Leaching of UNGG graphite Study of ^{36}Cl behaviour

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FROM RESEARCH TO INDUSTRY

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LEACHING OF UNGG GRAPHITE :

STUDY OF ^{36}CL BEHAVIOUR

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SCIENTIFIC BASIS FOR NUCLEAR WASTE MANAGEMENT XXXIX

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SOMMAIRE

NUCLEAR GRAPHITE WASTE

Nuclear graphite waste in France

- 9 UNGG reactors (graphite moderated, fueled with natural uranium, CO_2 cooled)
- 23000 t of irradiated graphite => 100 000 m^3 of conditioned waste in cementitious packages
- Nuclear graphite are classified as "Long Life Waste – Low Level" (^{14}C, ^{36}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

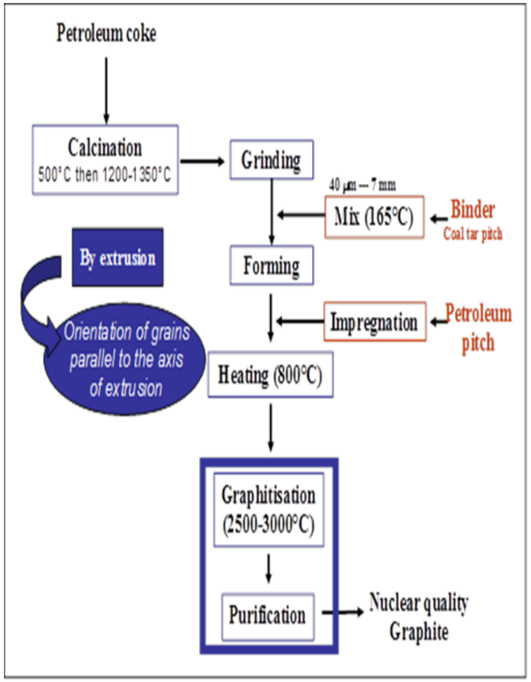
- Objective : **characterize ^{36}Cl source term** (leaching rate) on irradiated graphite.

^{36}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 ^{36}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 ^{36}Cl

IRRADIATED GRAPHITE ORIGIN OF CHLORINE 36



- **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_2..),…)
  - Brought by air pollution (end of the manufacture, during storage)
  - Present at low level in the coolant gas (Air, CO_2)

  Cl in nuclear graphite are around 5 to 40 ppm

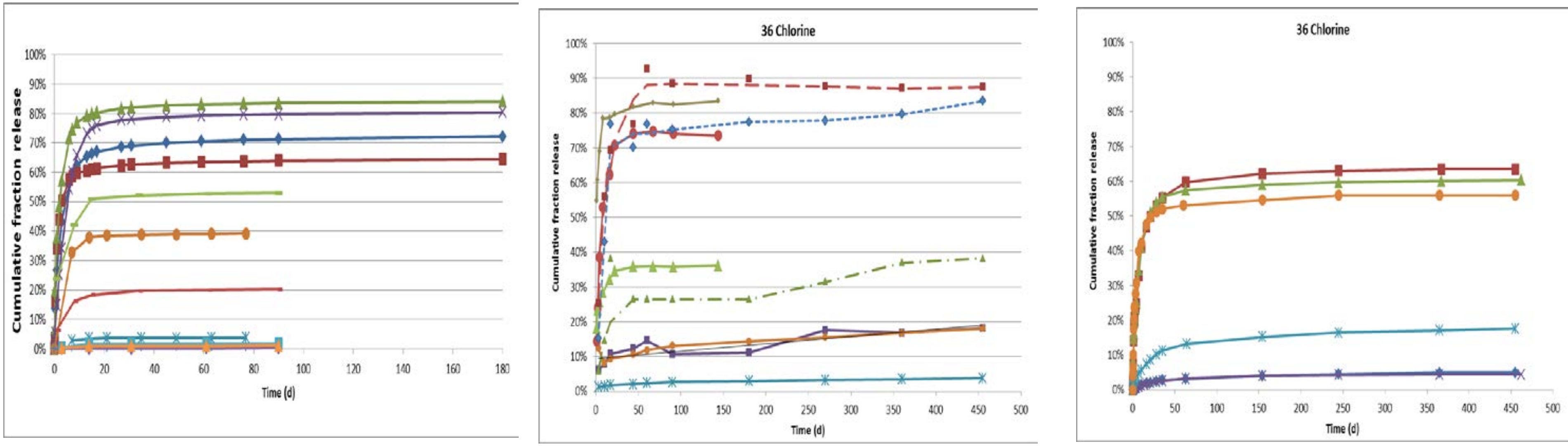
- **Origin of ^{36}Cl (long live radionuclide 3.10^{5}y, β^-)**
  - Production
    - Direct activation of ^{35}Cl (77,5%) 44 barns
    - Direct activation of ^{39}K (93,25%) 0,004 barns
    - Indirect activation of ^{34}S (4,2%) 0,34 barns

