Treatment and Disposal of Irradiated Graphite and other Carbonaceous Waste

Werner von Lensa
Forschungszentrum Juelich GmbH, Germany

Co-authors:
D. Bradbury, Bradtec Decon Technologies;
G. Pina, CIEMAT; M.J. Grave, Doosan Babcock Energy;
D. Vulpius, FZJ; A.W. Banford, NNL; B. Grambow, Subatech
Facts & Partners

- Start: April 2008 (4.5 years now)
- Duration: 60 Months
- Total Budget: ~ 11 Mio. EURO
- EU-Funding: 6 Mio. EUR

29 (31) Partners, 10 EU Countries & RSA

- 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, FTMC, FZJ, INR, JRC, LEI, UK NNL, NRG, SCK-CEN, NECSA)
- universities (EMN, CNRS-ENS, IPNL, The University of Manchester)

Co-sponsors (ANDRA, EDF, HSE, NDA, ONDRAF, BMBF etc.)

-> Prototype of Programme-related R&D
Objectives

- Integrated waste management approach on
  - irradiated graphite (i-graphite) &
  - other carbonaceous waste (e.g. backed carbon, pyrocarbon)
- Development of ‘Best Practices‘ in
  - Retrieval of i-graphite from reactor core,
  - Characterization of i-graphite features incl. origin of contamination,
  - Treatment / purification options,
  - Re-use / Recycling of i-graphite for different purposes,
  - Storage and Disposal behaviour
- ’Toolbox‘ for economical, environmental & sustainable options for
  - Legacy waste of reactors facing decommissioning
  - Management of i-graphite from future V/HTR, MSR & Fusionreactors
The first nuclear chain reaction
2nd of December, 1942

Painting by Gary Sheahan

EURADISS, Montpellier, France, October 26, 2011
Historical GCR Milestones

1938  Discovery of Nuclear Fission by Hahn / Strassmann
1942  First Self-sustained Chain Reaction (E. Fermi)
1943  3,5 MW Graphite-moderated Production Reactor (ORNL)
1947  Graphite-moderated GCR at Brookhaven
1948  36 MW_th British Experimental Pile Operation (BEPO)
1950  160 MW_th Windscale Plutonium Production Reactors
1951-53 UK studies on CO₂-cooled MAGNOX Reactors
1956-59 Commissioning of four (commercial) Calder-Hall Reactors (240 MW_el total)
1956-68 Air-cooled 1,7 MW_el G-1 at Marcoule, France
1957  First Commercial GCR in France: 70 MW_el Chinon A1
1963  30 MW_el Advanced GCR (AGR) in Windscale (400°C -> 650°C)
1976  First Commercial AGR at Hinkley Point B (625 MW_el / 41,5 %)

Very FIRST GENERATION to be DECOMMISSIONED FIRST !!!
Graphite-moderated Reactors in EU

United Kingdom:
• 26 MAGNOX (270 – 1760 MWth) NPW
• 14 Advanced Gas-Cooled Reactors (~ 1500 MWth / Unit)
• All AGR in operation (i-graphite lifetime)
• diverse experimental facilities and 2 Windscale Piles

France:
• 6 Natural Uranium Gas-cooled Reactors (UNGG)
• 3 Plutonium Production Reactors
• 2 Experimental Piles plus graphite in Fast Reactors

additionally:
• 1 MAGNOX in Italy, 1 UNGG in Spain; 2 HTR in Germany
• 2 RBMK in Lithuania
• Numerous Material Test Reactors
Dimension of the Problem

- About **250 000 tons** already accumulated, worldwide
- Origin from different reactor types & retrieval options
  - MAGNOX, UNGG, AGR, HTR
  - RBMK, MTR
- Various graphite grades and impurities
- Partially stored Wigner Energy
- Varying content of long-lived radioisotopes
  - $^{14}$C plus $^{3}$H, $^{36}$Cl, $^{41}$Ca, $^{60}$Co, $^{79}$Se, $^{99}$Tc, $^{129}$I, $^{135}$Cs, $^{152}/^{154}$Eu etc.
- Diverging national classifications (ILW, LLW, LLLLW)
- Different i-graphite management strategies
- **R&D devoted to operation; NOT to decommissioning**
Large amount of graphite in pile
AVR decommissioning dominated by dust, high contamination and missing disposal concept:
- Grouting of internals, removal / storage of RPV
- Extremely High Cost

