$^{14}$C Enrichment of Surface Deposits on Oldbury Reactor Core Graphite Determined by Secondary Ion Mass Spectrometry and Thermal Oxidation/Liquid Scintillation Techniques

Liam Payne, Peter J. Heard and Thomas B. Scott
Irradiated graphite

- Historically, the United Kingdom has built a number of graphite moderated reactors.
- Many of these reactors are in the process of decommissioning.
- Majority of the graphite classified as Intermediate Level Waste (ILW).
- Significant quantity for eventual disposal in a Geological Disposal Facility (GDF)
Sample provenance

- 49 samples
  - 6 x fuel channels
  - 2 x interstitial channels
- Oldbury reactor one
- Before receiving at UoB:
  - All samples had Bulk Density by Immersion (BDI)
  - One sample (Q15C5 6L/1) analysed for open pore volume and differential thermal oxidation

Blue = Fuel Channel
Red = Interstitial Channel
Scanning Electron Microscopy

Channel Wall Face

Inner Brick
Scanning Electron Microscopy

Channel Wall Face

Inner Brick
SEM-FIB

Channel Wall Face

Inner Brick
Channel Wall Face

Inner Brick

SEM-FIB
Secondary Ion Mass Spectrometry

- Incident gallium ion beam sputters the sample surface
- Secondary ion mass fragments generated
- Mass/Charge (m/z) ratio and intensity measured using Magnetic Sector mass spectrometer
- Corrections needed for interference peaks
- Low spectral resolution compared to commercial instruments
- **Ability to analyse radioactive samples**
SIMS Results

M10
4L: 55.3 ± 6.7 ppm
**EDND: 38.18**
7L: No coating present (< LOD)
**EDND: 42.14**

J01A4
4U: No coating present (< LOD)
**EDND: 15.42**
7U: No coating present (< LOD)
**EDND: 15.55**

F16
4L: 26.1 ± 3.1 ppm
**EDND: 38.18**
7L: 22.7 ± 5.5 ppm
**EDND: 42.14**

L13B2
4L: 28.8 ± 4.3 ppm
**EDND: 45.22**
7L: 12.8 ± 1.5 ppm
**EDND: 49.92**

Q15C5
2U: 20.8 ± 3.9 ppm
**EDND: 26.54**
7L: 13.2 ± 3.9 ppm
**EDND: 51.22**
11U: 5.3 ± 1.8 ppm
**EDND: 15.48**

N15A4
4U: 24.9 ± 8.9 ppm*
**EDND: 28.78**
8U: 19.2 ± 1.1 ppm
**EDND: 26.49**

J15B5
4L: 28.5 ± 4.9 ppm
**EDND: 45.52**
7L: 6.6 ± 0.6 ppm
**EDND: 49.92**

E19B5
4U: 24.6 ± 0.8 ppm
**EDND: 26.05**
7U: 5.4 ± 1.4 ppm
**EDND: 23.77**

*Indicates thin coating sample

EDND: Equivalent DIDO Nickel Dose
**ppm: Parts Per Million**
SIMS-Conclusions

- Inner brick slices give results below the limits of detection (estimated at approximately 2 ppm)
- Channel wall faces appear to be $^{14}\text{C}$ enriched when deposit is present
  - 5-60 ppm
  - Samples lower in the channel appear to have higher concentration
  - Does not appear to be correlated with lifetime neutron dose (EDND)
- Ion maps show the $^{14}\text{C}$ is uniformly distributed in the deposit

For full details see: L. Payne, P. J. Heard and T. B. Scott. “Enrichment of C-14 on surface deposits of Oldbury reactor graphite investigated with the use of Magnetic Sector Secondary Ion Mass Spectrometry (MS-SIMS).” WMSymposia2015 proceedings
Thermal Oxidation/LSC

- Oxidation Tube
- Air Supply
- Furnace
- Flow Meter
- Wash Bottle
- Bubbler System
Thermal Oxidation/LSC

Experimental run 1:
• 450 °C for 50 hours
• 50 mL/min air
• Copper catalyst
• Aliquots taken at 0, 1, 2, 3, 5, 8, 10, 25, 35 and 50 hours
• Counted using LSC for 60 minutes

Experimental run 2:
• 600 °C for up to 145 hours (full oxidation)
• 50 mL/min air
• Copper catalyst
• Aliquots taken at 0, 1, 2, 3, 5, 7 hours and others up to final duration (depending on lab access)
• Counted using LSC for 60 minutes
Thermal Oxidation/LSC

