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FROM RESEARCH TO INDUSTRY



LEACHING OF UNGG GRAPHITE : STUDY OF ^{36}Cl BEHAVIOUR

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SCIENTIFIC BASIS FOR NUCLEAR WASTE MANAGEMENT XXXIX

2ND TO 6TH NOVEMBER 2015

1- Commissariat à l'Energie Atomique et aux énergies alternatives (C.E.A.) –
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Chlorine 36 leaching data	P.05
Interpretation	P.06
Conclusion	P.08

■ Nuclear graphite waste in France

- 9 UNGG reactors (graphite moderated, fueled with natural uranium, CO₂ cooled)
- 23000 t of irradiated graphite => 100 000 m³ of conditioned waste in cementitious packages
- Nuclear graphite are classified as “**Long Life Waste – Low Level**” (¹⁴C, ³⁶Cl ..)
- 81% of the graphite still in reactor waiting for dismantling

The disposal behavior of the radionuclides is one of the main issues when considering graphite waste long-term management scenarios

■ Disposal studies

A “leaching test” program in accordance with EDF, ANDRA and CEA was initiated in 2008

- Objective : **characterize ³⁶Cl source term** (leaching rate) on irradiated graphite.
³⁶Cl is the main radionuclide which can contribute to the long term radiological impact of graphite in disposal due to his long lifetime, high mobility and solubility
- Methodologies : CEA develop leaching procedure optimized for ³⁶Cl measurement (similar to AIEA standards) with those followed specifications:
 1. Sampling times are defined to focus on diffusion mechanism and water uptake
 2. Analytical methodology was optimized to measure the ³⁶Cl

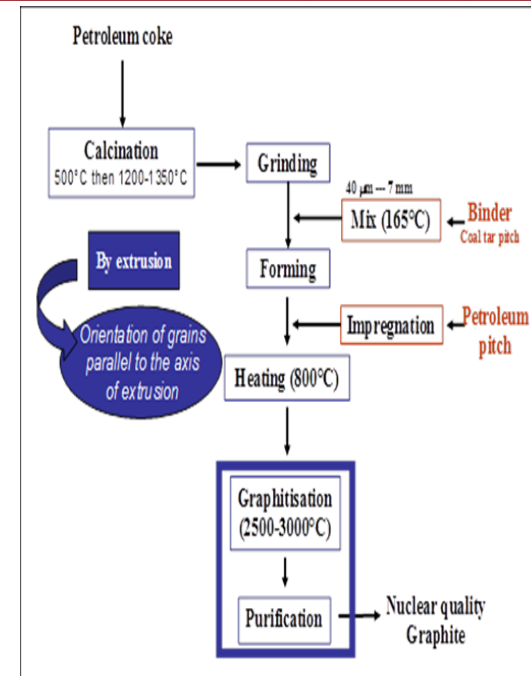
Origin of natural chlorine in nuclear graphite

- As an **impurity in the basic materials** used for the manufacture (Coke, Coal tar pitch, cleaning agents (NaF, MgF₂..),...)
 - Brought by **air pollution** (end of the manufacture, during storage)
 - Present at low level in the coolant gas (Air, CO₂)
- Cl in nuclear graphite are around 5 to 40 ppm

Origin of ³⁶Cl (long live radionuclide 3.10⁵y, β⁻)

- Production
 - Direct activation of ³⁵Cl (77,5%) 44 barns
 - Direct activation of ³⁹K (93,25%) 0,004 barns
 - Indirect activation of ³⁴S (4,2%) 0,34 barns

=>**³⁵Cl(n,g)³⁶Cl** is the predominant reaction for the formation of ³⁶Cl in irradiated graphite but with nuclear recoil ³⁶Cl location should be different from ³⁵Cl initial position (atoms are 'displaced', some maybe re-form covalent bonds =>different speciation of ³⁶Cl and ³⁵Cl)
=> ³⁶Cl activity **in French i-graphite is very low but with a huge variability** (1-10³ Bq/g) and a specific analytical procedure must be used (with low detection limit)



