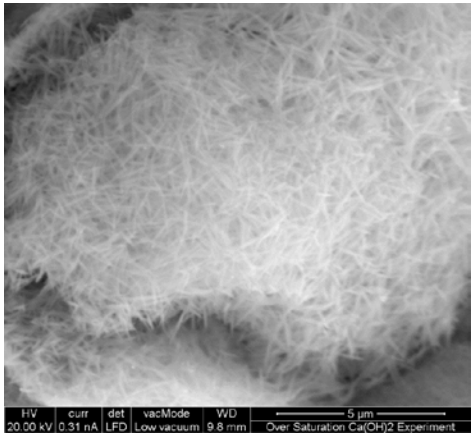
XRD	SEM-EDX		TEM
✓ Completed	✓ Completed		⌛ In progress
FTIR	**Raman**	**Synchrotron**	**TRLFS**
⌛ In progress	⌛ In progress	⌛ Application	Planned

Most solids show poor crystallinity in all media

Solubility Results: Status

➔ Monitoring of aqueous solubility:

- Cs, I, Se, Ni and U reach steady state (1-2y)
- Over- & under-saturation data converge
- Significant increase of solubility (2-3 orders of magnitude) of U and Ni in the presence of CDP

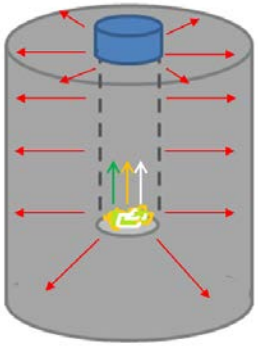


➔ Characterization of solids

- XRD shows poor crystallinity with negligible changes between solids from year 1 & 2
- SEM imaging shows most phases colloidal
- Se forms good crystals in the presence of Ca
- Fe surfaces in some experiments help nucleation

Diffusion Experiments

	Multi-elemental	Single-element (active isotopes)					
	Cs+I+Ni+Eu+Th+U	Cs	I	Th	U	Ni	Eu
NRVB	4 completed + 7 on-going	4	4	2	2	2	2
CDP	4 completed + 7 on-going	4	4	2	2	2	2



