# CarboSOLUTIONS

## Implementing Irradiated-Graphite Waste Management

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# CarboSOLUTIONS Objectives

- Innovative waste management SOLUTIONS on
  - Irradiated-graphite (i-graphite) &
  - other carbonaceous waste (e.g. backed carbon, pyrocarbon)
- Multi-scale investigations on i-graphite characteristics
  - Systematic correlation of influencing parameters (Temp., Atm. etc)
  - Predictive models for radionuclide releases
- Demonstration of 'Best Practices' in
  - Retrieval of i-graphite from reactor core,
  - Treatment / purification options (towards Pilot Scale),
  - Storage, Conditioning and Disposal,
  - Recycling of i-graphite for future V/HTR, MSR & Fusionreactors
- Synergies across near & medium-term decommissioning projects

# CarboSOLUTIONS Partners

***Carbo**SOLUTIONS partnership*

***will represent main actors and projects on***

***i-graphite management & research***

***in the EU & neighbour countries***

## Build upon CARBOWASTE Partnership*:

- **nuclear industries** (AMEC NNC, AREVA NP, Doosan Babcock, PBMR)
- **waste management companies** (Bradtec, Studsvik, Hyder, FNAG)
- **utilities** (EDF, Sogin, (EPRI))
- **graphite manufacturers** (GrafTech, SGL-Carbon)
- **waste management authorities** (ANDRA, NDA, ENRESA)
- **research** (CEA, CIEMAT, ENEA, FI, FZJ, INR, JRC, LEI, UK NNL, NRG, SCK•CEN, NECSA)
- **universities** (EMN, CNRS-ENS, IPNL, The University of Manchester)

**Additional partners** (from ‚CARBOWASTE countries‘ **plus** Ukraine, Russia etc.)

** Request for Expression-of-Interest in preparation*

# Dimension of the Problem

- About 250 000 tons already accumulated, worldwide
- Origin from different reactor types
  - MAGNOX (27), UNGG (7), AGR (14), HTR (3)
  - RBMK (2), Pu-Production Reactors & numerous MTR
- Various graphite grades and impurities
- Individual operational ‚histories'
- Varying content of long/short-lived radioisitopes
  - $^{14}C$ plus $^{3}H$, $^{36}Cl$, $^{60}Co$, $^{79}Se$, $^{99}Tc$, $^{129}I$, $^{135}Cs$, $^{152/154}Eu$ etc.
- Diverging national classifications (ILW, LLW, LL-LLW)
- Different i-graphite management strategies
- Closed ‚i-graphite cycle' essential for V/HTR & MSR (Gen IV)

More than 50 NPPs in EU !

# Near & Medium Term Projects

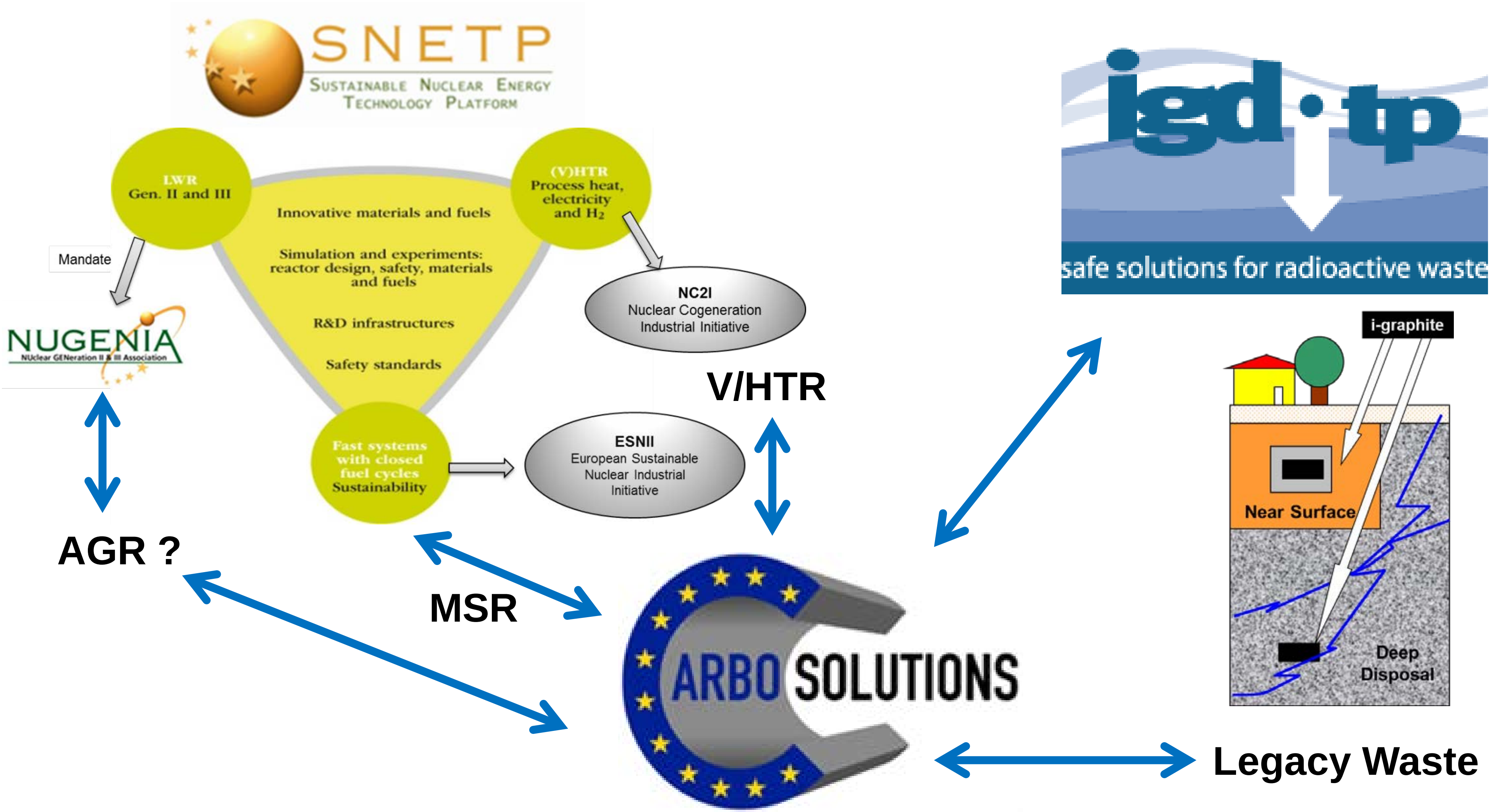
- **FR (Decommissioning of UNGG (e.g. Bugey, Sleeves) & G1 / G2)**
- **UK (BEPO, DRAGON, Windscale Piles, Hunterston, AGR Sleeves etc.)**
- **ES (Vandellos, UNGG Sleeves)**
- **IT (Latina)**
- **DE (AVR, THTR, MTRs, HTR-Fuel)**
- **ROM (MTRs)**
- **LT (Ignalina 1 & 2, Sleeves)**
- **UKR (Tscherobyl, Sleeves)**
- **RUS (RBMKs, Sleeves & early production reactors)**