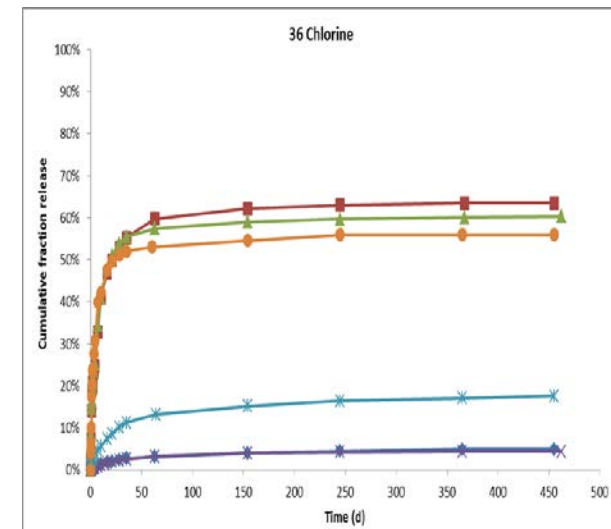
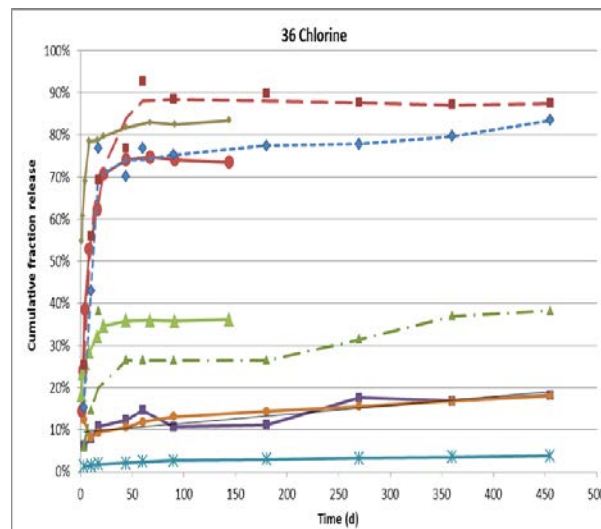
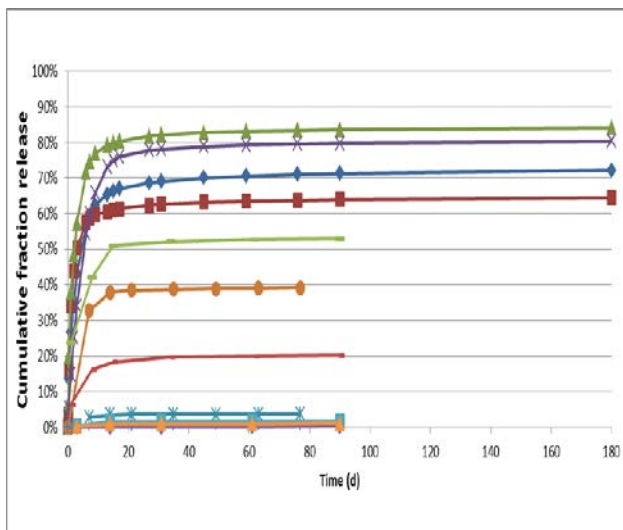
CHLORINE 36 LEACHING DATA

Overall leaching tests (^{36}Cl)

- High variability of the leaching rate (from few % to 90%)
- ^{36}Cl is release in liquid phase in two stages
 1. With a very quick release kinetics (called “labile fraction”)
 2. Slow release kinetics (called “non labile fraction”)
- No release in the contact gas phase (Air, N_2 , Ar)

Others common points

- Water uptake kinetics are fast in irradiated graphite samples (70 % of the open porosity is filled within a few days)



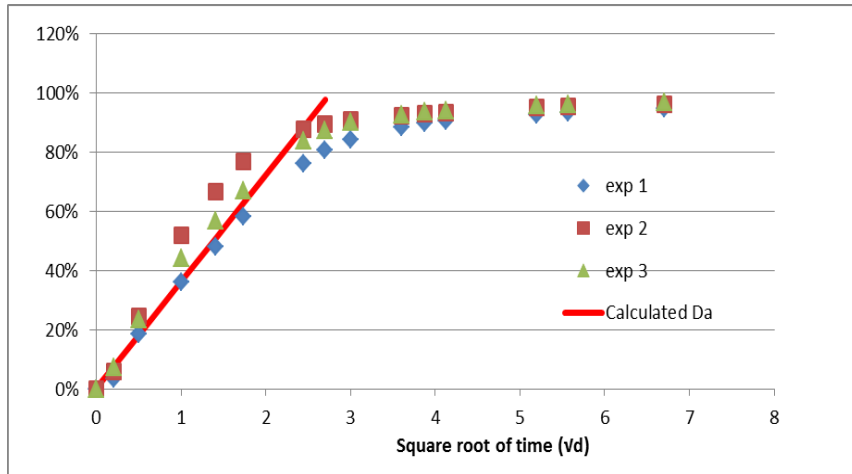
Chlorine 36 cumulative fractional release as a function of time for irradiated graphite samples. Tests performed with pure water or lime water under air or inert atmosphere

