



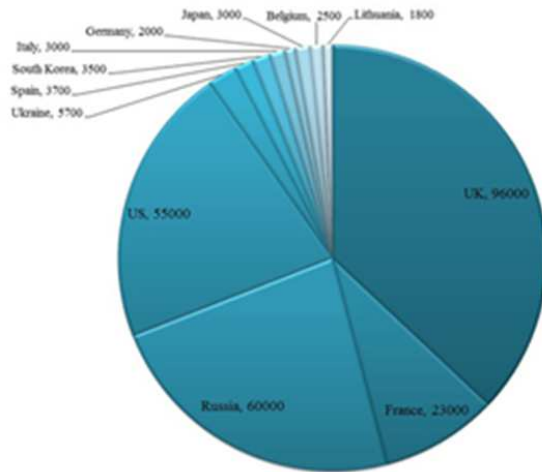
# **$^{36}\text{CI}$ ASSESSMENT OF EDF GRAPHITE WASTE AND THE LATEST SUGGESTED DEVELOPMENTS**

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# I-GRAPHITE CONTEXT (1/2)



**La Hague (Areva)**  
Graphites sleeves from Chinon reactors & fuel treatment waste stored in silos



**Saint Laurent A1(EDF), 460 Mwe, 1969→ 1990**  
**Saint Laurent A2(EDF), 515 Mwe, 1971→ 1992**  
Sleeves are stored in silos



**Chinon A1(EDF), 70 Mwe, 1963→ 1973**  
**Chinon A2(EDF), 210 Mwe, 1965→ 1985**  
**Chinon A3(EDF), 400 Mwe, 1966→ 1990**



Several experimental reactors (CEA)

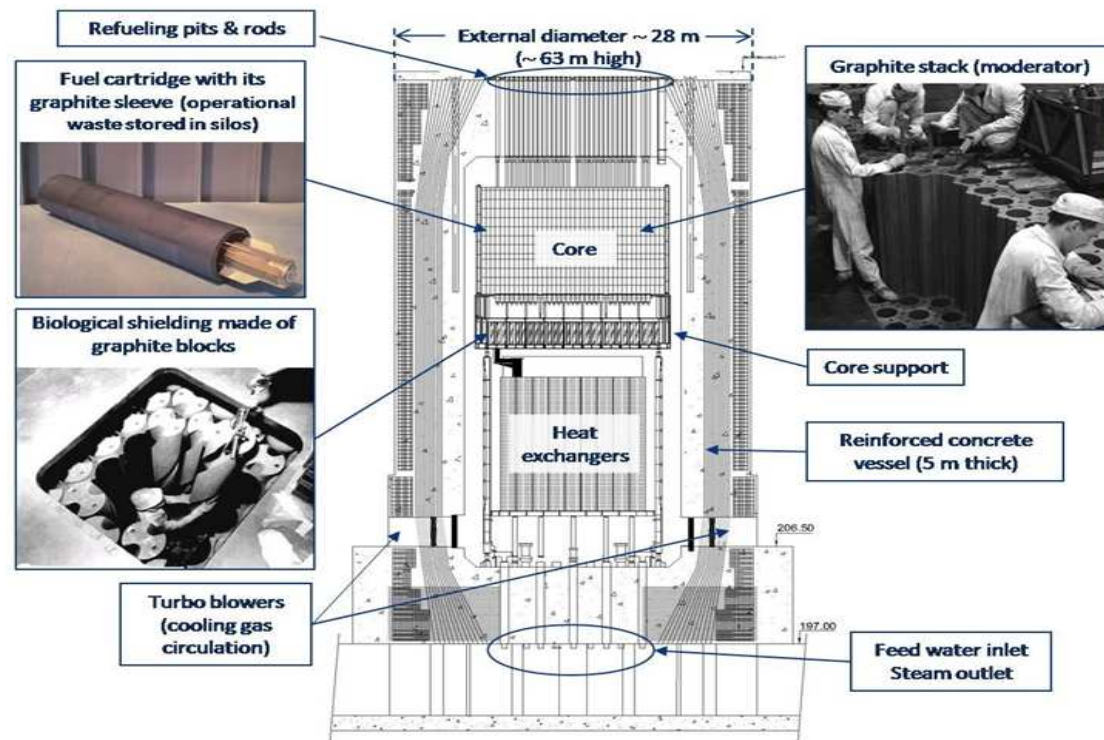


**Bugey 1 (EDF)**  
540 MWe  
1972→ 1994



**G1 (CEA, air cooled), 2 Mwe, 1956→ 1958**  
**G2(CEA), 38 Mwe, 1958→ 1980**  
**G3 (CEA), 38 Mwe, 1959→ 1984**  
+Chinon graphite sleeves stored in silos

# I-GRAPHITE CONTEXT (2/2)



The units are all UNGG (Uranium Naturel Graphite Gaz) plants, a reactor design developed in France. UNGG reactors were graphite moderated, cooled by carbon dioxide, and fuelled with natural uranium metal.

