Development of Technologies and Management Options for Irradiated Graphite and Carbonaceous Waste

AtomEco 2013 (Moscow)

05 November 2013 | Werner von Lensa, Corrado Rizzato, Natalia A. Girke, Hans- Jürgen Steinmetz
Reactor Graphite - Dimension of the Problem

- About **250.000 Mg** already accumulated, worldwide
- Origin from different reactor types & retrieval option
  - (MAGNOX, UNGG, AGR, HTR, RBMK, MTR, TRIGA etc.)
- Types and grades with various impurities
- Individual irradiation „history“ and contamination sources
- Varying content of long-lived radioisotopes
  - (Radiocarbon $^{14}$C plus $^{36}$Cl, $^{3}$H, $^{129}$I, $^{99}$Tc, $^{79}$Se, $^{135}$Cs etc.)

- Significant amounts of Radiocarbon $^{14}$C (5730 y half-life)
  - From $^{14}$N(n,p)$^{14}$C (approx. 90%, 1,81 barn)
    Nitrogen as nitrides and N$_2$ absorbed in graphite matrix
  - From $^{13}$C (1,1%; 0,0009 barn) and $^{17}$O (0,037%, 0,235 barn)
Reactor Graphite – German Situation

More than 1,000 Mg of graphite (including carbon bricks)

Operating and decommissioned reactors

→ Power Reactor THTR

→ Research Reactors AVR, DIDO, MERLIN, TRIGA-MHH, FRF, RFR, FRM, BER etc.

### AVR - Specific inventory of components in Bq/g ¹)

<table>
<thead>
<tr>
<th></th>
<th>Graphite (65Mg)</th>
<th>Carbon bricks (158 Mg)</th>
<th>Steam generator (42,5 Mg)</th>
<th>Thermal shield (141,5 Mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-14</td>
<td>7,1</td>
<td>1,8 E+06</td>
<td>4,2 E+01</td>
<td>6,2 E+01</td>
</tr>
<tr>
<td>H-3</td>
<td>5,5</td>
<td>1,8 E+07</td>
<td>6,4 E+04</td>
<td>9,2 E+04</td>
</tr>
<tr>
<td>Co-60</td>
<td>8,0</td>
<td>8,2 E+05</td>
<td>2,8 E+04</td>
<td>3,9 E+04</td>
</tr>
<tr>
<td>Cl-36</td>
<td>2,3</td>
<td>3,7 E+02</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cs-137</td>
<td>1,0</td>
<td>2,0 E+04</td>
<td>7,0 E+05</td>
<td>3,0 E+03</td>
</tr>
<tr>
<td>Sr-90</td>
<td>1,0</td>
<td>5,0 E+04</td>
<td>7,1 E+05</td>
<td>1,0 E+03</td>
</tr>
</tbody>
</table>

¹) Source: PKS
Current disposal option in mine KONRAD

KONRAD
LAW/MAW
former iron ore mine
licensed, operating ≥ 2018

Source: www.deutschland.de/aufeinenblick/deutschlandkarte
Activity limits for C-14 in mine KONRAD

Volume repository „KONRAD“: 303.000 cbm
Total C-14 activity permitted: 4 E+14 Bq

Average activity per cbm: 1,32 E+09 Bq/cbm

Typical volume of „Konrad-Container“ (Typ V): ca. 10 cbm

average load of typical waste container: 1,32 E+10 Bq

In addition limits from 3 safety analyses have to be considered:
⇒ Most restrictive 14C limits for internal operation

<table>
<thead>
<tr>
<th>C-14 (condition)</th>
<th>Limited activity* [Bq / Container]</th>
</tr>
</thead>
<tbody>
<tr>
<td>non specified</td>
<td>1,8 E+08 – 2,0 E+08</td>
</tr>
<tr>
<td>volatile fraction (&lt; 1 % and ≤ 10 %)</td>
<td>1,8 E+09 – 2,0 E+09</td>
</tr>
<tr>
<td>low volatile fraction (≤ 1 %)</td>
<td>1,8 E+10 – 2,0 E+10</td>
</tr>
</tbody>
</table>

*depending on tightness of waste package

For optimum usage most of 14C should be on hand as < 1 % volatile

Source: Ironwork Bassum
What does that "de facto" mean?

- How many containers do we need to dispose 4E+14 Bq of C-14???