Chlorine 36 labile fraction

- The release kinetics of labile ^{36}Cl can be described by a diffusion model of dissolved Chlorine (Cl^-) through the graphite porosity
- Chlorine 36 release is not limited by water up-take
- Low impact of leaching parameters (water chemistry, pH, temperature)

Comparison of ^{36}Cl release with a diffusion model

The overall release is normalized to 100% of ^{36}Cl labile fraction



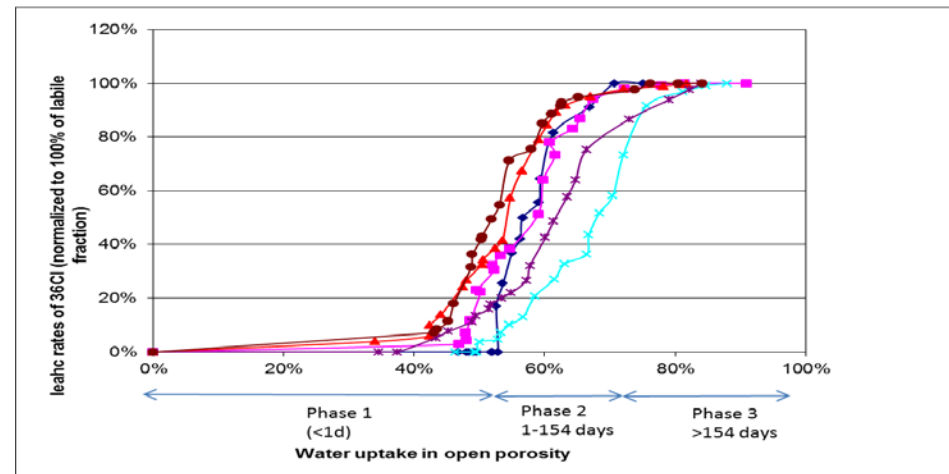
Diffusion calculations are performed by adjusting the value of the diffusion coefficients to reproduce the experimental data of the leaching tests according to Equation

$$F = 2 \cdot \frac{S}{V} \sqrt{\frac{D_a \cdot t}{\pi}}$$

F: Leached fraction
S: Geometric area subject to leaching
V: Geometric volume of sample
t: Time
Da: Apparent diffusion coefficient

Correlation between ^{36}Cl labile fraction leach rate and water uptake in graphite open porosity

The overall release is normalized to 100% of ^{36}Cl labile fraction

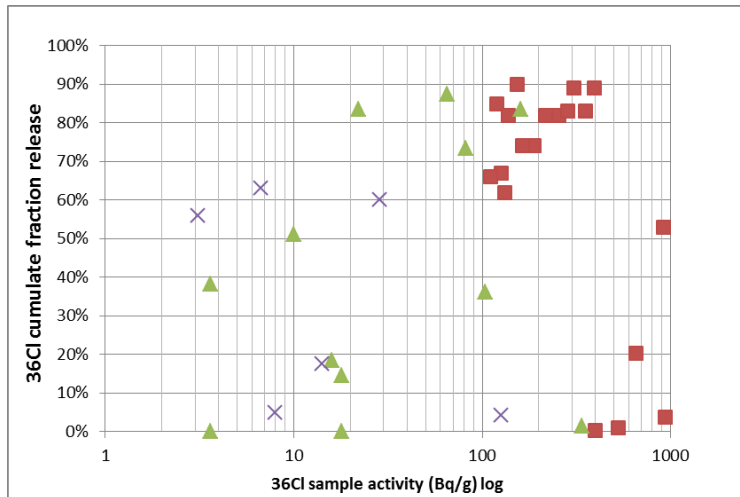


Coke	Mean Da (m ² .s ⁻¹)	Mean De (m ² .s ⁻¹)
« Spécial »	3.10 ⁻¹¹	6.10 ⁻¹²
« Lockport »	9.10 ⁻¹²	2.10 ⁻¹³
« Lima »	3.10 ⁻¹²	6,5.10 ⁻¹³