Through diffusion in radial configuration

Two aqueous phases:
- NRVB-equilibrated water
- NRVB + CDP

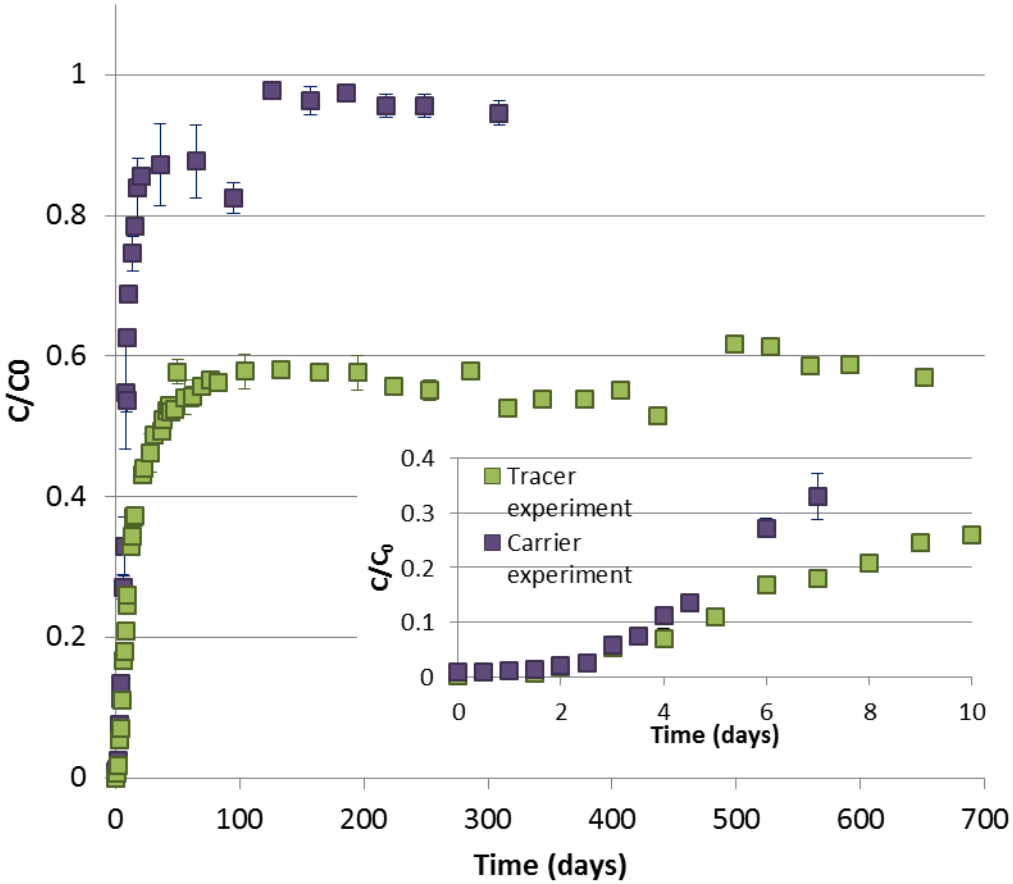
All under N_2 atmosphere

Status of Diffusion Experiments

		NRVB	CDP
Multi-element	Cs	✓ Breakthrough	✓ Breakthrough
	I	✓ Breakthrough	✓ Breakthrough
	U	⌛ On going	⌛ On going
	Th	⌛ On going	⌛ On going
	Ni	⌛ On going	⌛ On going
	Eu	⌛ On going	⌛ On going
Single-element	Cs	✓ Breakthrough	✓ Breakthrough
	I	✓ Breakthrough	✓ Breakthrough
	U	⌛ On going	⌛ On going
	Th	⌛ On going	⌛ On going
	Ni	⌛ On going	✓ Breakthrough
	Eu	⌛ On going	⌛ On going

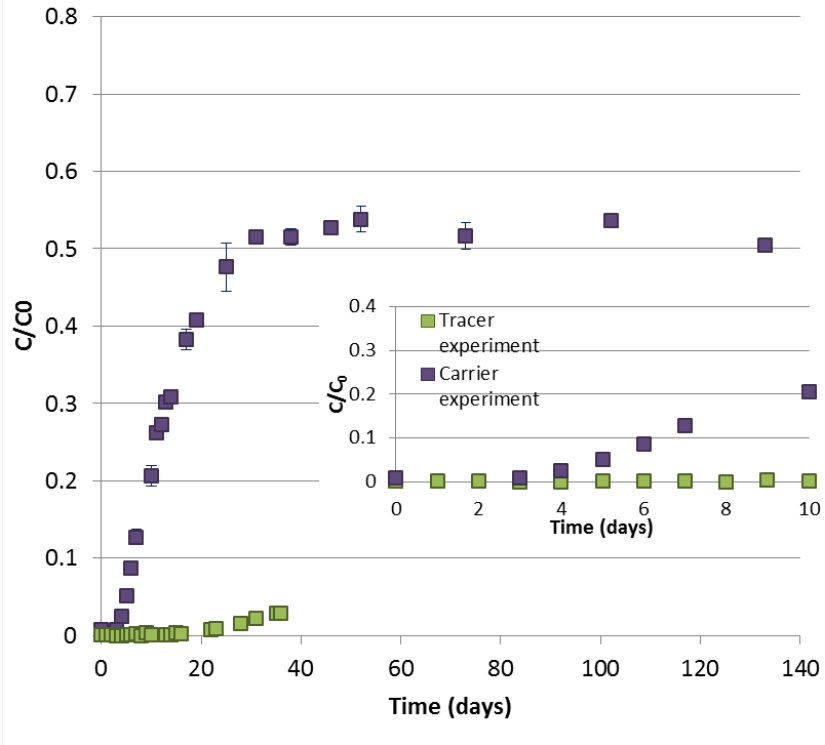
Diffusion Results: Caesium

NRVB



- Breakthrough after 2 days
- Tracer experiments show higher % retention than the carrier tests