<table>
<thead>
<tr>
<th>C-14 (condition)</th>
<th>Limited activity [Bq/container]</th>
<th>Hypothetical waste containers for 4 E+14 Bq</th>
</tr>
</thead>
<tbody>
<tr>
<td>non specified</td>
<td>1.8 E+08</td>
<td>2.222.000</td>
</tr>
<tr>
<td>volatile (&gt; 1 % and ≤ 10 %)</td>
<td>1.8 E+09</td>
<td>222.000</td>
</tr>
<tr>
<td>volatile (≤ 1 %)</td>
<td>1.8 E+10</td>
<td>22.000</td>
</tr>
</tbody>
</table>

For disposal of $^{14}$C waste KONRAD can only be used effectively if condition of $^{14}$C meets the requirement: low volatile fraction ≤ 1%
CARBODisp:
Disposal of Irradiated Graphite in Mine KONRAD

**Aim:** Development of concepts and methods for the final disposal of irradiated graphite in KONRAD (or other possible German repositories)

**Funded by BMBF, 2010-2014, Budget ~ 1. Mio. Euro**

**Objectives**
- Bond type of $^{14}$C in i-graphite and release form
- Release factors, rates and paths
- Release rates from conditioned waste packages under various storages and handling conditions

**Scientific cooperation with MEPhI (Moscow)**

**Supported by the Russian-German committee of Rosatom and BMWi**

A. Bushuev, V. Zubarev, E. Petrova et al.
Comparative measurements on C-14 release (MEPhI)

Graphite from air cooled reactor
Storage approx. 9-10 years (NPT), only quantitative, no systematical analysis

<table>
<thead>
<tr>
<th>Sample Nr.</th>
<th>Data</th>
<th>C-14 [$10^6$ Bq/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2001</td>
<td>0,50</td>
</tr>
<tr>
<td></td>
<td>2009</td>
<td>0,44</td>
</tr>
<tr>
<td>2</td>
<td>1999</td>
<td>1,63</td>
</tr>
<tr>
<td></td>
<td>2010</td>
<td>1,63</td>
</tr>
<tr>
<td>3</td>
<td>1999</td>
<td>1,62</td>
</tr>
<tr>
<td></td>
<td>2010</td>
<td>1,47</td>
</tr>
<tr>
<td>4</td>
<td>1999</td>
<td>0,80</td>
</tr>
<tr>
<td></td>
<td>2010</td>
<td>0,96</td>
</tr>
<tr>
<td>5</td>
<td>2001</td>
<td>0,37</td>
</tr>
<tr>
<td></td>
<td>2010</td>
<td>0,43</td>
</tr>
<tr>
<td>6</td>
<td>2001</td>
<td>0,40</td>
</tr>
<tr>
<td></td>
<td>2010</td>
<td>0,44</td>
</tr>
</tbody>
</table>

No changes observed within the accuracy of the method
Releases under different Storage Conditions

Releases under basic pH?
Releases under moist air?

What is the impact of the storage conditions?
And sample form? (block, powder, pellet)

<table>
<thead>
<tr>
<th>Release of C-14</th>
<th>Relative Fractional release [%]</th>
<th>Time [y]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>0.0018</td>
<td>1.56</td>
</tr>
<tr>
<td>Moist Air</td>
<td>0.07629</td>
<td>1.56</td>
</tr>
<tr>
<td>Packed in PE</td>
<td>0.00730</td>
<td>0.94</td>
</tr>
</tbody>
</table>
Nuclear Graphite: Influencing Variables

- **MANUFACTURE**
  - Impurities from raw materials/air/purification

- **IRRADIATION**
  - Partial release ($^{36}$Cl, $^{14}$C)
  - $^{36}$Cl and $^{14}$C formation
  - Additional precursors (N2)

- **RETRIEVAL / TREATMENT**
  - Releases of $^{14}$C, $^{36}$Cl
  - Recycle/reuse of graphite

- **TRANSPORT / STORAGE**
  - Releases of $^{14}$C, $^{36}$Cl
  - Radioactive decay
  - Cross-contamination (mixed waste)

- **DISPOSAL**
  - Releases of $^{14}$C, $^{36}$Cl
  - Radioactive decay
CARBOWASTE:
Treatment and Disposal of Irradiated Nuclear Graphite and other Carbonaceous Waste

Coordinated by Dr. Werner von Lensa

Objectives:
1. Retrieval and Segregation
2. Characterization and Modelling
3. Treatment Options
4. Re-use and Recycle
5. Disposal Behaviour

- Development of „Best Practices“
- Providing a „Toolbox“ of sustainable and economic options for decommissioning and management of i-graphite
Carbowaste: Facts and Partners

- **Start:** April 2008
- **Duration:** 60 Months \(\text{(48)}\)
- **Total Budget:** \(\sim 11\) Mio. EURO
- **EU-Funding:** 6 Mio. EUR

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, \(\text{(EPRI)}\))
- **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)
- **Co-sponsors** (ANDRA, EDF, HSE, NDA etc.)
Manufacture of Nuclear Graphite

Several influencing variables even in virgin material

Different graphite grades result in different i-graphite characteristics
Impact of Operational Conditions?

