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## Leaching of UNGG graphite Study of $^{36}\text{Cl}$ behaviour

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FROM RESEARCH TO INDUSTRY



# LEACHING OF UNGG GRAPHITE : STUDY OF $^{36}\text{Cl}$ BEHAVIOUR

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## SCIENTIFIC BASIS FOR NUCLEAR WASTE MANAGEMENT XXXIX

2<sup>ND</sup> TO 6<sup>TH</sup> NOVEMBER 2015

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## ■ Nuclear graphite waste in France

- 9 UNGG reactors (graphite moderated, fueled with natural uranium, CO<sub>2</sub> cooled)
- 23000 t of irradiated graphite => 100 000 m<sup>3</sup> of conditioned waste in cementitious packages
- Nuclear graphite are classified as “**Long Life Waste – Low Level**” (<sup>14</sup>C, <sup>36</sup>Cl ..)
- 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 <sup>36</sup>Cl source term** (leaching rate) on irradiated graphite.  
<sup>36</sup>Cl 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 <sup>36</sup>Cl 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 <sup>36</sup>Cl

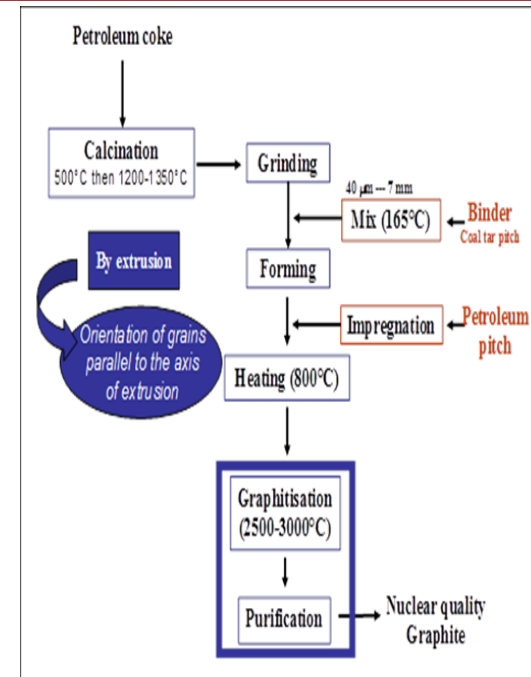
## Origin of natural chlorine in nuclear graphite

- As an **impurity in the basic materials** used for the manufacture (Coke, Coal tar pitch, cleaning agents (NaF, MgF<sub>2</sub>..),...)
  - Brought by **air pollution** (end of the manufacture, during storage)
  - Present at low level in the coolant gas (Air, CO<sub>2</sub>)
- Cl in nuclear graphite are around 5 to 40 ppm

## Origin of <sup>36</sup>Cl (long live radionuclide 3.10<sup>5</sup>y, β<sup>-</sup>)

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

=>**<sup>35</sup>Cl(n,g)<sup>36</sup>Cl** is the predominant reaction for the formation of <sup>36</sup>Cl in irradiated graphite but with nuclear recoil <sup>36</sup>Cl location should be different from <sup>35</sup>Cl initial position (atoms are 'displaced', some maybe re-form covalent bonds =>different speciation of <sup>36</sup>Cl and <sup>35</sup>Cl)  
=> <sup>36</sup>Cl activity **in French i-graphite is very low but with a huge variability** (1-10<sup>3</sup> Bq/g) and a specific analytical procedure must be used (with low detection limit)