**Synergies: common reactor types, graphite grades, disposal routes etc.**

**National programmes underway or scheduled, structural funds (e.g. Ignalina)**

**Fulfills ‚Programme Related Logics‘ for FP8**

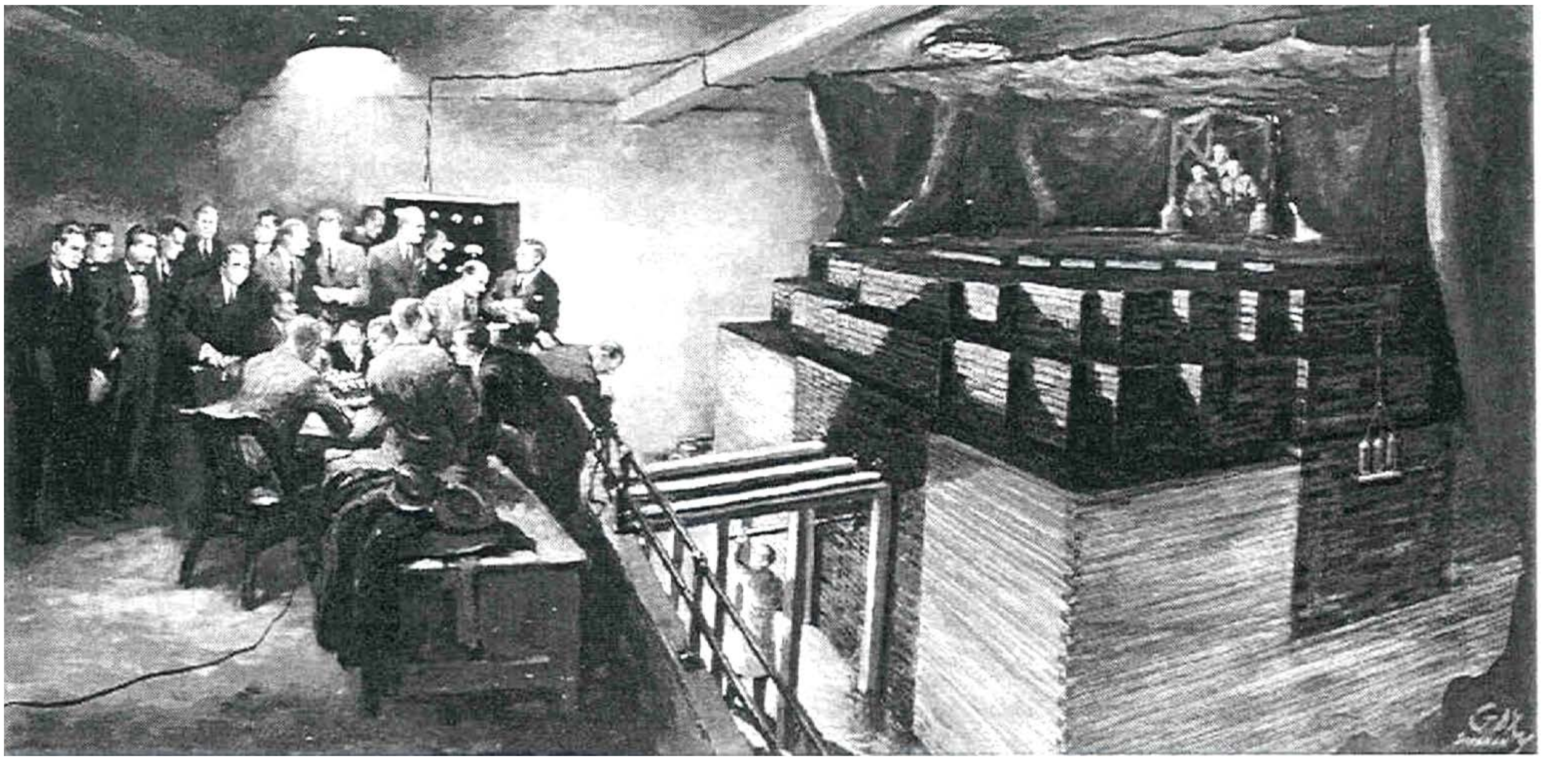
# Between Technology Platforms



# The Beginning of i-Graphite History

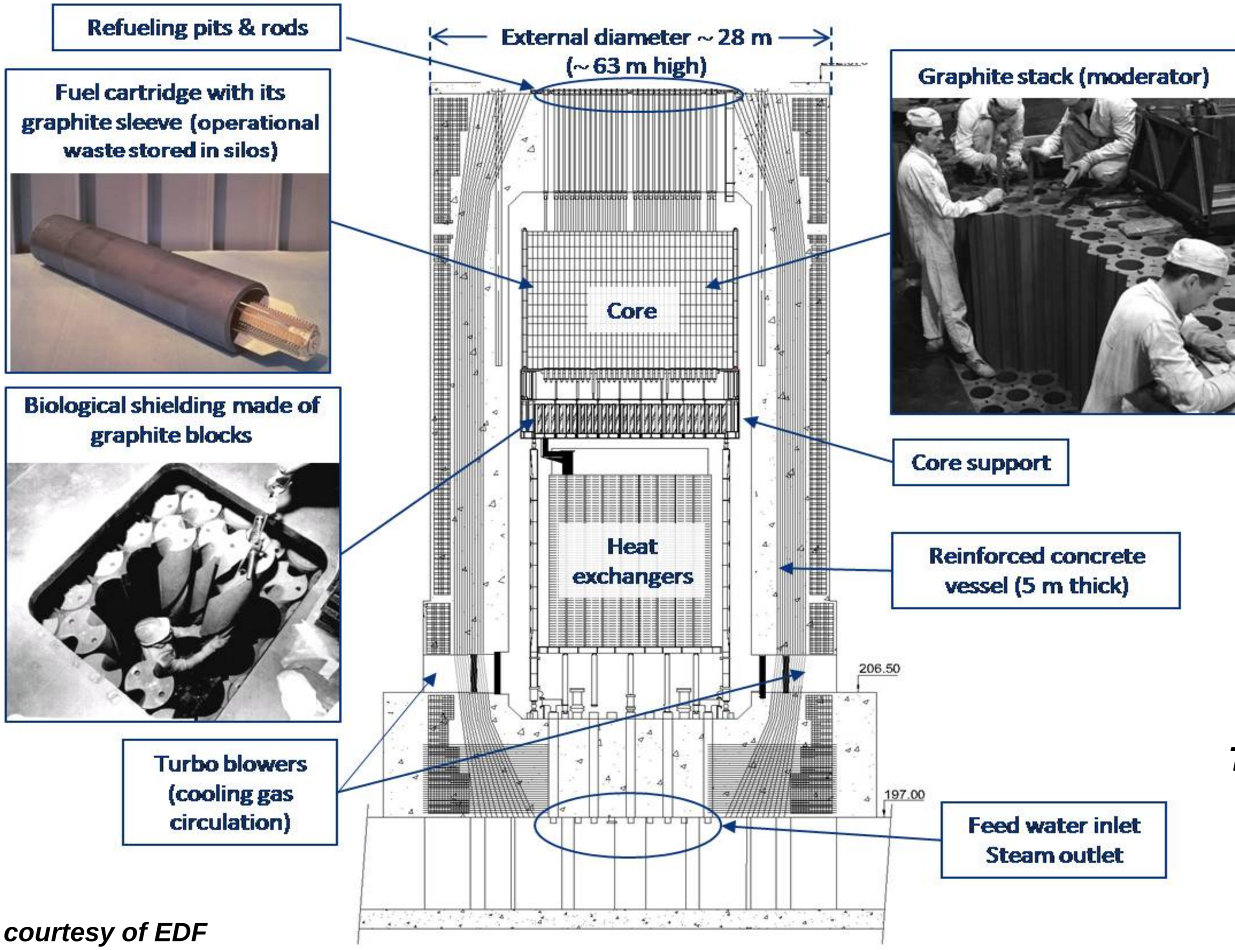
**First nuclear chain reaction**

**2nd of December,1942**



*Painting by Gary Sheahan*

# Graphite in gas-cooled reactors



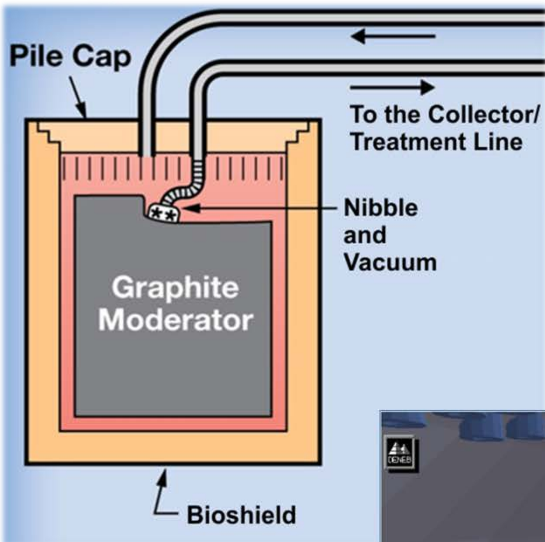

By courtesy of EDF

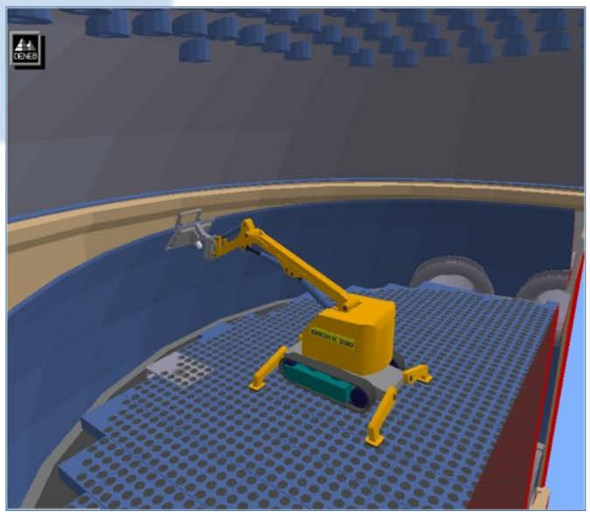
*Example of an UNGG "integrated vessel" type reactor*

