

FROM RESEARCH TO INDUSTRY



*METHODOLOGY FOR MEASURING AND
EVALUATION OF INVENTORY IN THE
WASTE CHLORE-36 GRAPHITE*

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CETAMA WORKSHOP

« SAMPLING AND CHARACTERISATION »

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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

Determine the radionuclide content of the graphite waste is an obligation for safety reasons and to determine the best strategy for their management

Main French studies

- Objective : **characterize ³⁶Cl source term** (inventory) in irradiated graphite.
³⁶Cl (301000y half-life) 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 analytical procedure optimized for ³⁶Cl measurement with those followed specifications:
 1. Strategies are defined to take into account the **huge variability of ³⁶Cl**
 2. Methodology for sample homogenization
 3. Analytical methodology optimized to measure ³⁶Cl

IRRADIATED GRAPHITE ORIGIN OF CHLORINE 36

Origin of natural chlorine in nuclear graphite

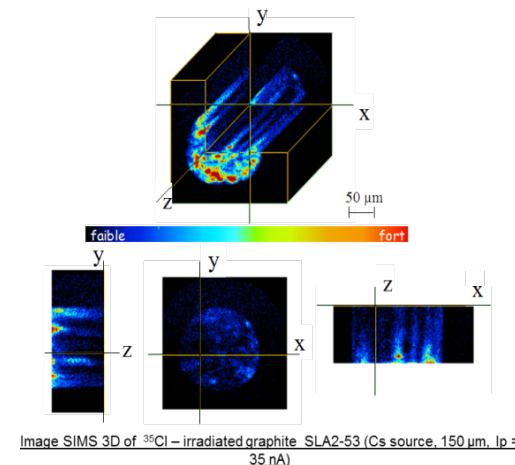
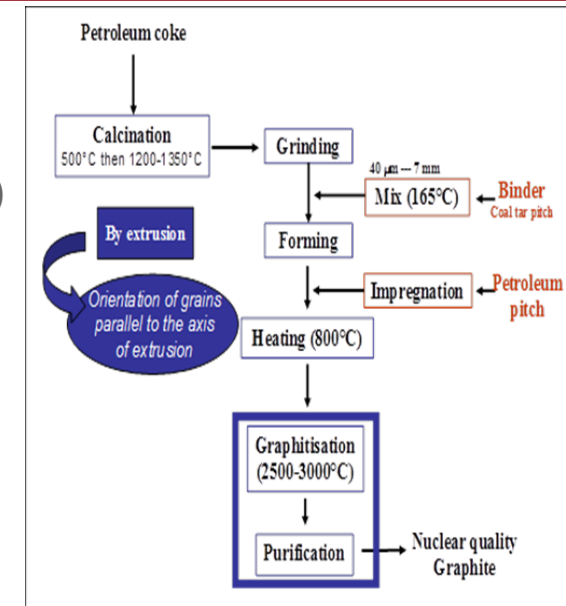
- As an **impurity in the basic materials** used for the manufacture (Coke, Coal tar pitch, cleaning agents(NaF , MgF_2 ..),...)
 - Brought by **air pollution** (end of the manufacture, during storage)
 - Present at low level in the coolant gas (Air , CO_2)
- Cl in nuclear graphite is around 5 to 40 ppm

Origin of ^{36}Cl (long live radionuclide 3.10^5y , 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

$\Rightarrow ^{35}\text{Cl}(\text{n},\text{g})^{36}\text{Cl}$ 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 $\Rightarrow$ different speciation of ^{36}Cl and ^{35}Cl)

$\Rightarrow ^{36}\text{Cl}$ activity in French i-graphite is very low but with a huge variability ($1\text{-}10^3\text{ Bq/g}$) and a specific analytical procedure must be used (with low detection limit)

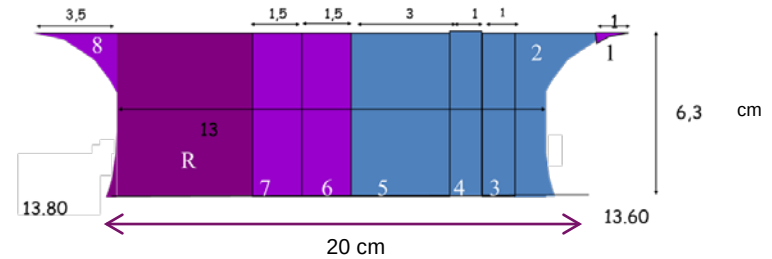
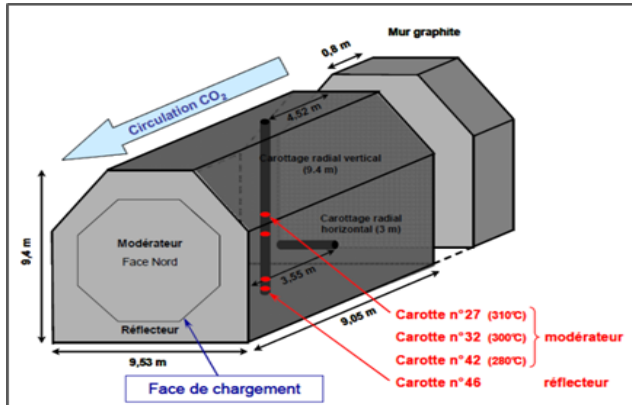