Diffusion Results: Iodide

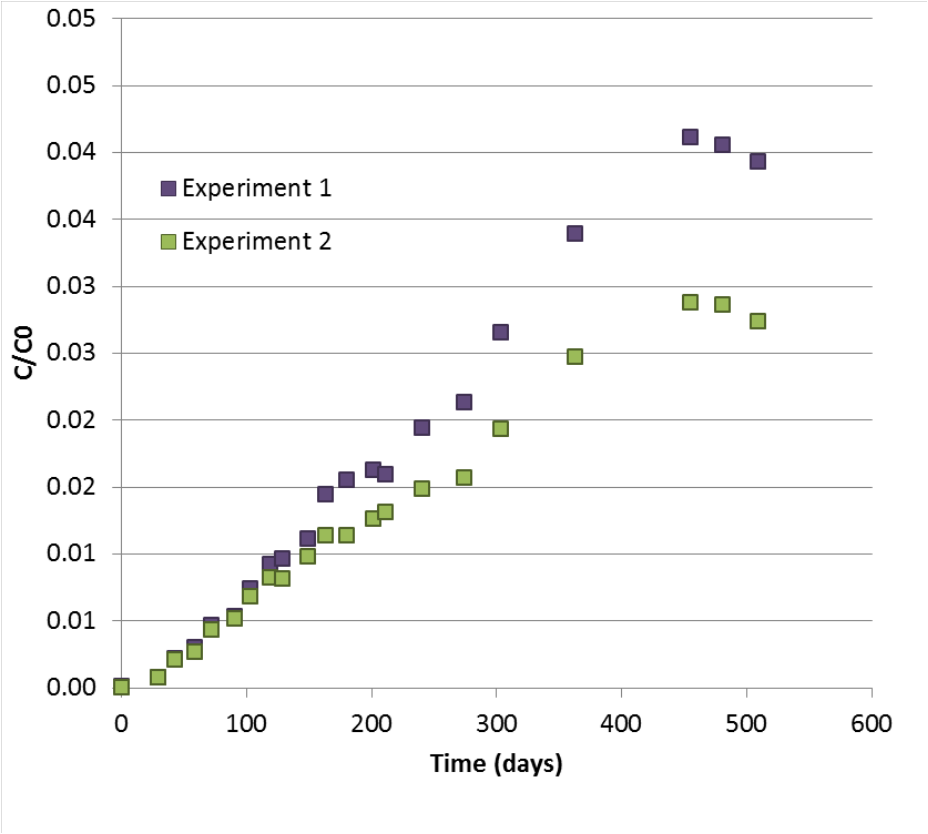


NRVB

- Experiments at tracer levels (^{125}I only) show very little breakthrough
- Breakthrough after 4 days for the carrier experiments
- Significant retention observed, ≅50%, at carrier levels (^{125}I + KI)

CDP reduce uptake of I by NRVB (30% cf. 50%)

Diffusion Results: Nickel



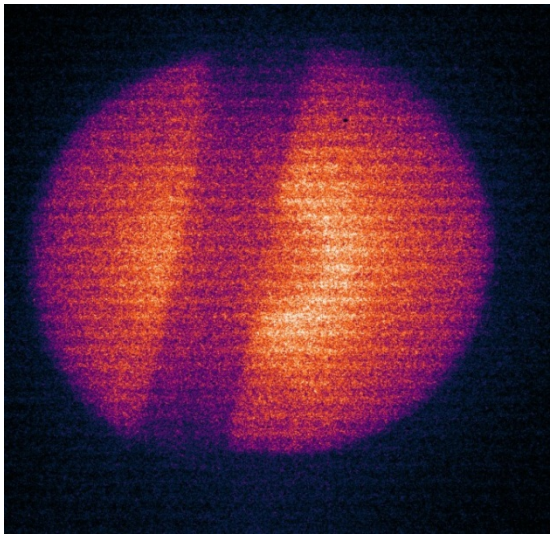
CDP

^{63}Ni + carrier

Slow but measurable breakthrough with CDP present

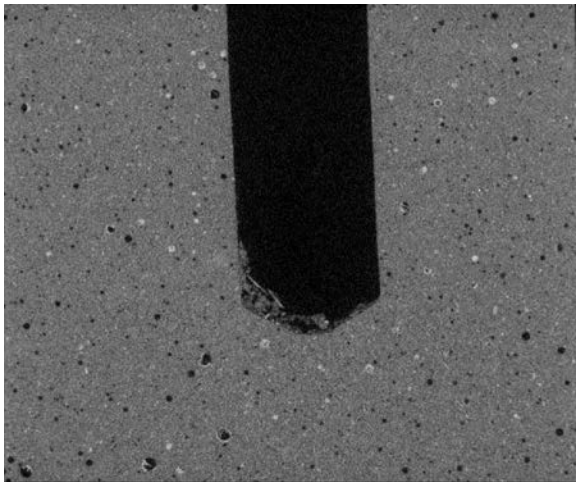
No signs of breakthrough in absence of CDP