Red - 600 °C
Black - 450 °C

Q15C5 2U Slice 1

Q15C5 2U Slice 2

Q15C5 7L Slice 1

Q15C5 11U Slice 1
450 °C

Q15C5 2U Slice 1

Q15C5 2U Slice 2

Q15C5 7L Slice 1

Q15C5 11U Slice 1
600 °C

Q15C5 2U Slice 1

Q15C5 2U Slice 2

Q15C5 7L Slice 1

Q15C5 11U Slice 1
Activity per mass

![Graph showing Activity per mass](image)

- **$^{14}$C activity (Bq/g)**
- **Temperature (°C)**

**Legend:**
- Q15C5 2U 1
- Q15C5 2U 2
- Q15C5 7L 1
- Q15C5 11U 1
Total activity

$^{14}\text{C}$ activity (Bq)

Temperature (°C)

- Q15C5 2U 1
- Q15C5 2U 2
- Q15C5 7L 1
- Q15C5 11U 1
Comparison between SIMS/LSC

Mass of $^{14}$C (g) = Activity of $^{14}$C (Bq)/Specific activity of $^{14}$C ($1.65 \times 10^{11}$ Bq/g)

$^{14}$C concentration (ppm) = Mass of $^{14}$C (g)/Mass of material (g)

<table>
<thead>
<tr>
<th>Sample</th>
<th>$^{14}$C concentration SIMS (ppm)</th>
<th>$^{14}$C concentration LSC (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q15C5 2U Slice 1</td>
<td>20.8 ± 3.9</td>
<td>20.9</td>
</tr>
<tr>
<td>Q15C5 2U Slice 2</td>
<td>4.1 ± 3.4</td>
<td>2.8</td>
</tr>
<tr>
<td>Q15C5 7L Slice 1</td>
<td>13.2 ± 3.9</td>
<td>9.9</td>
</tr>
<tr>
<td>Q15C5 11U Slice 1</td>
<td>5.3 ± 1.8</td>
<td>3.5</td>
</tr>
</tbody>
</table>
Thermal Oxidation/LSC
Conclusions

• Rapid initial release of $^{14}$C at 450 °C from channel wall face samples with significant deposit.
  • Inner brick sample still shows significant $^{14}$C release at 450 °C
    • Adsorbed precursor species
• Initial release of $^{14}$C at 600 °C from all samples
  • Surface (and subsurface) complexes from coolant gas
• Slow later release of $^{14}$C at 600 °C from all samples
  • Precursor species located in the graphite lattice
Conclusions

• Samples exposed to channel wall face (usually) have a pronounced carbonaceous deposit present

• Inner brick samples do not have such a deposit but have microstructural changes present associated with a lifetime in a nuclear reactor

• SIMS and LSC analysis highlights a relative enrichment in $^{14}$C on the channel wall face deposits.
  • This enrichment appears to be influenced by location within the reactor but not with lifetime neutron dose

• $^{14}$C located in this deposit could be more labile than $^{14}$C located in bulk graphite
Acknowledgements

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SIMS - Irradiated Graphite

Counts vs. m/z

- 16 = O⁻
- 24 = $^{12}$C₂⁻
- 26 = $^{12}$C$^{14}$C⁻
- 28 = $^{14}$C$^{14}$N⁻
- 28 = $^{12}$C$^{16}$O⁻
SIMS- Ratios

- **m/z 14:**
  - $^{14}\text{C}$
  - $^{14}\text{N}$
  - $^{12}\text{CH}_2$

- **m/z 28:**
  - $^{14}\text{C}_2$
  - $^{14}\text{C}^{14}\text{N}$
  - $^{14}\text{C}^{12}\text{CH}_2$
  - $^{12}\text{C}^{16}\text{O}$
  - $\text{N}_2$
  - $^{12}\text{CH}_2\text{N}$
  - Si

More possible $^{14}\text{C}$ containing species
Can investigate effects of oxygen
EDX data suggest these are not present
- Isobaric mass interference effects still present in raw spectra
- Geometrical and location effects on signal
  - use of ratios negates these effects
    - 28:24
    - 16:24
Irradiated PGA graphite samples

- Depth profile 1800 seconds on 300 µm² area
- Depth approximately 300nm
- Six repeats of different areas on each surface
- Ratios calculated
  - 28:24 (¹⁴C₂:¹²C₂)
  - 16:24 (¹⁶O:¹²C₂)
  - 24:(24+26)(¹²C₂:¹²C₂+¹²CN)
**SIMS- Concentration Calculation**

- Linear regression performed on oxygen experiment data
- Difference calculated between \( x_1 \) and \( x_0 \) at point \( y_1 \)
- Calculated difference in parts per million
- Corrected for CN contribution

**ASSUMPTIONS**

- Signal arising from \(^{12}C_2^-\) is constant
- CO species signal generated by injecting oxygen is similar to that found if oxygen is already present
- Corrected signal arising at 28 Da is due to \(^{14}C_2^-\)