TYPE OF « GRAPHITE » SAMPLE

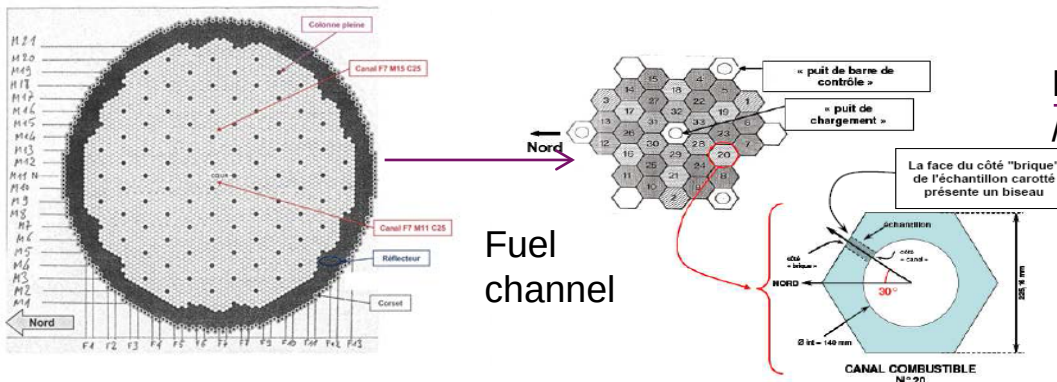
Type of sample

Massive Sample (example : sample from G2 reactor from 0,6 to 1,5 kg)

- Sub sample are made by cutting slices and grinding
- Cutting powder is also used



Samples coming from coring inside the fuel channel (example : G1 or EDF reactor)



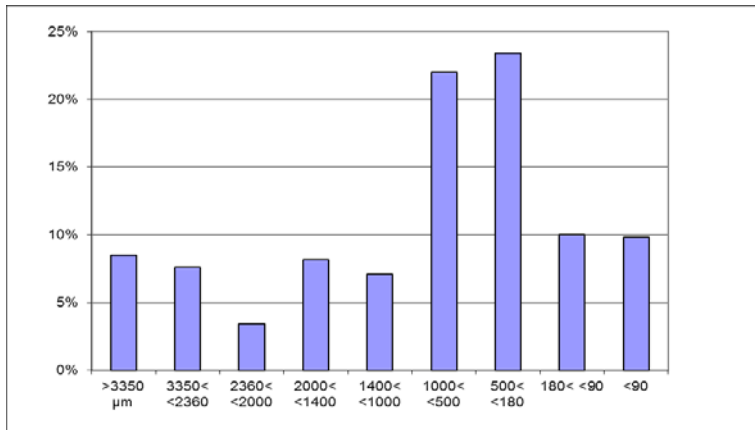
Many samples
/Height



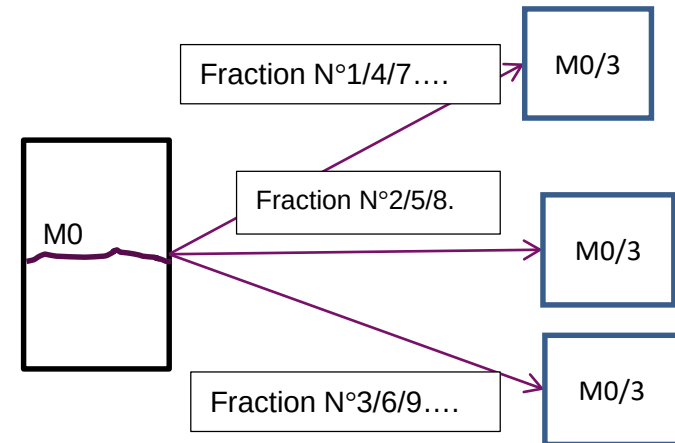
$M=5-25g$ $\Phi 16$ to 18 mm $L=30$ to 60 mm