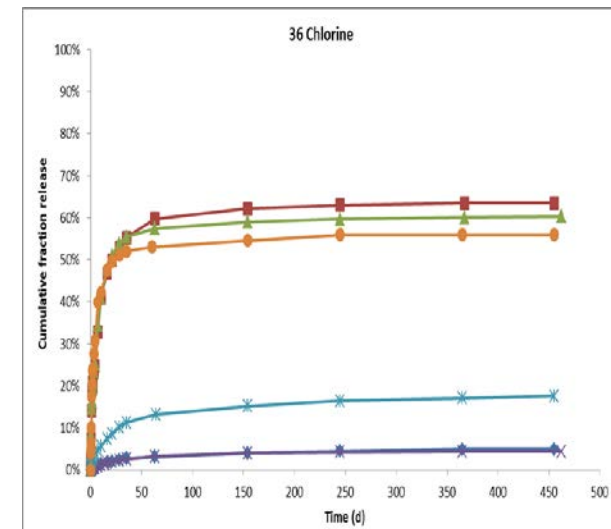
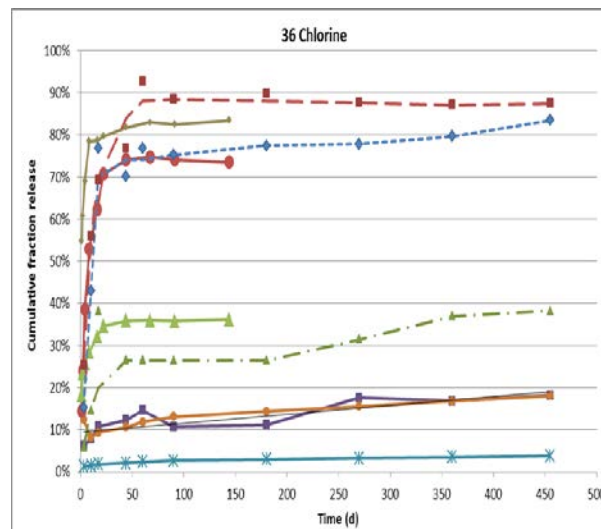
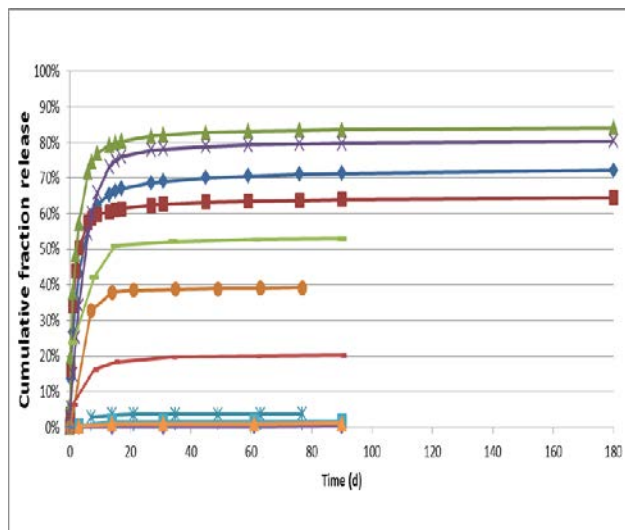
# CHLORINE 36 LEACHING DATA

## Overall leaching tests ( $^{36}\text{Cl}$ )

- High variability of the leaching rate (from few % to 90%)
- $^{36}\text{Cl}$  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,  $\text{N}_2$ , Ar)

## Others common points

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



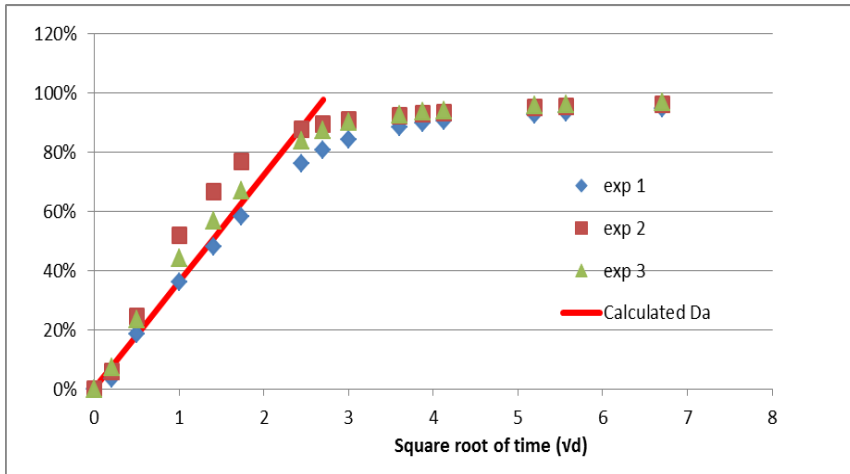
**Chlorine 36 cumulative fractional release as a function of time for irradiated graphite samples. Tests performed with pure water or lime water under air or inert atmosphere**

## Chlorine 36 labile fraction

- The release kinetics of labile  $^{36}\text{Cl}$  can be described by a diffusion model of dissolved Chlorine ( $\text{Cl}^-$ ) 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 $^{36}\text{Cl}$ release with a diffusion model

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



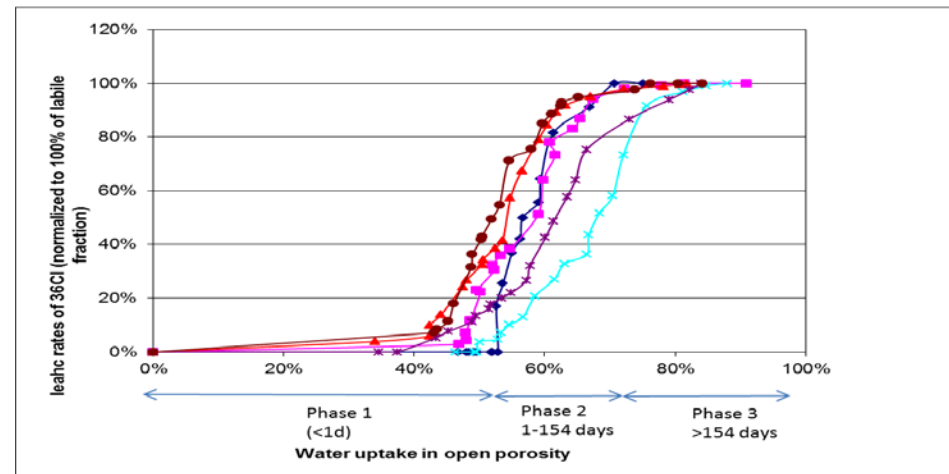
Diffusion calculations are performed by adjusting the value of the diffusion coefficients to reproduce the experimental data of the leaching tests according to Equation