High variability of release rates

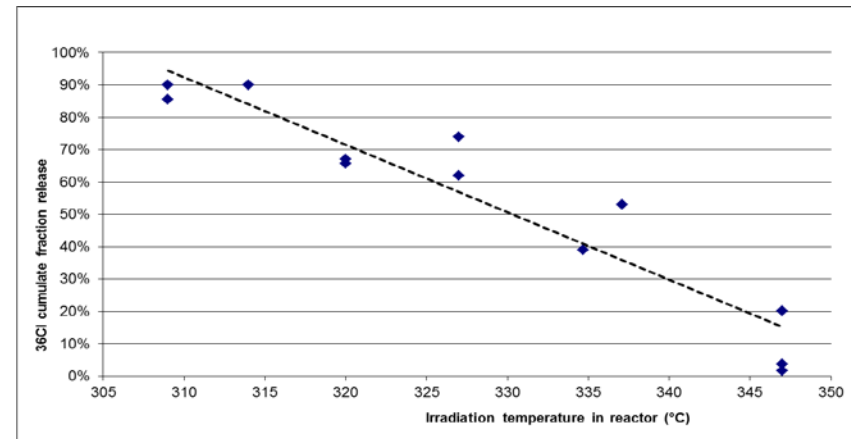
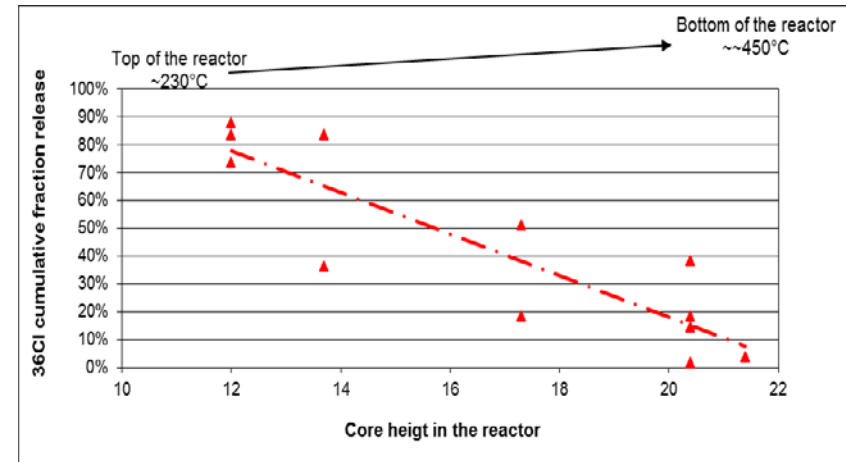
- Not correlated to the initial activity of graphite
- Correlation between the sample temperature and position during reactor operation and the quantity of labile ^{36}Cl (confirmed on 3 reactors)

Low leaching rate => Irradiated at high temperature
High leaching rate => Irradiated at low temperature



Chlorine 36 leaching rates as a function of samples initial activity in Bq.g^{-1} (logarithmic scale)

Chlorine 36 cumulative fractional release as a function of core height and temperature



- Leaching tests demonstrate :
 - Two forms / localization of ^{36}Cl in irradiated graphite
 - One labile form, controlled by a diffusion process through graphite porosity
 - A second stage showing slow release kinetics (non-labile fraction)
 - ^{36}Cl leaching rate depends on i-graphite operating temperature
 - **Low leaching rate => Irradiated at high temperature**
 - **High leaching rate => Irradiated at low temperature**

- Perspectives of work
 - Study the correlation of the variability of leaching rate with graphite structural evolution
 - Influence of the coke/reactor /other graphite waste need to be clarified
 - Study the non labile fraction (speciation / localization)

- Perspectives for disposal
 - To get a better understanding of the underlying mechanisms which govern chlorine 36 release in order to increase confidence in the demonstration of long term safety
 - To assess long term chlorine 36 release rate to improve the source term model and therefore the safety assessment

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