*Typically 2000 – 3000 Mg of graphite / reactor (plus Sleeves)*

**Retrieval of i-graphite mostly not considered in the design phase !**

# Challenging Retrieval



**Block-by-Block or In-situ Removal ?**

Retrieval Options

Cutting/Removal Techniques

Under Air

Under Water

Under Inert Gas

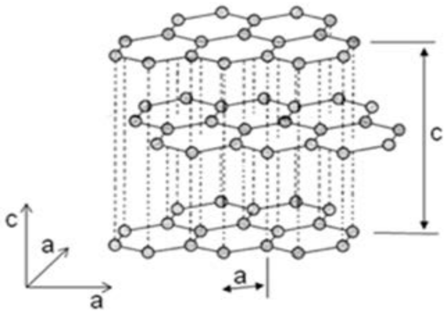
**Demonstration of principal options (e.g. wet or dry retrieval) necessary !**

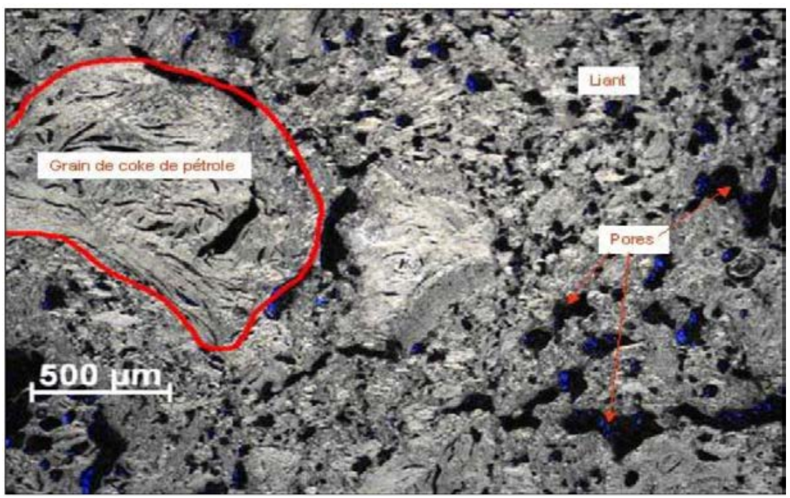
# What is special with i-graphite ?

- **Significant amounts of $^{14}C$ (5730 y half-life)**
  - From $^{14}N$ *(1,81 barn)*, nitrides and absorbed $N_2$
  - From $^{13}C$ *(1,1%; 0,0009 barn)* and $^{17}O$ *(0,037%, 0,235 barn)*
- **Significant amounts of $^{36}Cl$ (300 000 y half-life)**
  - From $^{35}Cl$ left behind on purification from neutron poisons
- **Wigner energy** *(Stored Energy)*
  - function of neutron flux, temperature and irradiation history
  - Potentially releasable, acceleration of corrosion ?
- **Various other contaminants** and
- **Mix of different materials & dimensions**

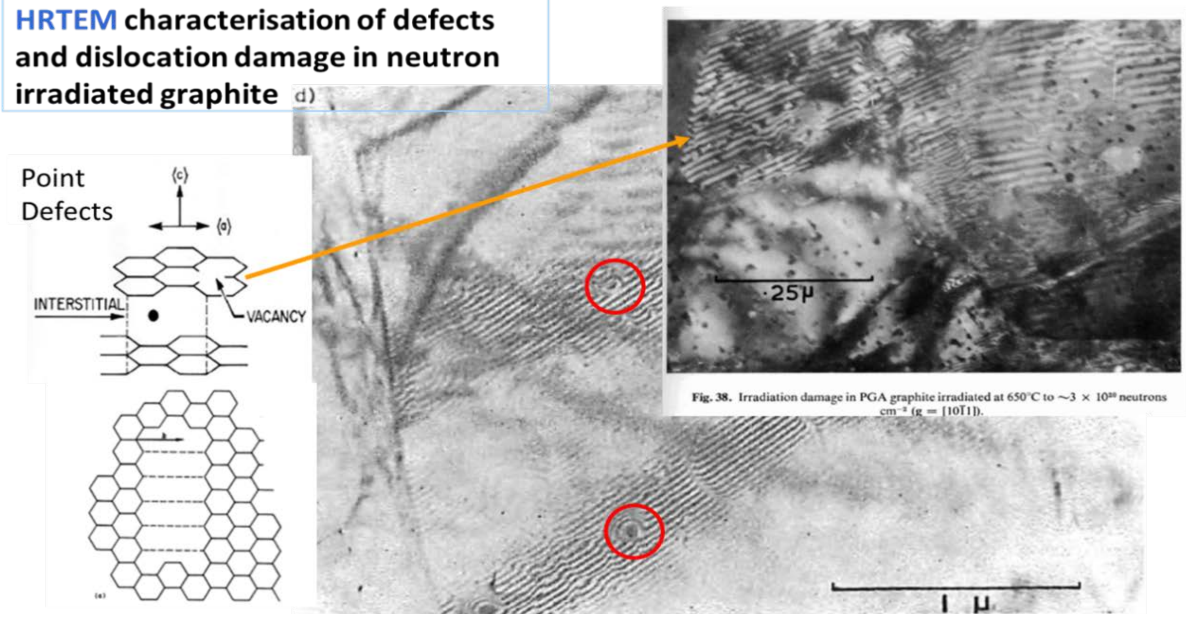
# I-Graphite: No ideal graphite lattice

**Nuclear graphite is a porous *polycristalline material with well graphitized and amorphous zones***




**HRTEM characterisation of defects and dislocation damage in neutron irradiated graphite**




**Systematic approach needed to establish predictive models on radionuclide speciation, location & releases**

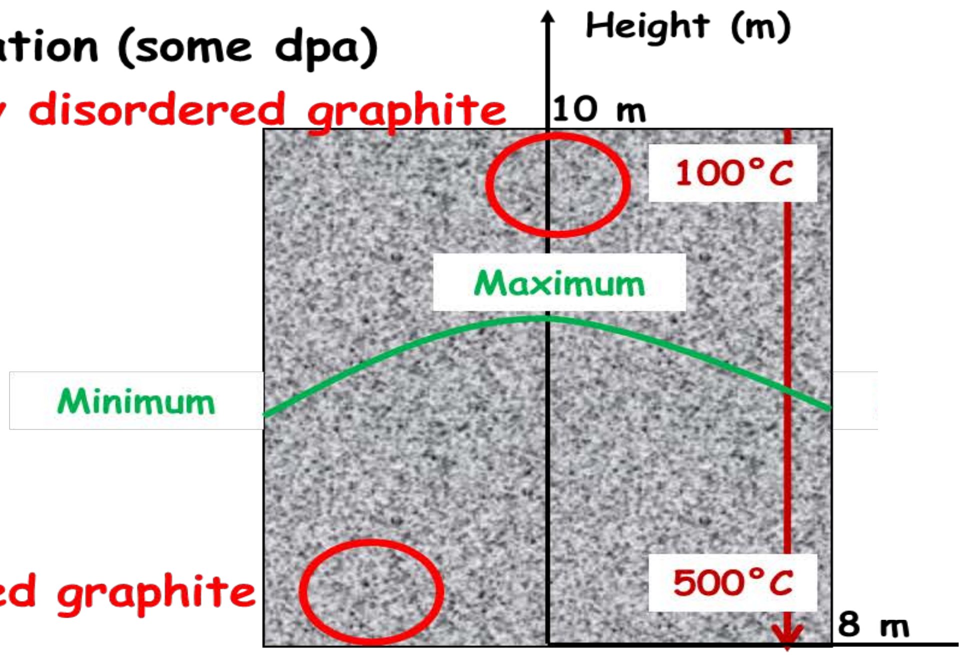
# Impact of operational conditions?

Neutron flux VS Temperature

Neutron flux → Destructuration (some dpa)

Temperature → Reordering

Very disordered graphite




Less disordered graphite

Moderator graphite

**Radiolytical Corrosion**

- Release of impurities ?
- Release of activation products ?