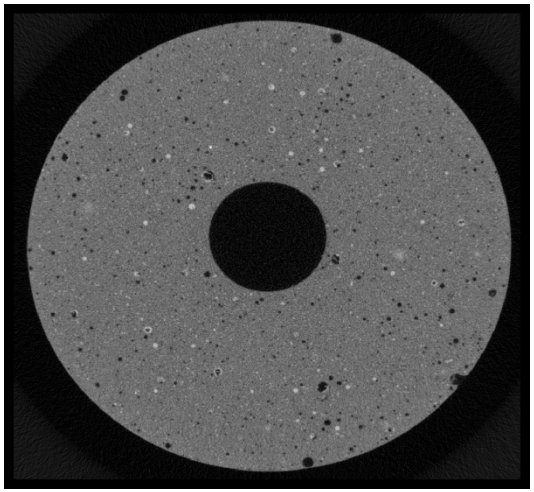
Diffusion Results: Iodide (AutoRad & XRT)

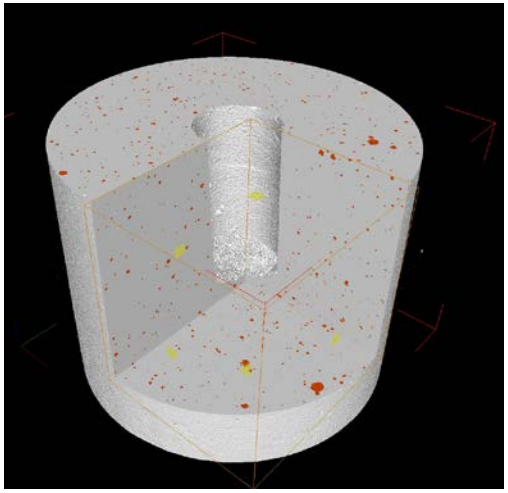


Radial distribution is homogenous

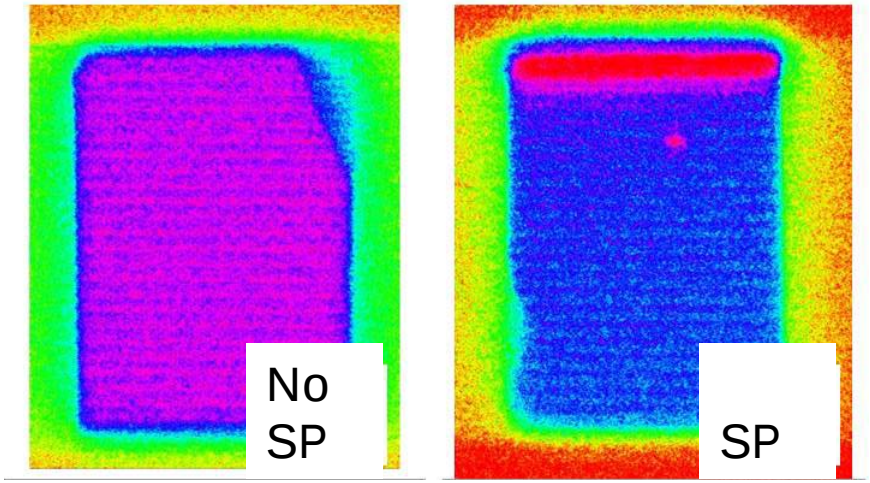
Migration through the NRVB matrix and not through micro-fissures







Superplasticisers – Polycarboxylates



➔ Increase solubility of radionuclides in solution

➔ Inhibit uptake by cement

➔ Lead to bleed in some blends

➔ Developing bespoke SP to minimise complexation of r.n.