Underwater Fort Saint Vrain

Contamination dominates GLEEP

Radiation Dominates WAGR

RANGE OF SOLUTIONS
Characterisation Methods

- **Autoradiography** – visual representation of isotopic distribution and location
- **Optical microscopy** – detail the comparison between microstructure, pore size and filler distribution at low resolution
- **Electron Microscopy** including FIB and TEM,
- **Scanning Electron Microscopy and EDX** – elemental analysis and impurity distribution
- **Raman Spectroscopy** – structural characterisation, phase purity and crystallite size
- **X-ray powder diffraction analysis (XRD)** - crystallinity
- **X-ray Tomography** – porosity and location of high attenuation impurities, investigate density.
Synchrotron X-ray Tomography

- Experimental time at the Paul Scherrer institute, Swiss Light Source, to perform I-graphite experiments
- 3D reconstruction enables to differentiate Microstructure
  - Porosity
  - Matrix/Filler
  - Volume fraction
  - Other regions of density
    - High Attenuation
Secondary ion mass spectrometry (SIMS)
In-depth profiling of trace elements in graphite
-> Chemisorbed N, H, OH, O

X-ray photoelectron spectroscopy (XPS)
Identification of chemical bonds / binding energies

Prompt-gamma neutron activation analysis (PGNAA)
Non-destructive way to determine the concentration of trace elements

Gas chromatography (GC) with a scintillation detector
For measurements of radioactive gases containing H-3, C-14 and Kr-85, e.g. HTO, $^{14}$CO$_2$ etc.
Impact of the i-graphite structure?

- **Porosity** allows access to contamination within the pore system
  - During operation by reactive gases, e.g. formed by radiolysis
  - During treatment for extraction of radionuclides
  - During disposal by leachants

- **Filler** particles and **Binder** regions show different features regarding
  - impurities & resulting activation
  - Crystallinity & chemical reactivity
  - Different cokes, pitches etc.

- Large **Hetereogeneity** (hot spots)

- **Radiation Damage** (amorphisation)
Impact of the Graphite Surfaces

Plausible organic compounds forming on graphite surface due to oxygen adsorption [El-Genk 2011]

Strong Physi- & Chemisorption of Oxygen, Hydrogen, Nitrogen & CARBON on microscopic surfaces within the pore system

Idealised structure of graphene oxide [Hamilton 2009]
Chemisorption of gases on surface of pore system (e.g. H₂, O₂, N₂)

- Significant concentrations of nitrogen found by PGNAA

Hypothesis:

- $^{14}$C from nitrogen near to pore system surface
- $^{14}$C from $^{13}$C as interstitial in the graphite lattice (diffusion?)
- At least two different locations / chemical bonds

Similar observations for other radionuclides

- Organic chlorine in the bulk, inorganic forms at the inner surfaces
- Tritium as H-T, C-T, C-OT, hydrocarbons (isotope exchange !)
- Metals as carbides or ionic bonds
C-13 Activation Process

(LAMMPS, Potentials: AIREBO, LCBOP)
Impact of Activation Process?