Sampling

- Grinding under 150 Ton press
- Mixing/ homogenization /sampling of the sample powder by fractional method (*ISO 11648 standard*)
- A minimum of two sub samples is taken



Granulometry spectrum of powder after grinding under 150Ton



Mineralization process

Mineralization is performed in pressurized O₂ closed reactor in the presence of chlorine for chemical tracer yield

Mass sample is around 0.6 g of graphite powder

=> Mineralization in close system : no lost of chlorine



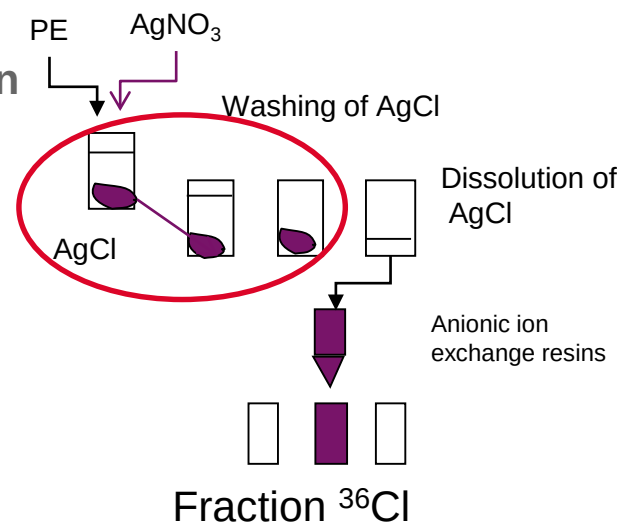
Chemical purification

Methodology employed use two steps of chemical separation

1. Precipitation of silver chloride (AgCl) in acidic media
2. Separation of chlorine by ion exchange resins after dissolution in $\text{Na}_2\text{S}_2\text{O}_3$ 0.2M media

=> Total separation RN (Global FD > 10^4) checked by impurity determination by gamma ray spectrometry, ^{14}C measurement...

=> Chemical yield is around 90% (Ionic Chromatography)



Measurement methodology

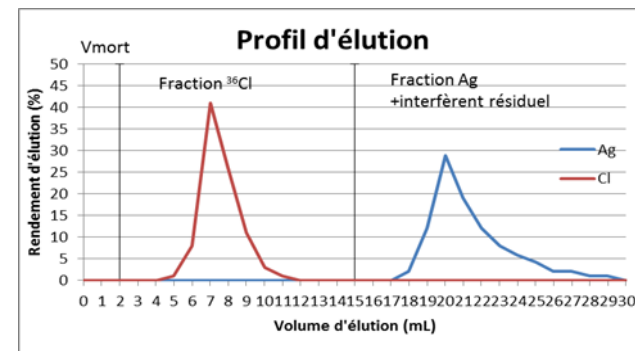
Liquid Scintillation Counting measurement (LSC)

Equipment : Ultra Low level Liquid Scintillation QUANTULUS, Perkin Elmer

Complete methodology

Detection limit : < 0,5 Bq/g of I-graphite

Uncertainty of measurement : <10% for 5 Bq/g



CHARACTERIZATION METHODOLOGY VALIDATION

1. CETAMA circuit ^{36}Cl [2007] on synthetic solution
2. Round Robin test on irradiated graphite sample during **CARBOWASTE** project « *Treatment and Disposal of Irradiated Graphite and Other Carbonaceous Waste* » FP7-211333 [2008-2013]