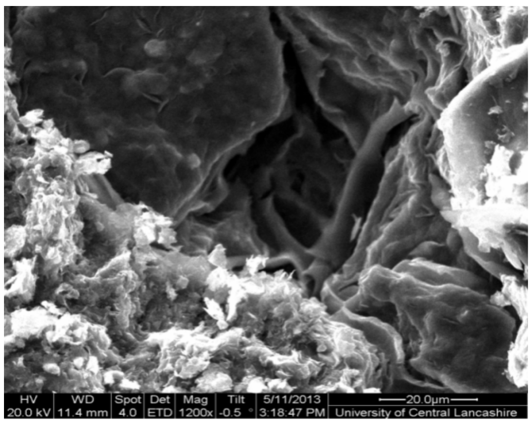
⇒ **i-graphite characteristics even differ within the same reactor !**

⇒ **Correlation with operational conditions necessary !**

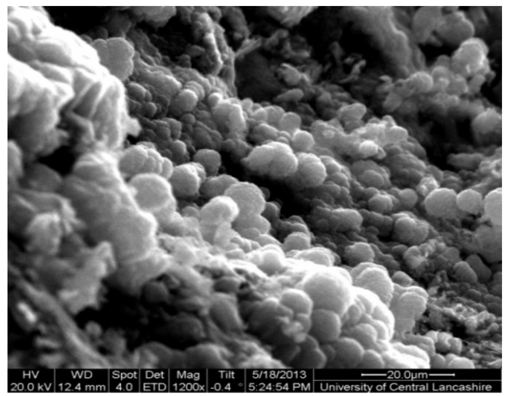
# Deposits & Bioavailability of RN ?

## Carbonaceous deposit found on <u>UK Magnox</u> i-graphite

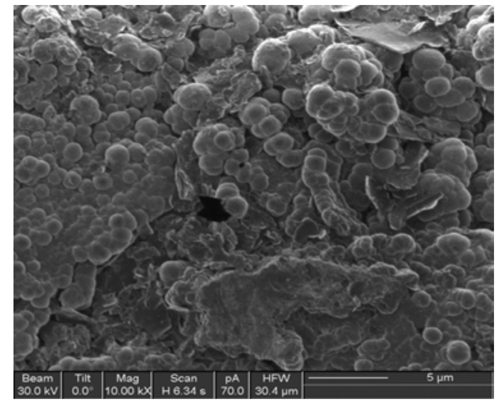
simulated on virgin Magnox graphite by depositing C-13 from a C-13 precursor onto a graphite surface bears a strong resemblance to i-graphite deposit (see SEMs below).



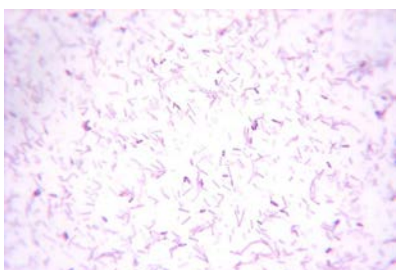

**Virgin Magnox Graphite**




**Magnox Graphite**
**(C-13 Deposit)**



**Irradiated Magnox**
**(Carbonaceous Deposit)**



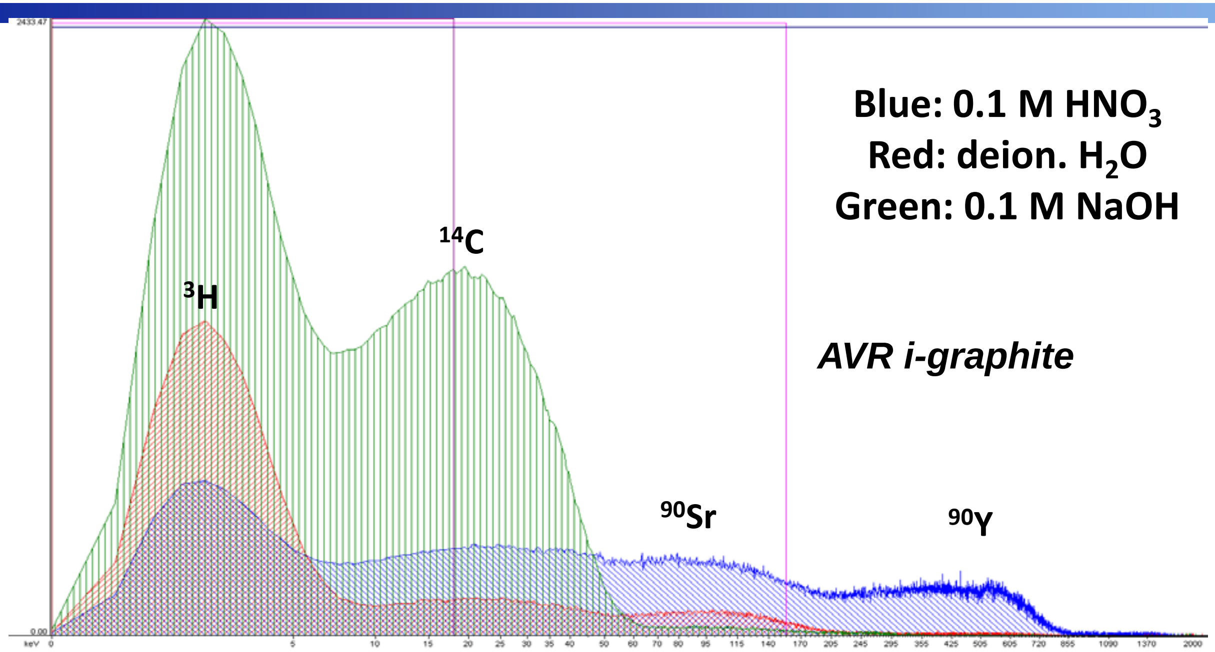
## Microorganisms found on cement control samples

Diffusivity rates with the presence of microorganisms at least five times greater !

**Not addressed in detail, yet**

*By couttesy of UCLAN*

# Impact of storage & conditioning ?




**Releases under basic pH?**

**Releases under moist air?**

| Release of C-14 | Relative Fractional release [%] | Time [y] |
|---|---|---|
| Air | 0,0018 | 1.56 |
| **Moist Air** | **0,07629** | 1.56 |
| Packed in PE | 0,00730 | 0.94 |

**What is the best conditioning for i-graphite ?**

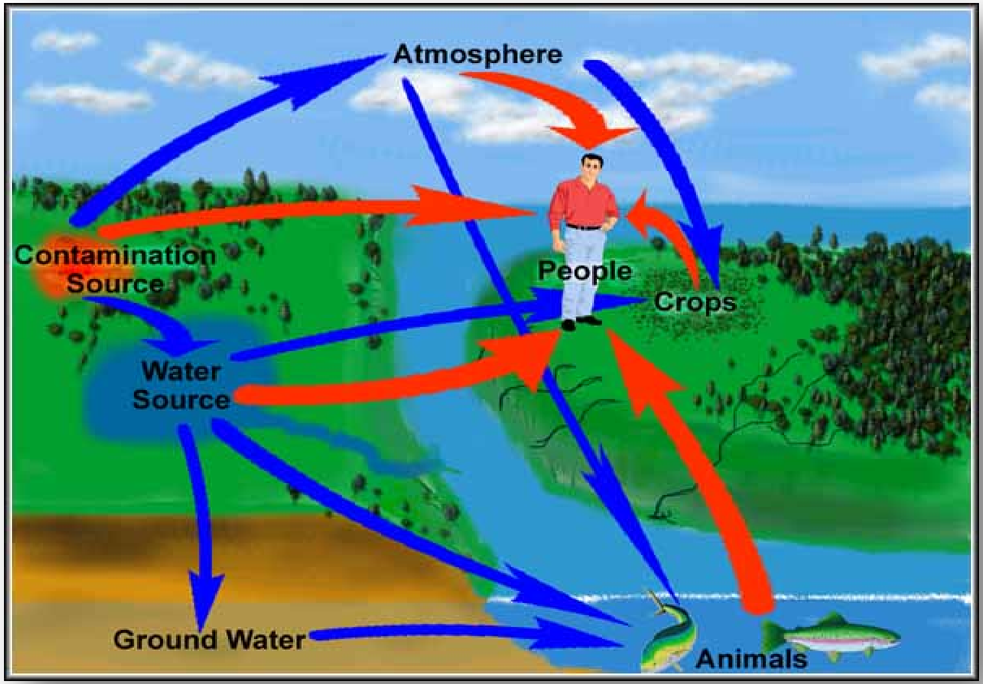
# Radionuclides of Interest

- **Mobile/volatile species**

➢ **Tritium**
- **Generally high activity (≥ $A_{C-14}$)**
- **Relatively short $T_{1/2}$ (12,32 y)**
- **Safe enclosure?**

➢ **Radiocarbon**
- **Generally high activity (1-1000 kBq/g)**
- **Long $T_{1/2}$ (5730 y)**
- **Identical chemical behaviour of C-12**
- **Biocompatibility**