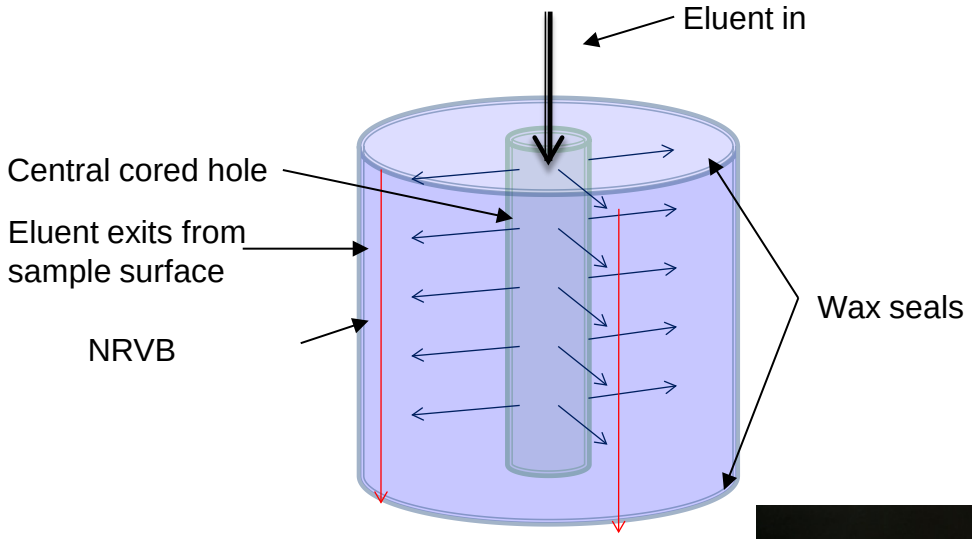
But: Grouts very different to backfill

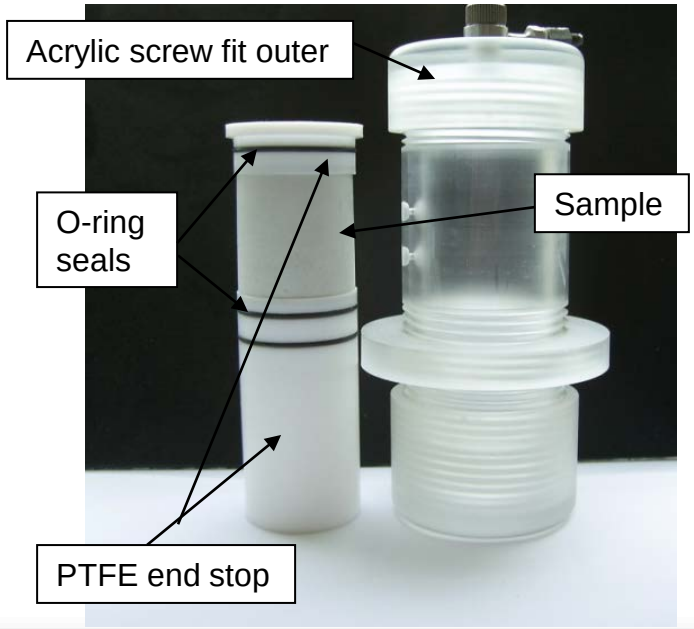
A. Young, P. Warwick, A. Milodowski and D. Read. Behaviour of radionuclides in the presence of superplasticiser."Adv. Cem. Res. **25**: 32-43 (2013).