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

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

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

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

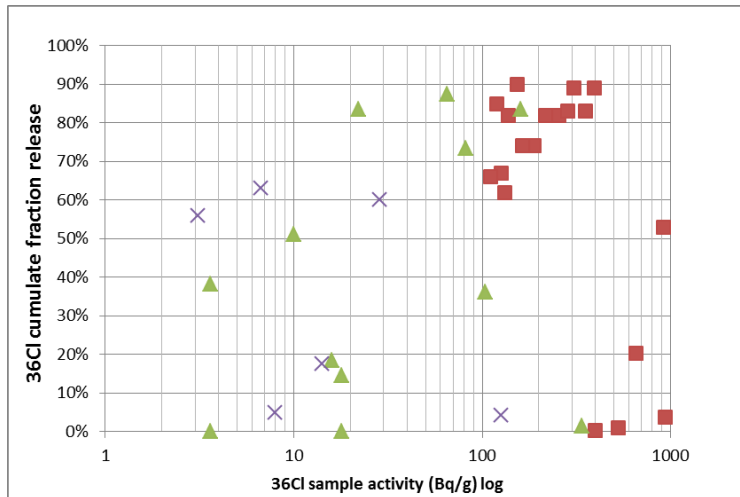


Coke	Mean $D_a$ ( $\text{m}^2 \cdot \text{s}^{-1}$ )	Mean $D_e$ ( $\text{m}^2 \cdot \text{s}^{-1}$ )
« Spécial »	$3 \cdot 10^{-11}$	$6 \cdot 10^{-12}$
« Lockport »	$9 \cdot 10^{-12}$	$2 \cdot 10^{-13}$
« Lima »	$3 \cdot 10^{-12}$	$6,5 \cdot 10^{-13}$

## High variability of release rates

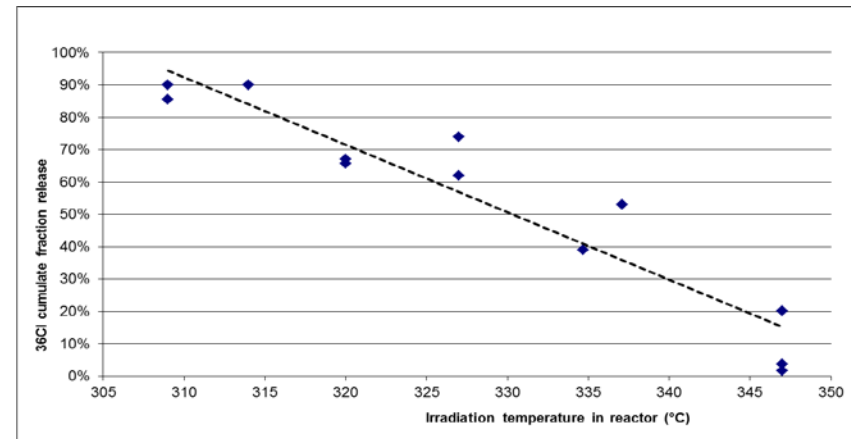
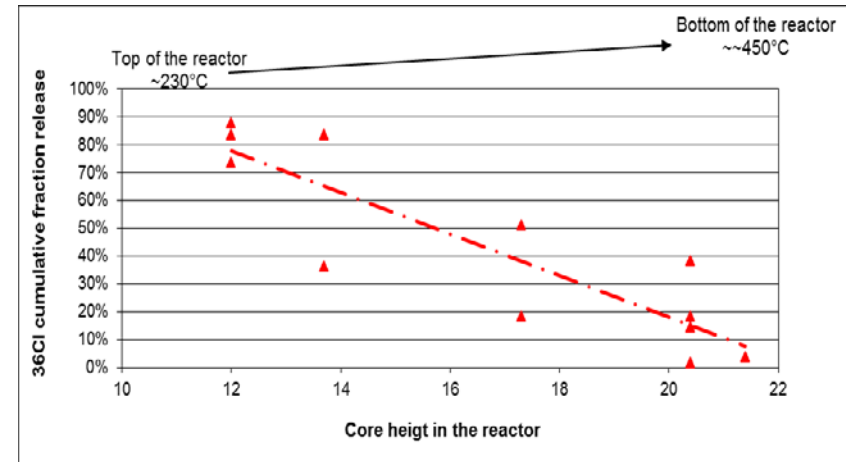
- Not correlated to the initial activity of graphite
- Correlation between the sample temperature and position during reactor operation and the quantity of **labile  $^{36}\text{Cl}$**  (confirmed on 3 reactors)

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  $\text{Bq.g}^{-1}$  (logarithmic scale)**

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





- Leaching tests demonstrate :
  - Two forms / localization of  $^{36}\text{Cl}$  in irradiated graphite
    - One labile form, controlled by a diffusion process through graphite porosity
    - A second stage showing slow release kinetics (non-labile fraction)
  - $^{36}\text{Cl}$  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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