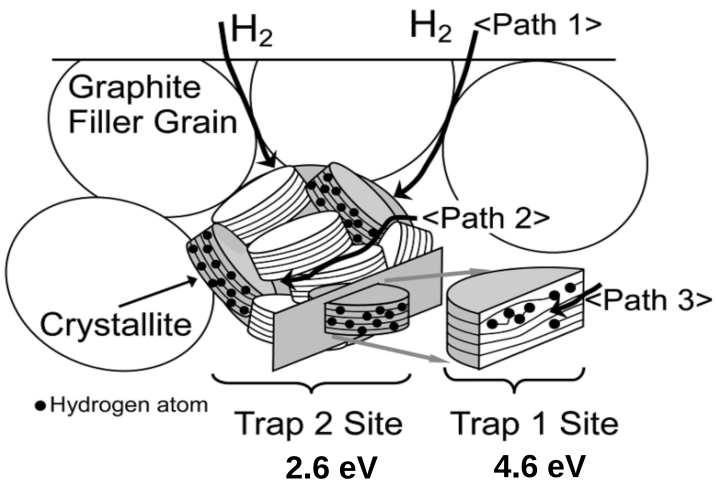
➢ **Chlorine-36**
- **Generally low to very low activity (10-100 Bq/g for UNGG)**
- **Long $T_{1/2}$ (301000 y)**
- **High mobility**



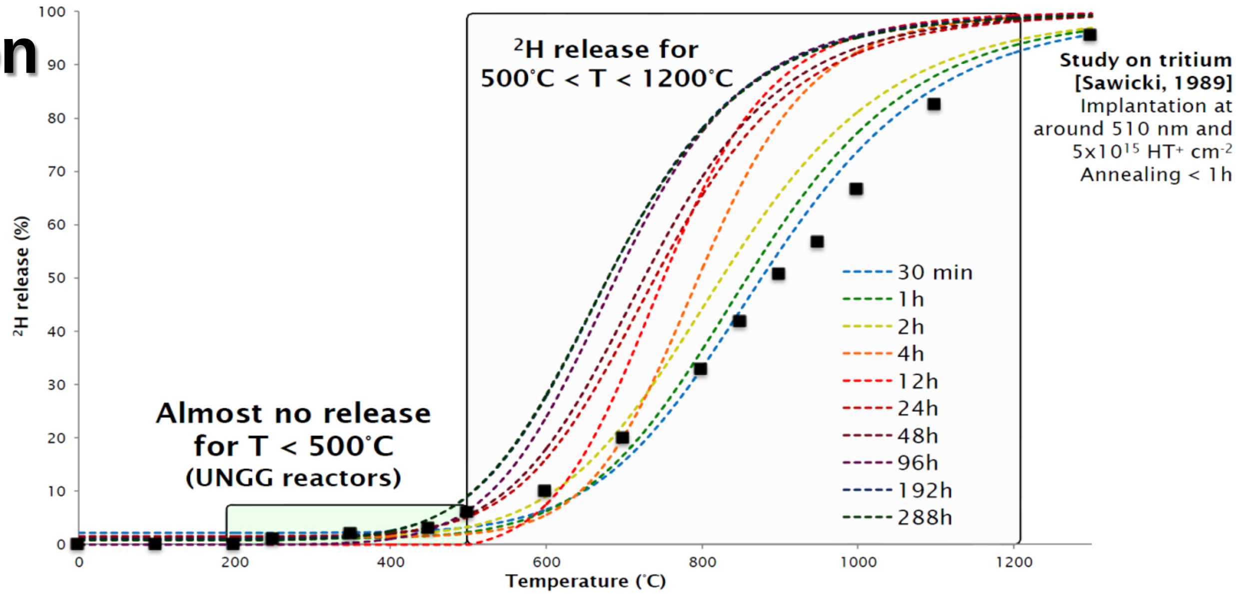
# Tritium

- **Origin: Li & B activation**
  - **Removal:**
    - **Thermal Treatment**
      - **Inert Gas > 1200°C**

**Removable up to 100% !!!**




1.3 eV: when trapping is not significant




N. Toulhoat et al., IPNL

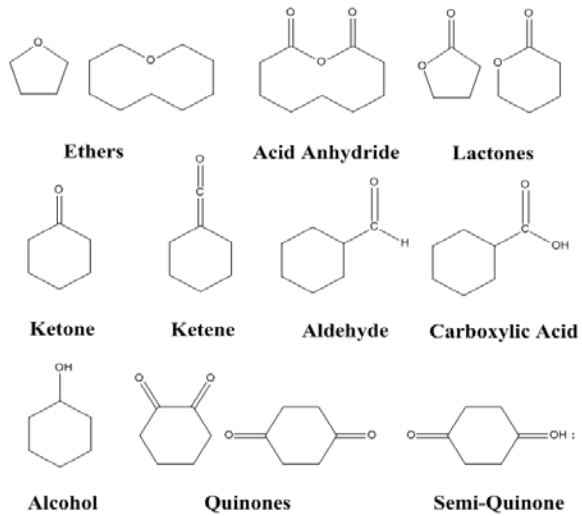
*Tests made with implanted $^{2}H$ as simulant for tritium*

**Open Issues:**

- **Treatment Process Optimization**
- **Secondary waste management**
- **Larger samples**

# Radiocarbon

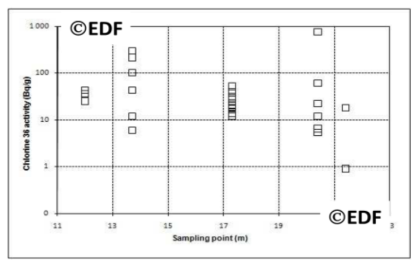
- **Origin ($^{14}N(n,p)^{14}C$, $^{13}C(n,\gamma)^{14}C$, $^{17}O(n,\alpha)^{14}C$ )**
- **Chemical Form(s)**
  - **Mainly elemental, covalently bonded**
  - **Multitude of organic compounds**
  - **Coexistance with functional groups on the crystalline surfaces**




- **Two ‚Macro' Locations identified**
  - **Homogeneous within the crystallites via $^{13}C$ activation (more stable)**
  - **Heterogeneous in hot spots or enriched on surfaces (releasable)**
- **$^{14}C$ Removal**
  - **Up to 80% total radiocarbon removal at ~10% mass loss**
  - **Removable fraction depends on i-graphite ‚history' (pre-corrosion)**
  - **New treatment processes under development** (-> lower mass loss)

# Chlorine-36

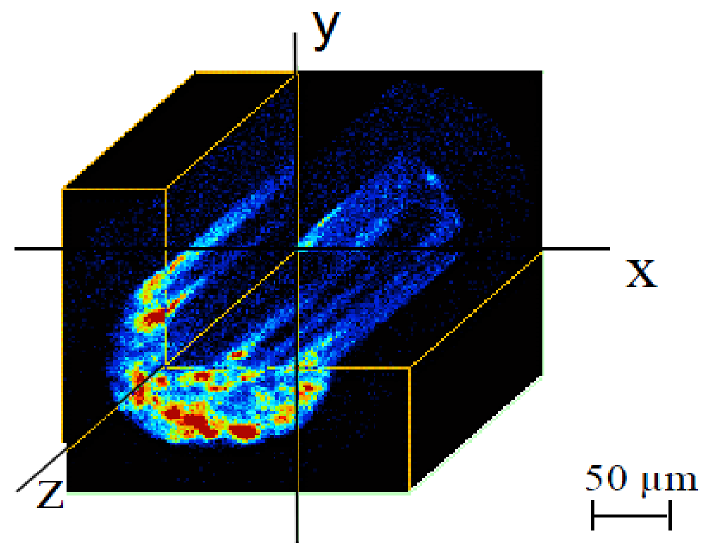
- **Origin**
  - **Impurities in the raw materials**
  - **Cl added during ‚purification'**
  - **Air pollution (e.g. near-sea sites)**
- **Chemical Form**
  - **Organic (C-Cl) → Less mobile**
  - **Inorganic**
    - **Oxychlorine compounds (stable)**
    - **Hydrogen Chloride (Thermal treatment effective)**
- **Location (SIMS)**
  - **Hot Spots**
  - **Huge Variability**




- **Cl releases already during operation**

**Open Issues: Impact of operational conditions**
**Purification methods for $^{36}Cl$**

| Reaction | $\sigma(E_{th})$ [b] |
|---|---|
| $^{35}Cl(n,\gamma)$ | 44 |
| $^{34}S(n,\gamma)^{35}S \rightarrow ^{35}Cl(n,\gamma)$ | 0,34 |
| $^{39}K(n,\alpha)$ | 0,004 |