^{36}Cl EVALUATION

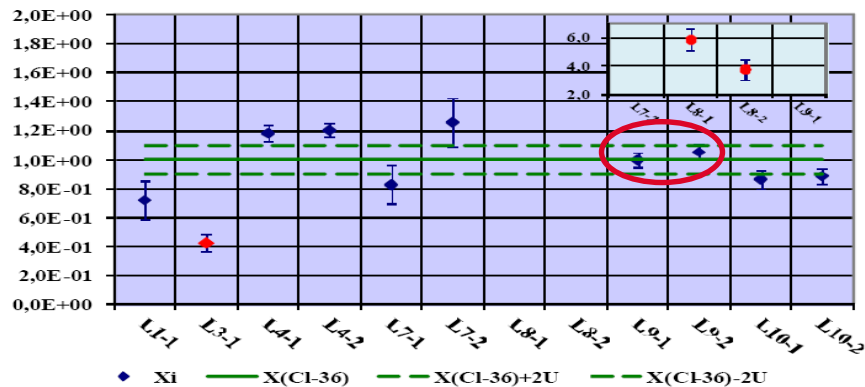


Figure 15. Results for Cl-36 evaluation

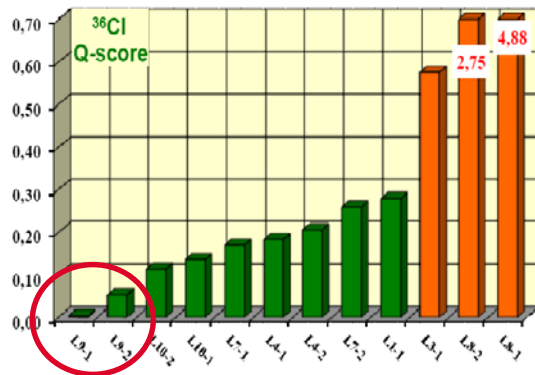


Figure 16. Q-score for Cl-36 evaluation

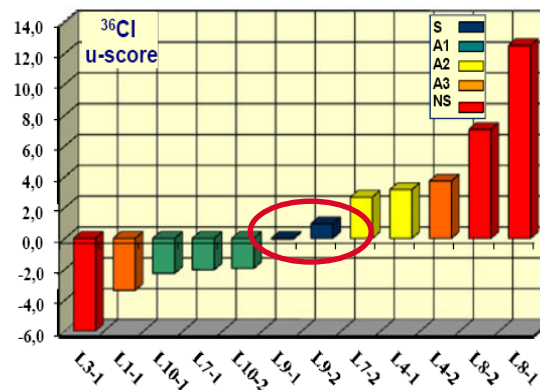
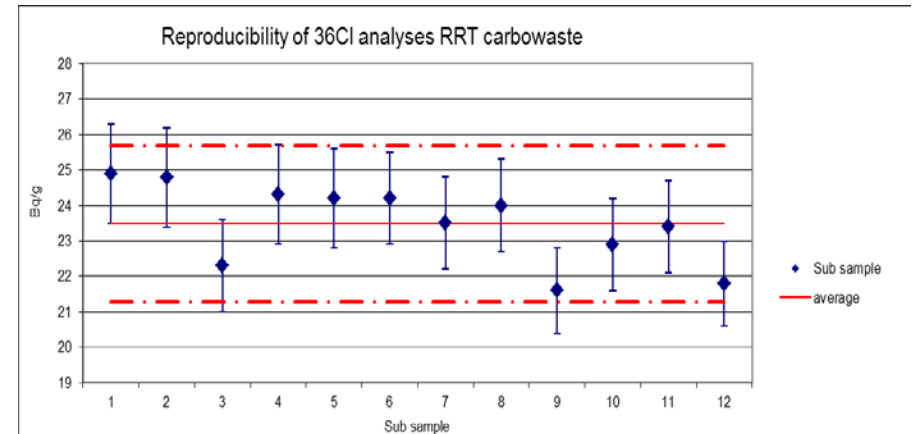


Figure 18. U-score chlorine-36 evaluation

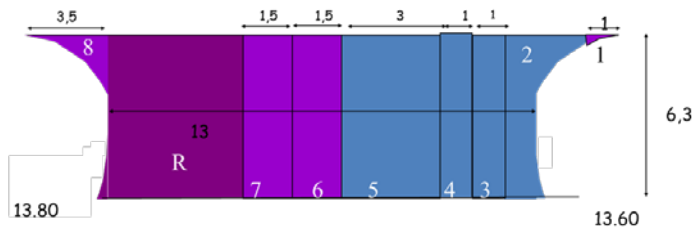
Test for

- Accuracy,
- Trueness,
- Precision,
- Repeatability,
- Reproducibility

VARIABILITY CONSIDERATION

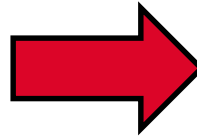
For largest sample (G2) : estimation of heterogeneity / variability to have the “best average value”

- 1) Mass weighted average in order to take account of the Volume/mass of each sample
- 2) cutting powder : homogenous powder made during cutting



Sample	Cutting powder
^{36}Cl (Bq/g)	180 ± 24

	^{36}Cl (Bq/g)
Average	195 ± 90
Mass weighted average	184 ± 26
Cutting powder	180 ± 24



Sample	G2-27-8	G2-27-R	G2-27-7	G2-27-7	G2-27-1
mass (g)	6	80	12	12	3
^{36}Cl (Bq/g)	256 ± 30	182 ± 29	180 ± 30	180 ± 24	230 ± 27

For smaller sample : homogenization by grinding all the sample

But this analytical methodology (grinding and analytical process) were not sufficient to have a “best estimate value” for inventory we need to develop

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