- Neutron flux
- Temperature

<table>
<thead>
<tr>
<th>Neutron flux</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>VS</td>
<td>Reordering</td>
</tr>
<tr>
<td>Height (m)</td>
<td>Width (m)</td>
</tr>
<tr>
<td>10 m</td>
<td>8 m</td>
</tr>
<tr>
<td>Maximum</td>
<td>Minimum</td>
</tr>
<tr>
<td>100°C</td>
<td>500°C</td>
</tr>
</tbody>
</table>

- Deuteration (some dpa)
- Very disordered graphite
- Less disordered graphite

- Wigner Energy
  - strongly bonded with T

- Corrosion
  - Release of impurities
  - Release of activation products

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

Nuclear graphite is an heterogeneous material very far from mono-crystalline graphite: high porosity, polycrystalline material with well graphitized and amorphous zones

More a graphitized carbon/carbon composite!

⇒ Characterization of its multiscale organisation not trivial!
Irradiation-Induced Structural Changes

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

Point Defects

**Fig. 38.** Irradiation damage in PGA graphite irradiated at 650°C to ~3 × 10^21 neutrons cm^-2 (g = [10\(\bar{1}\)])
Treatment Options

- **Purpose:**
  - Selective removal of (volatile) radionuclides / Decontamination
  - Improving the disposal behaviour
  - Closing the Graphite/C-14-cycle (Recycling)

- **Options:**
  - Thermal Treatments
    - High/Low Temperature Gas Oxidation (O2) (FZJ)
    - Low Temperature-Pressure Gas Oxidation (O2) (FZJ)
    - Steam Reforming (Studsvik)
    - Thermal Reaction of reloaded reactants (FZJ)
  - Chemical Treatments
    - Wet Oxidation (Ciemat, ENEA, INR)
    - Acid solution treatment (Subatech)

- **Conditioning:**
  - Pore Sealing with glass (Impermeable Glass Matrix)
  - Pore Closing with Silicone
  - Embedding in Geopolymer
Carbon-14 Release by Thermal Treatment

<table>
<thead>
<tr>
<th>Sample [No.]</th>
<th>Heating Temperature [°C]</th>
<th>C-14 Content [Bq/g]</th>
<th>Release C-14 [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NPT (start)</td>
<td>7.44E+05</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>1500</td>
<td>6.44E+05</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1500</td>
<td>6.74E+05</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>NPT</td>
<td>9.91E+05</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>1500</td>
<td>1.01E+06</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1500</td>
<td>8.99E+05</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>NPT (start)</td>
<td>9.62E+05</td>
<td>(-1)</td>
</tr>
<tr>
<td></td>
<td>1500</td>
<td>1.06E+06</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1500</td>
<td>8.83E+05</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>NPT (start)</td>
<td>1.34E+06</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>2200</td>
<td>1.30E+06</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2200</td>
<td>1.25E+06</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>NPT (start)</td>
<td>1.28E+06</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>2200</td>
<td>1.20E+06</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2200</td>
<td>1.24E+06</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>NPT (start)</td>
<td>1.17E+06</td>
<td>(-2)</td>
</tr>
<tr>
<td></td>
<td>2200</td>
<td>1.17E+06</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2200</td>
<td>1.21E+06</td>
<td></td>
</tr>
</tbody>
</table>

accuracy: +/- 10 %

No significant release has been observed within the precision of the method. More Systematic investigations are necessary for better understanding.
Carbon-14 Release by Thermal Treatment (inert)

- Oxidants already adsorbed on the graphitic matrix (soon exhausted)
- Inert Atmosphere with low amount of impurities (up to 20 ppm O₂)*

**Limitation:**
Exhaustion of Adsorbed Reactants

*Depending on the experimental equipment implied*
Carbon-14 Removal by Thermal Treatment (steam)

Fractional release of $^{14}$C [%]

Fractional release of total C [%]

Effective on Removal but HIGH mass losses compare to the previous case
New Approach

- C-14 removal is a local effect: removed by oxidation
- Continuous provision of reactants is not efficient (temperature vs reaction rate)

⇒ Separate reactant loading and chemical reactions
Conclusions

The CARBOWASTE Project:

• Revealed that the relevant RN exist in different chemical forms & locations
• Explored the existance of mobile & stable / less mobile fractions of RN
• Provided a much better understanding of RN behaviour in i-graphite
• Offers a 'Tool Box' for i-graphite management strategies on MCDA basis
• Showed the impact of 'Manufacture and Operation Histories' on i-graphite
• i-graphite disposability is supported by the generated performance assessment data
• Treatment/decontamination have been demonstrated as viable options

Created a basis for innovative i-graphite management options

CarboSOLUTIONS
Thanks for Your Attention
CarboSOLUTIONS
Implementing i-graphite Waste Management

- 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,
  - Storage, Conditioning and Disposal,
  - Recycling of i-graphite for future V/HTR, MSR & Fusion reactors

- Synergies across near & medium-term decommissioning projects

⇒ High Relevance within FP8