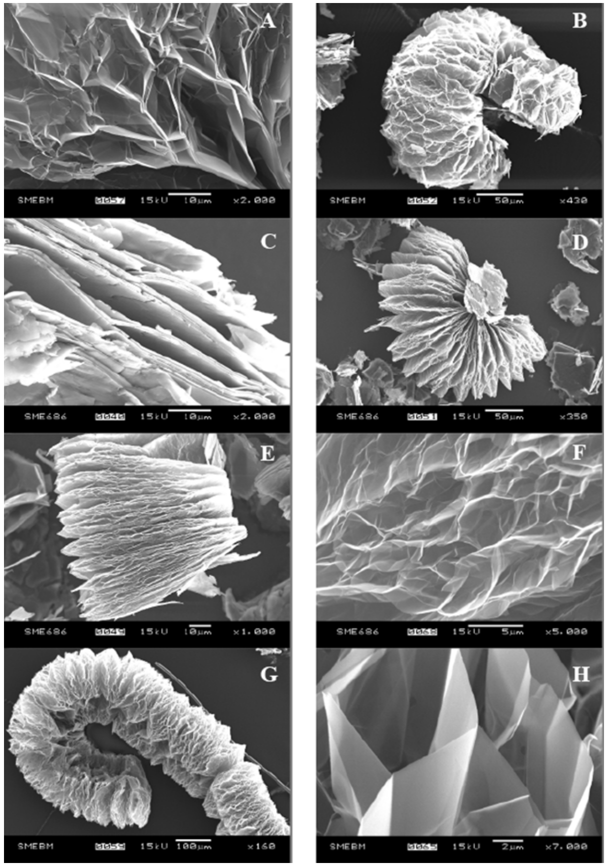

SIMS 3D Image of $^{35}Cl$
irradiated graphite SLA2-53 (CEA)

# Other Radionuclides

- **Activation Products, Uranium and Transuranics**
  - **Efficient and selective removal through chemical treatment(s) !**

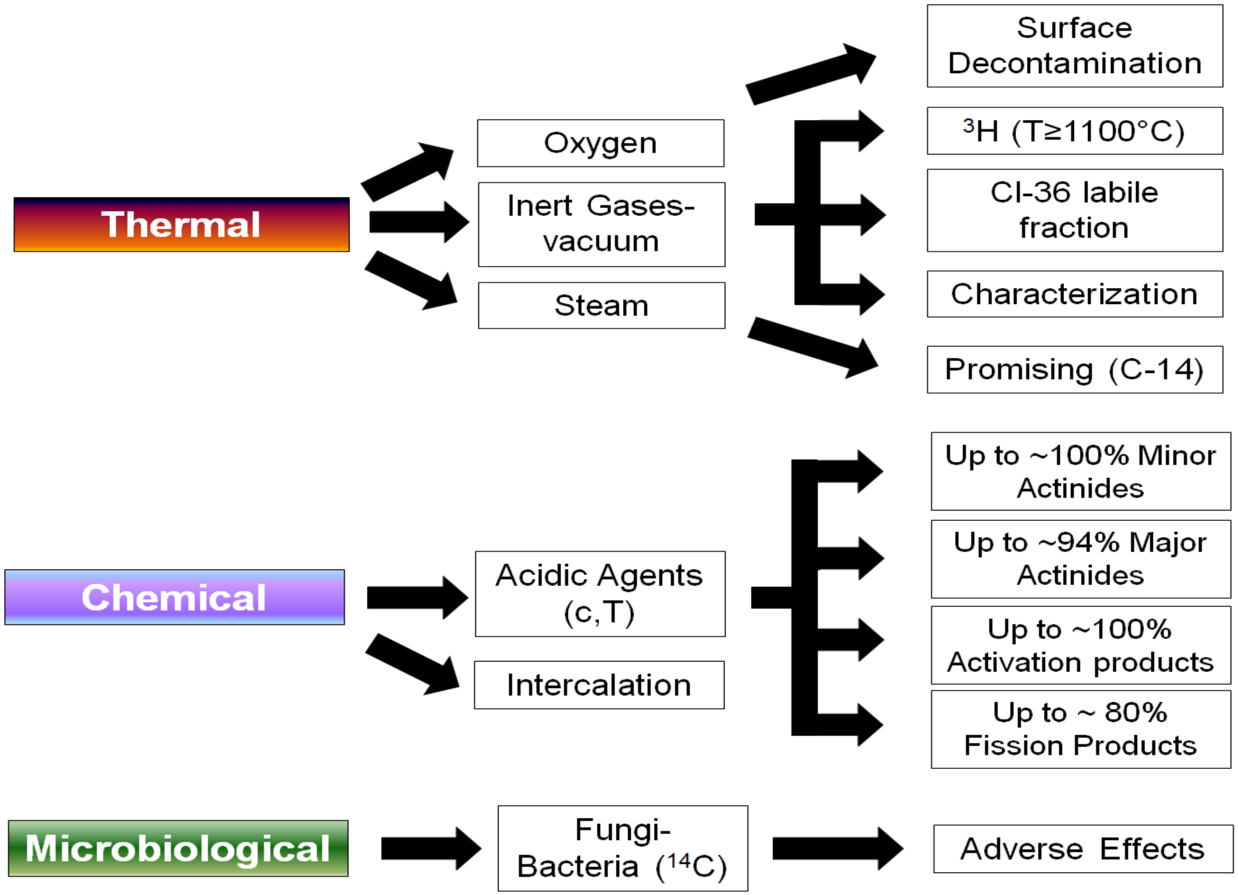
| Nuclide | Agent(s) used | Maximal Removed Fraction (%) |
|---|---|---|
| $^{60}Co$ | 3M HCl or $H_2SO_4$ | 90% |
| $^{152/154}Eu$ | Any acid+complexing agent | 100% |
| $^{134/137}Cs$ | $H_2SO_4$ + $H_3PO_4$ | 100% |
| $^{94}Nb$ | 3M HCl | 77% |
| Gross b | HCl+$H_2SO_4$ | 70% |

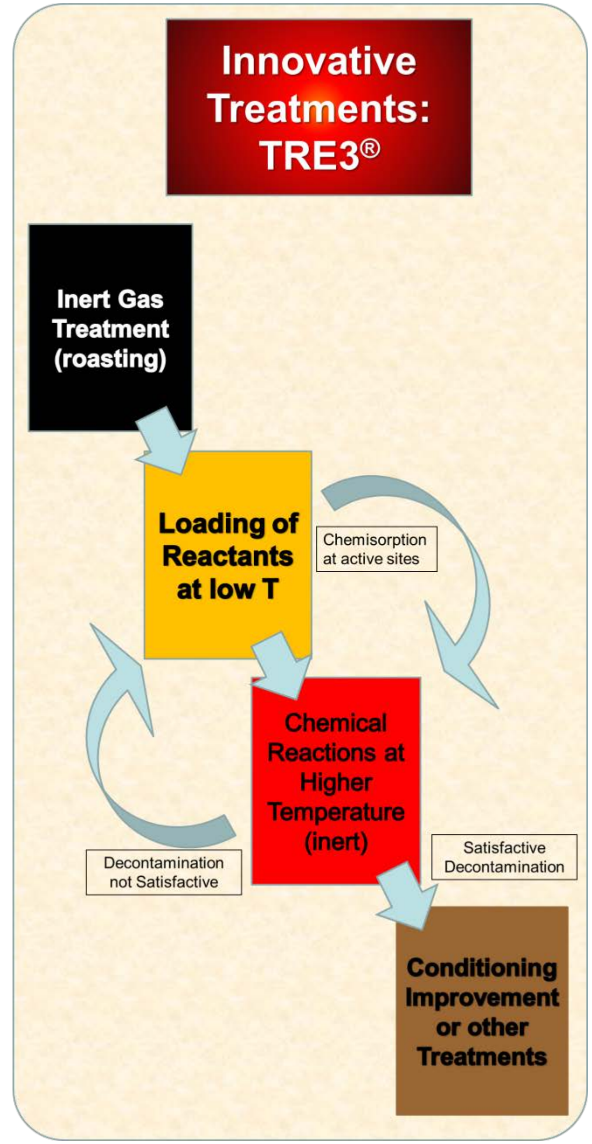
| Nuclide | Agent(s) used | Maximal Removed Fraction (%) |
|---|---|---|
| $^{241}Am$ | HCl or $H_2SO_4$ | 100% |
| $^{239/240}Pu$ | $H_2SO_4$ | 94% |
| $^{3}H$ | $H_2SO_4$+$HNO_3$ | 90% |
| $^{14}C$ | Organic solvents | 27% |