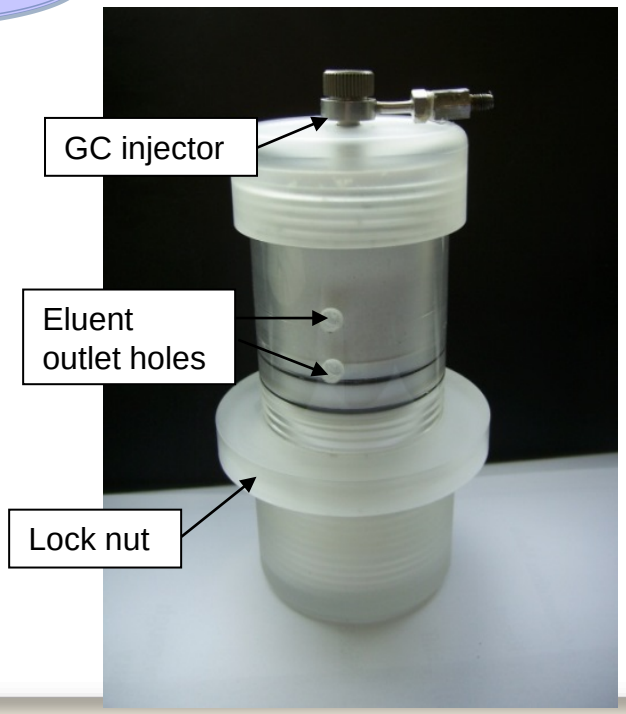
Diffusion Results: Summary

- ➔ Simple, robust and cost-effective methodology
- ➔ Breakthrough of Cs and I plus Ni in the presence of CDP
- ➔ CDP reduces the breakthrough time and retention for both cationic and anionic species
- ➔ Diffusion experiments at tracer level showed higher retention than those in the presence of carrier
- ➔ U, Th and Eu show no signs of breakthrough after 2 years