- Relevant activation processes show significant recoil energies

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Max. released Energy (MeV)</th>
<th>Recoil Energy of Activation Product (keV)</th>
<th>Nucl. Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-3</td>
<td>6.25</td>
<td>7.0</td>
<td>$6\text{Li}(n,\alpha)\text{H}_3$</td>
</tr>
<tr>
<td>C-14</td>
<td>0.58 (p)</td>
<td>41.4</td>
<td>$14\text{N}(n,p)\text{C}_{14}$</td>
</tr>
<tr>
<td>C-14</td>
<td>8.17</td>
<td>2.60</td>
<td>$13\text{C}(n,\gamma)\text{C}_{14}$</td>
</tr>
<tr>
<td>O-17</td>
<td>2.42</td>
<td>0.19</td>
<td>$17\text{O}(n,\alpha)\text{C}_{14}$</td>
</tr>
<tr>
<td>Cl-36</td>
<td>7.80</td>
<td>0.91</td>
<td>$35\text{Cl}(n,\gamma)\text{Cl}_{36}$</td>
</tr>
<tr>
<td>Co-60</td>
<td>6.70</td>
<td>0.40</td>
<td>$59\text{Co}(n,\gamma)\text{Co}_{60}$</td>
</tr>
</tbody>
</table>

- Recoil energy breaking pre-existing chemical bonds
- Activation product is more or less delocated
- Ionized activation product can form new chemical bonds
Main features of i-graphite are already ‘manufactured’ into the material during the production process:

- Impurities are origin of neutron activation processes
- Locations of impurities determine location of activation products

Construction, Operation, Retrieval & Storage History?

- Manufacture History
- History during construction
- Operation History \((n, \text{atm},T)\)
- Storage History after irradiation

Investigation on Virgin Materials

Investigation on Radioactive Materials
Impact of operational conditions?

Neutron flux

Destructuration (some dpa)

Very disordered graphite

Temperature

Reordering

VS

Height (m)

10 m

100°C

Maximum

Minimum

Less disordered graphite

Moderator graphite

8 m

500°C

« Cold » zones of minimum flux :
Less structured: chlorine more accessible

« Hot » zones of maximum flux :
More structured: chlorine less accessible

EURADISS, Montpellier, France, October 26, 2011
Impact on Treatment and Disposal?

- **Exposed locations** of radionuclides at (pore) surfaces
- **Stable locations** within the crystallites
- **Migration** of interstitials to grain boundaries, influenced by radiation damage
- **Labile and stable** chemical forms

**Hypothesis:**

- Exposed and labile fractions may be removed by treatment and/or leaching
- Stable fractions may withstand long-term leach attack

Treatment Options

- Treatment is addressing a spectrum of radionuclides ($^3$H, $^{14}$C, $^{36}$Cl, $^{60}$Co, U, Pu etc)
- Different treatment options
  - Physical (roasting)
  - Chemical (gases, liquids)
  - Electrochemical
  - Microbiological
- Significant decontamination factors achieved
The highest enrichment rates (more than 200:1) are attained by thermal treatment in inert gas (→ massive sample, 1300 °C, nitrogen).

Massive samples are more effective than pulverised samples.
The highest enrichment rates (more than 20:1) are attained by thermal treatment in inert gas (→ massive sample, 1060 °C, argon).

Massive samples are more effective than pulverised samples.
Disposal Behaviour

- Three disposal options
  - Surface / Near surface
  - Shallow disposal (< 200 m)
  - Deep geological disposal
- Release kinetics of LLRN ($^3$H, $^{14}$C, $^{36}$Cl etc)
- Development of specific Waste Containers
- Inorganic & organic $^{14}$C and $^{36}$Cl releases
- Impermeable Glas / Graphite Matrix
- Geochemical Modelling of RN transport
- Repository Performance Assessment
Concluding Remarks

- Dissemination activities
  - within Large-Scale Collaborative Project
  - Collaboration with EPRI and IAEA
  - Publications, Conferences (>50)

- Strong Education & Training component (> 30 BSc, MSc, PhD)

- CARBOWASTE is already PROGRAMME-RELATED
  - Significant contributions from national programmes (UK, FR, DE, ES, BE …)
  - Strong inclusion of stakeholders (Utilities, WMO, industry, research, …)

- Near-term Implementation (FR, LIT, UKR, UK, ES, IT, DE, BE, …)
  -> Confederation of Implementation Phase ???

I-graphite management remains a technical & scientific challenge!
First CARBOWASTE Baby

Thanks for Your Attention!

EURADISS, Montpellier, France, October 26, 2011