**New Option: Use of Intercalation Process**

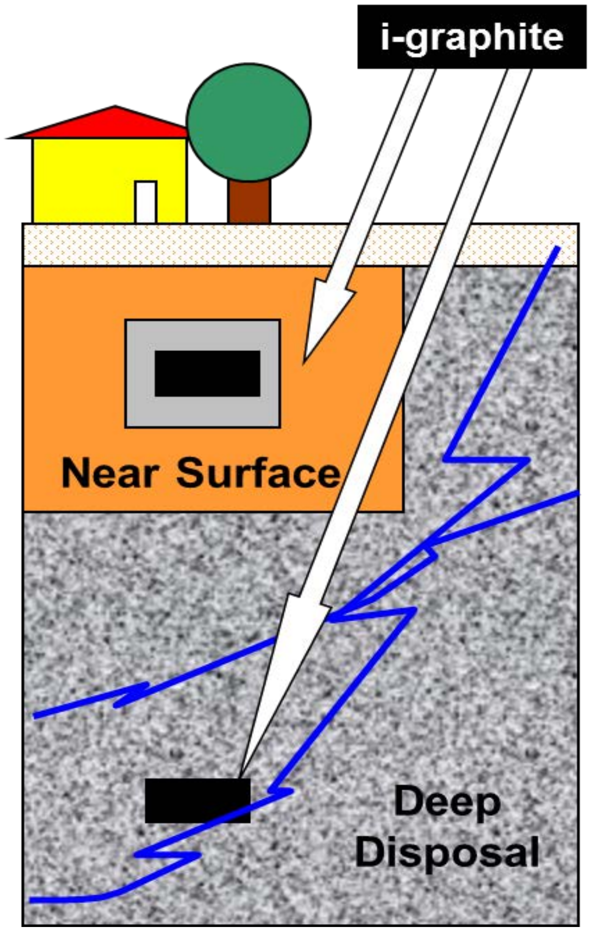
# Treatment Options




**Open Issues: - Process Optimisation to i-graphite grades**
**- Larger samples (Pilot scale)**

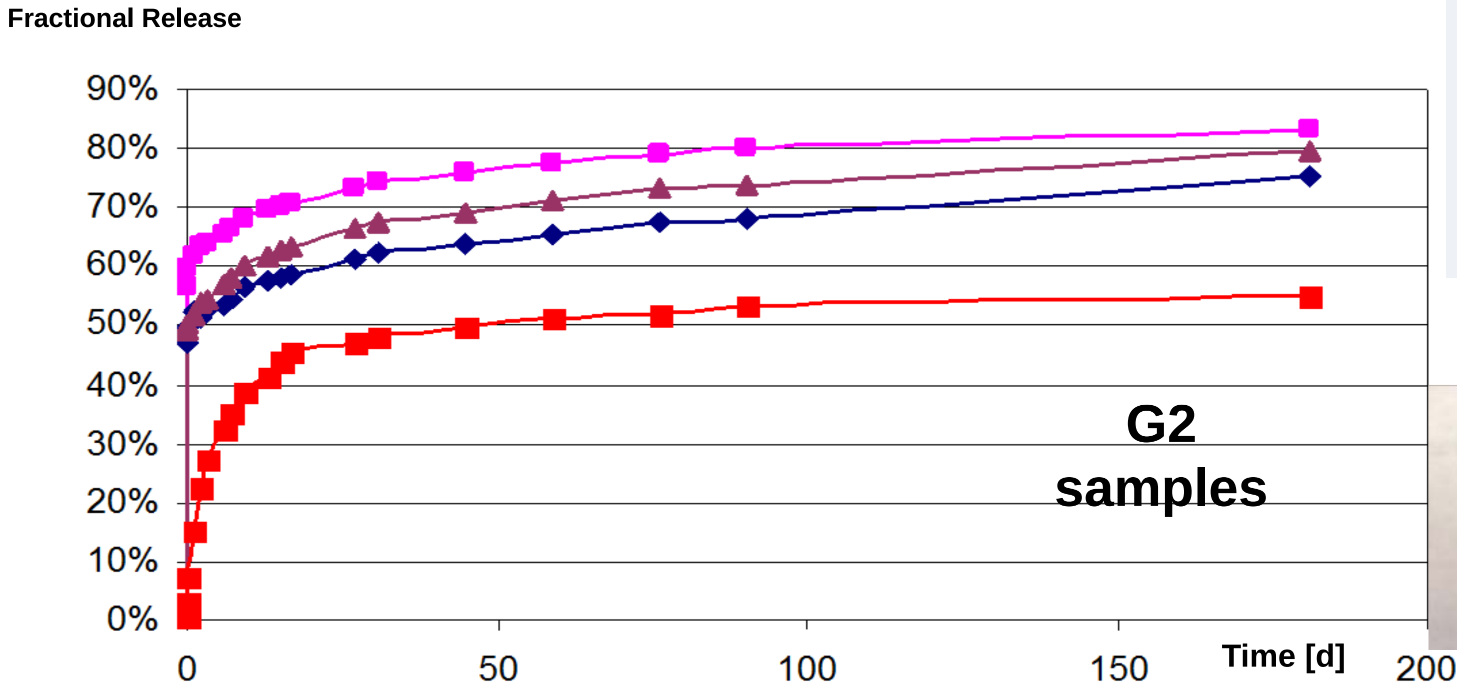
# Disposal issues

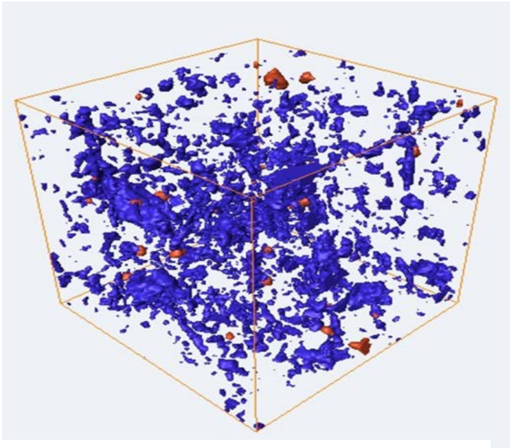



- ***Three disposal options***
  - *Surface / Near surface*
  - *Shallow disposal (< 200 m)*
  - *Deep geological disposal*
- **i-Graphite is a chemically inert & stable matrix**
- **Release kinetics of LLRN ($^{14}C$, $^{36}Cl$ etc)**
- **Inorganic & organic $^{14}C$ and $^{36}Cl$ releases**
- **Development of specific Waste Containers**
- **Geochemical Modelling of RN transport**
- **Repository Performance Assessment**
- **International Waste Acceptance Criteria**

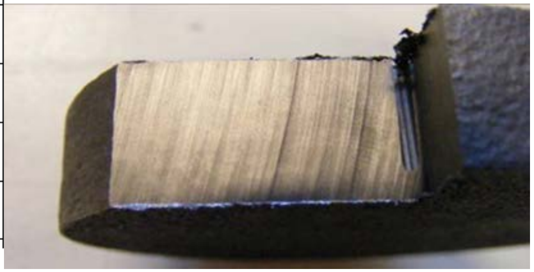
# Water penetration behaviour

- **Kinetics of water penetration for irradiated graphite**
  - **Water impregnation is fast (<100 days) and does not limit RN release**
    - **Water occupies between 50% to 80% of the total porosity**
      - **Dependent on graphite grades**



3D volume reconstruction of 1 mm³ BEPO Graphite showing porosity and impurities - UoM



**Alternative: Impermeable Glas / Graphite Matrix (IGM)**

# Leaching of $^{14}C$ and $^{36}Cl$

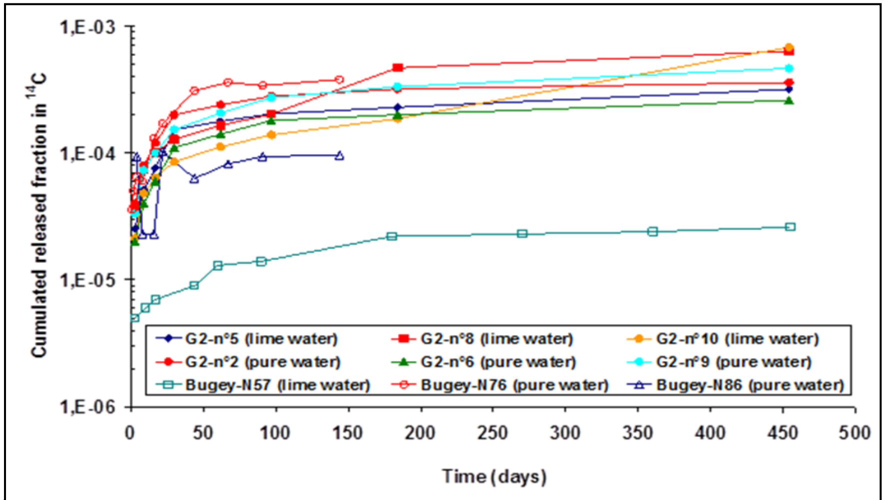
**Releases in 2 stages**

1. **Very rapid release kinetics (labile fraction)**
2. **Slow release kinetics (non-labile fraction)**