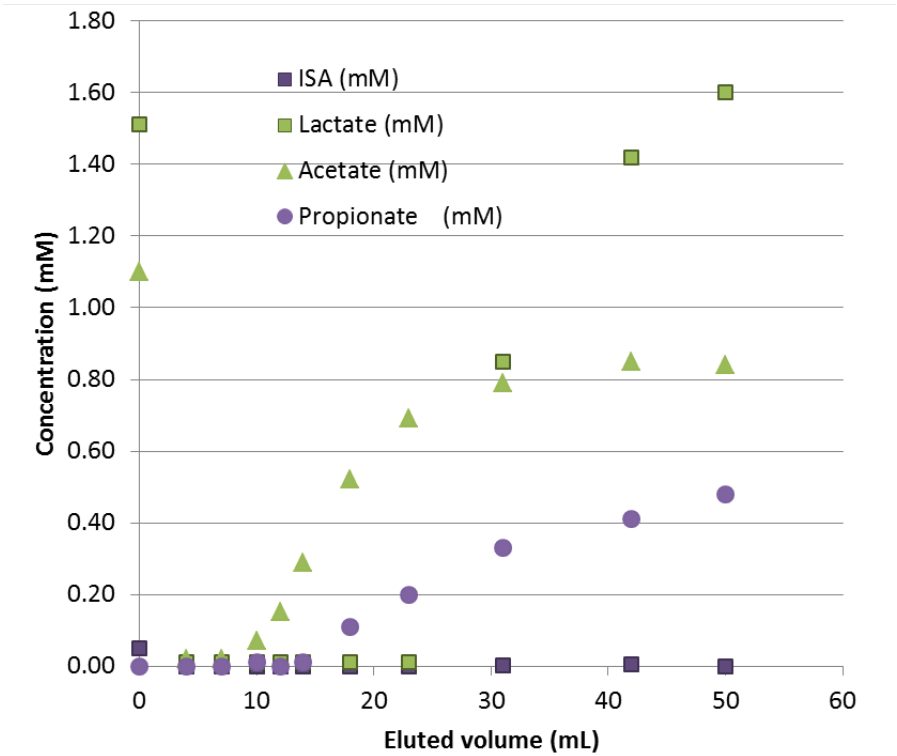
Advection: Experimental Setup







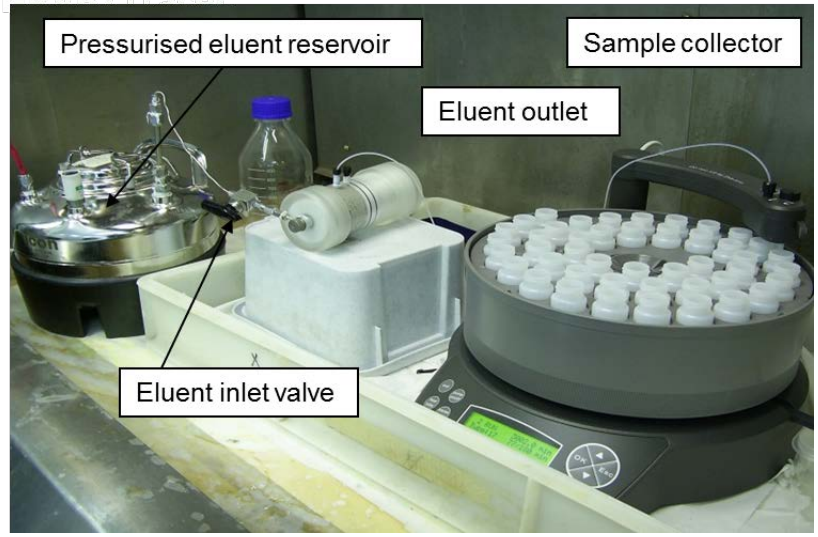
Advection Results



CDP

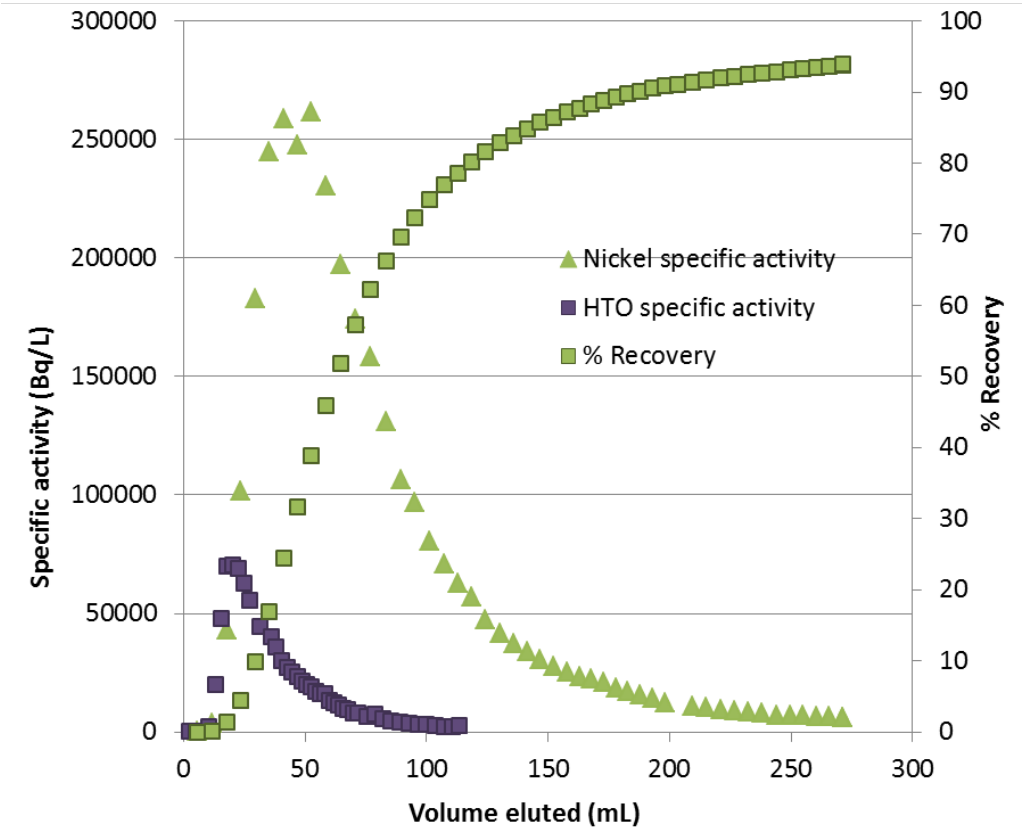
- The NRVB block was equilibrated with CDP before injection of ^{63}Ni
- Not all components of CDP behave in the same way

- ISA disappears from the eluate whereas concentration of propionate increases



Advection Results: Nickel

CDP



- Rapid elution of ^{63}Ni, almost as fast as HTO
- 95% of the injected Ni is recovered from the block (no carrier added)

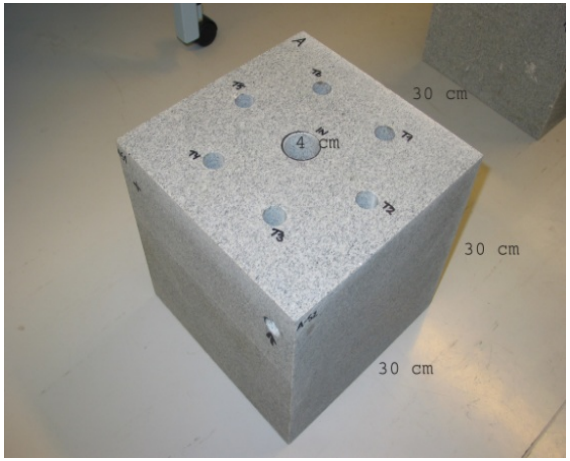
Results to Date

- Simple protocol allows large number of experiments & delivers reproducible data
- Empirical evidence of NRVB retention for higher valence ions
- Limited retention for monovalent cations (Cs^+) & anions (I^-)
- Characterisation of immobilisation phases & determination of stability essential for predictive modelling
- Greater mobility of trace radionuclides in presence of carrier
- CDP reduce uptake & shorten breakthrough times
- Methodology for deriving representative p.a. input