=>^{35}Cl(n,g)^{36}Cl is the predominant reaction for the formation of ^{36}Cl in irradiated graphite but with nuclear recoil ^{36}Cl location should be different from ^{35}Cl initial position (atoms are 'displaced', some maybe re-form covalent bonds =>different speciation of ^{36}Cl and ^{35}Cl)

=> ^{36}Cl activity in French i-graphite is very low but with a huge variability (1-10^3 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

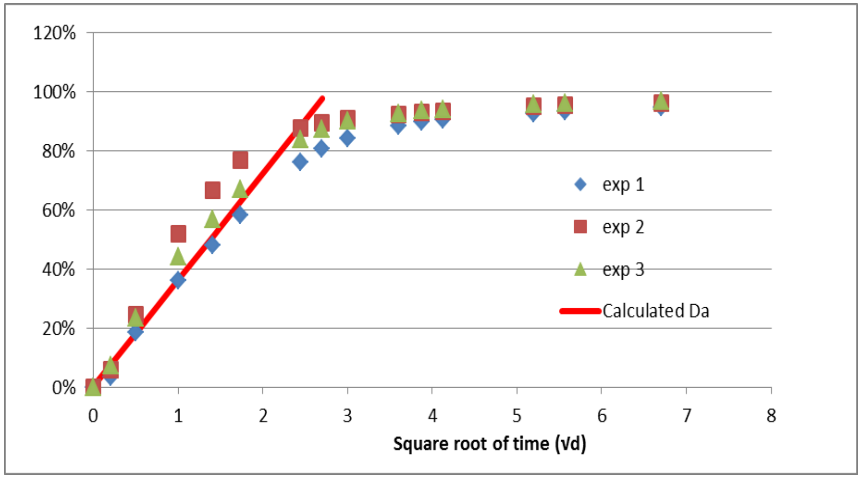
INTERPRETATION

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)

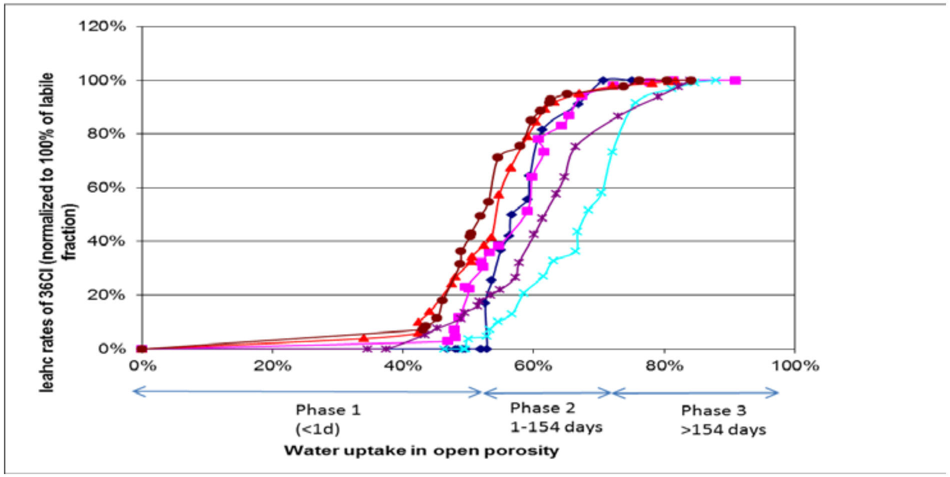
Comparison of ^{36}Cl release with a diffusion model