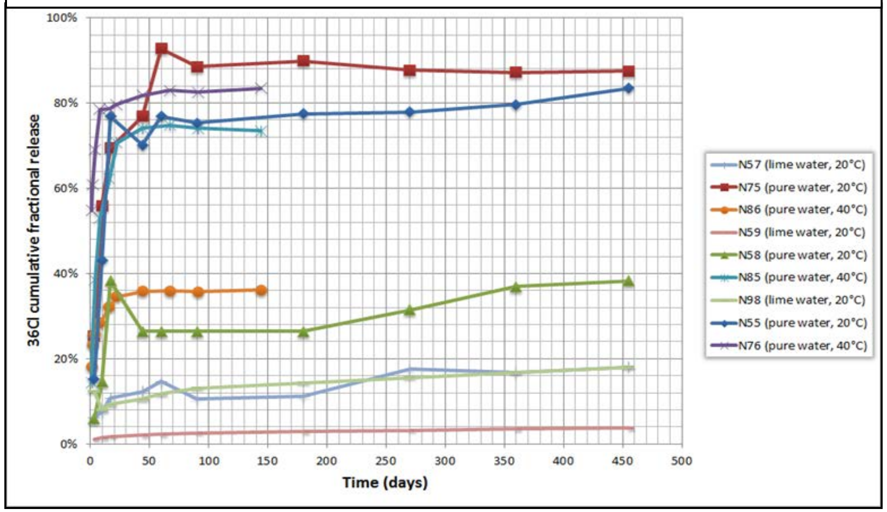
***R&D Challenge:***

- ***Determination of chemical speciation in gases and liquids***
- ***Removal of labile fractions by i-graphite treatment***
- ***Predictive analytical model for release mechanisms***

$^{14}C$




$^{36}Cl$



# Surface Disposal Facilities

## Case of El Cabril (ENRESA)

| Isotope | Radiological Inventory of El Cabril | Disposed Activity at El Cabril (14/10/2011) | Disposed vs. Radiological Inventory | Graphite Activity Per UNGG | Graphite vs. Inventory percentage |
|---|---|---|---|---|---|
| | (MBq) | (MBq) | (%) | (MBq) | (%) |
| H-3 | 2,0E+08 | 3,14E+06 | 1,57 | 4,22E+08 | 211 |
| C-14 | 2,0E+07 | 2,84E+06 | 14,2 | 1,65E+08 | 825 |
| Co-60 | 2,0E+10 | 2,64e+08 | 1,32 | 1,57E+07 | 0,08 |
| Ni-63 | 2,0E+09 | 9,13E+07 | 4,57 | 5,41E+07 | 2,7 |

- i-graphite from 1 UNGG exceeds Waste Acceptance Criteria!
- Removal of tritium / reduction of $^{14}C$ by thermal treatment
- Volume reduction beneficial
- Grinding/mixing with concrete
- Inclusion into pore-free matrix (e.g. IGM)

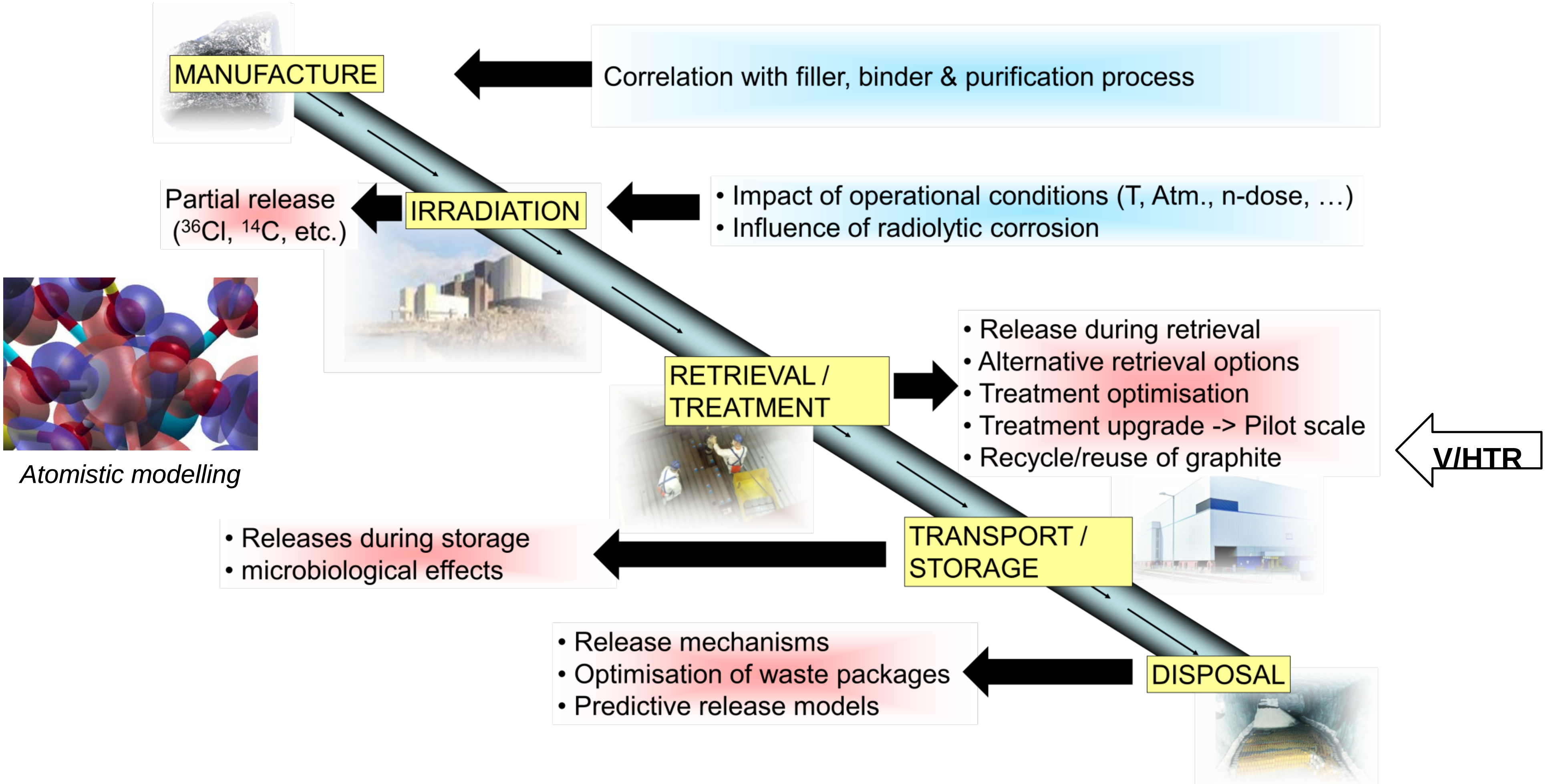
**Demonstration with i-graphite !**

# Deep Geological Disposal (UK)

- **Analyses not bonded to specific disposal concept, geospheres & depth**
- **Calculations made for UK inventory** (~95,000 tonnes, ~ 6000 TBq $^{14}C$, ~26 TBq $^{36}Cl$)
- **<u>Regulatory guidelines satisfied even with conservative assumptions</u> for vaults containing only packages of i-graphite wastes & backfill**
  - ***Predictable behaviour of i-graphite in isolation***
  - ***Improved performance (transport in gas not likely)***
  - ***Simplified safety arguments & safety case***
- **Difficult to generically assess <u>co-disposal with other ILW</u>**
  - ***Bulk gas generation (i.e. metals, organics, strongly irradiating wastes)***
  - ***Incorporation of $^{14}C$ in methane gas (e.g. by autrophic bacteria)***
  - ***Container integrity relevant***
- **Human intrusion relevant, but less significant than for other ILW** (strong γ & α)
- **Unlikely large scale disruption could lead to significant doses** ($^{14}C$ in food chain)

***<u>A wider range of disposal systems might be suitable if the residual uncertainties were further reduced !</u>***

# Challenging R&D Programme




## ‚New Waste' the more we know about it

CARBO SOLUTIONS