Future Work

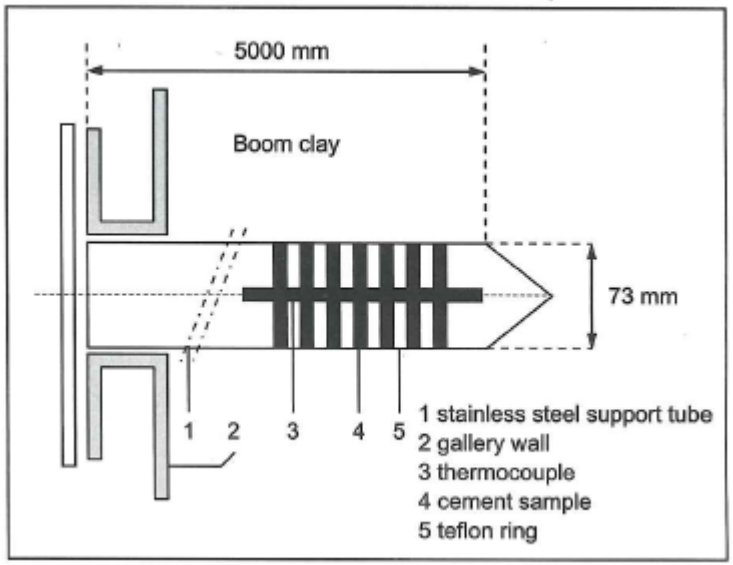
- ➔ Detailed characterisation of incipient mineral phases
- ➔ New experiments (^{99}Tc, ^{36}Cl and ^{75}Se) to help differentiate the solid phases formed in the different systems
- ➔ Advanced spectroscopic methods to elucidate nature of local chemical environment (SSNMR, ISIS, DIAMOND).
- ➔ Up-scaling to more representative dimensions (block, URL)
- ➔ Effect of organics (*e.g.* SP) in (re-)mobilisation
- ➔ Integrate parallel developments in cement & concrete "printing" (additive manufacturing)

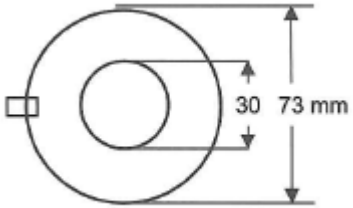
Up-scaling



Up-scaling

➔ In-situ experiments: HADES underground laboratory (depth 220 m, Mol, Belgium)[1]





- Assessment of the effect of different cement formulations on Boom Clay
- 12-18 months
- 25º or 80ºC

- Potential application of this methodology to other host rocks
- Characterisation of mineralogical changes on the cement–rock interface (dissolution/precipitation)
- Diffusive behaviour of key radionuclides through interface
- Effect of cement additives (e.g. superplasticisers)

*1.- D. Read et al. Mineralogical and microstructural changes accompanying the interaction of Boom Clay with ordinary Portland cement. Advances in Cement Research, **13**, 175-183 (2001)*

Supporting Evidence for Chemical Containment

- ➔ Natural Analogues
  - ➔ Maqarin, Oman, Cyprus
  - ➔ Harpur Hill

- ➔ Industrial Analogues
  - ➔ Ancient structures (*e.g.* Hadrian's Wall)
  - ➔ Encapsulation of radioactive industrial (NORM) waste

- ➔ Underground laboratory tests (Mol, Åspö),Related research (*e.g.* SKIN)

Key Uncertainties

- ➔ Nature of solubility limiting phases

- ➔ Effect of CDP, SP & other additives

- ➔ Porosity-permeability (cracking modes, carbonation etc.) + coupled chemical transport, mineralisation & phase evolution

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