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



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

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

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

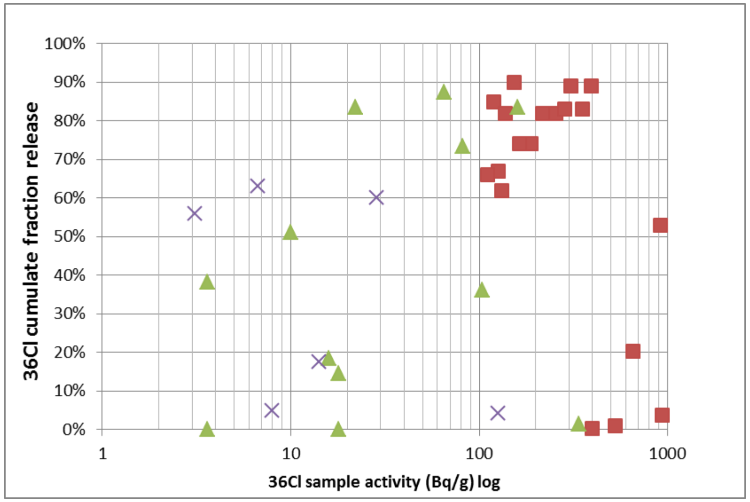
F: Leached fraction
S: Geometric area subject to leaching
V: Geometric volume of sample
t: Time
Da: Apparent diffusion coefficient

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}	$6,5.10^{-13}$

INTERPRETATION

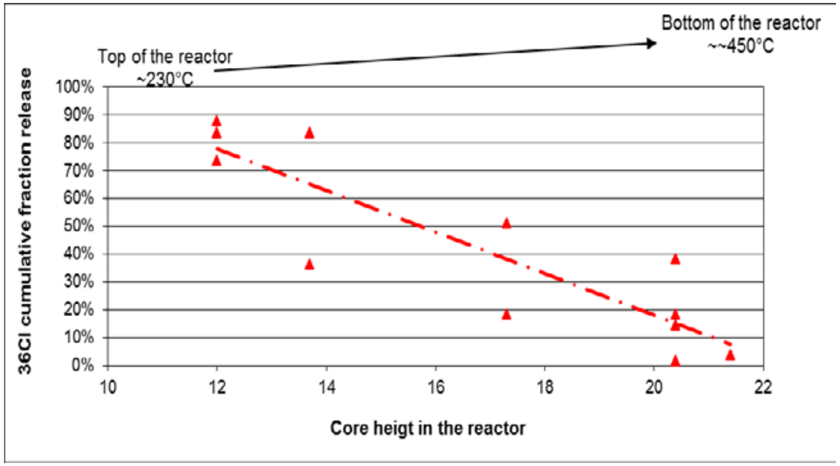
- **High variability of release rates**
  - Not correlated to the initial activity of graphite
  - Correlation between the sample temperature and position during reactor operation and the quantity of labile ^{36}Cl (confirmed on 3 reactors)

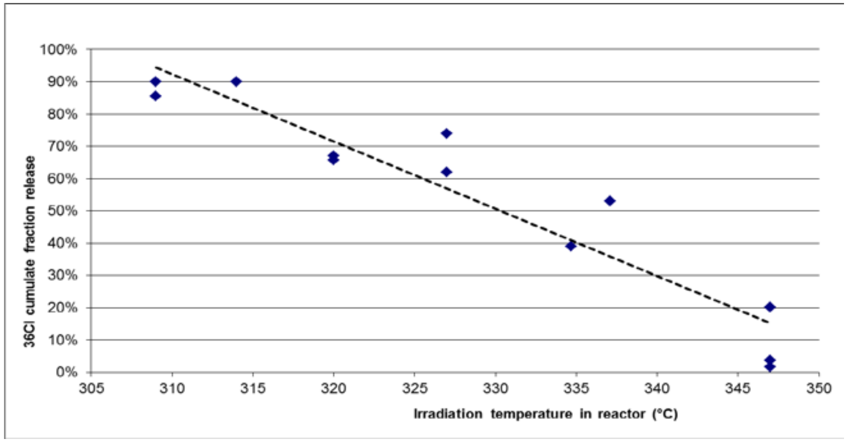
Low leaching rate => Irradiated at high temperature
High leaching rate => Irradiated at low temperature



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





CONCLUSION

- 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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