There are two main types of graphite waste:

- Graphite stacks, still in reactors ( $\approx 88\%$  in weight)
- Sleeves initially containing uranium cartridges, placed in the channels and removed while defueling

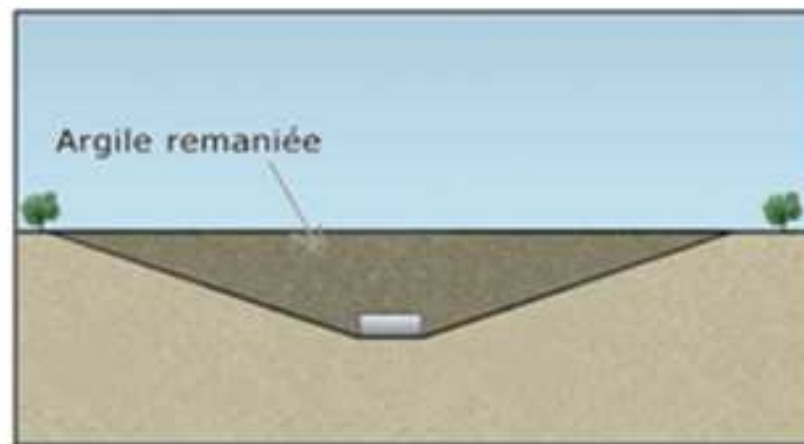
# FRENCH DISMANTLING WASTE TYPOLOGY

Mass activity (Bq/g)	Type of waste	Short life i.e. Long life (>30 years) below CSA (Soulaines) acceptance level	Long life (>30 years) above CSA acceptance level
≈100	VLLW	Very Low Level Surface disposal in CIREs (Morvilliers) in operation	
1.00E+06	LLW	Shallow repository in CSA (Soulaines) in operation and in CSM (Manche) now closed	Site under investigation
1.00E+09	ILW		CIGEO (near Bures in 2030)
From operation	HLW	CIGEO (opening near Bures in 2030)	

Graphite waste is a part of long life Low Level Wastes (LL-LLW)

- Long life (>30 years)
- Radiological inventory dominated by C-14 and radionuclides with very low or low mass activities produced from activation of impurities in graphite.

A repository site is under investigation by ANDRA (French governmental radioactive waste management agency)



Sub-surface repository concept for LL-LLWastes



# PURITY OF NUCLEAR GRAPHITE, A KEY POINT

It is necessary to avoid the temptation of making sweeping generalizations, i.e., the apparent homogeneity of graphite material, while a rigorous analysis convinces us of its prodigious heterogeneity.

This is important because the false intuition of homogeneity leads:

1. to indulge in penny-pinching for sampling and measurements,
2. to lose confidence in radiochemical measurements in graphite,
3. to choose maximum values to quantify inventories and
4. to shamelessly show measurements shape matching neutron flux shape even if it is simply not possible and only to avoid losing face.

To realize that these generalizations are huge mistakes, it must be understood that everything comes from the purity of nuclear graphite. During the UNGG period of operation, uranium without enrichment (or with very little enrichment) required high density graphite to significantly increase the proportion of thermal neutrons and high purity to decrease the absorbed number of neutrons.

It was the only way to enable a fission chain reaction.

As inversely proportional to the impurity concentration, the Pierre Gy formula explains that the relative variance is very high. This heterogeneity, coming from purity, needs to be taken into account to compute a radiological inventory based on impurity activation.

# RADIOLOGICAL INVENTORY ASSESSMENT

The precise assessment of the radiological inventory is the fundamental step in decommissioning programs. This assessment has to be performed very carefully, particularly avoiding any simplifications that can lead to over-estimation and early as possible, because its results are essential to any relevant decision making for disposal and later, for the dismantling method.

In France, in the case of graphite waste, the key issue is to confirm its' acceptability in the future repository currently under investigation. It is only since 1980 that Cl-36 inventory has been considered as a key point.

Initially, the calculation is simplified by taking margins and if the results are not satisfactory, some simplifications are removed in order to meet the objectives. Prior to 2005, given the huge variability of the measurement results of Cl-36, without any correlation with the neutron flux, temperature or anything else, the initial version was based on the maximum value of measures.

French law of 28 June 2006 asked to commission a graphite disposal in 2013. In 2008, with a significant number of radiochemical measurements on its stacks of graphite, EDF developed a scientific method to assess this inventory by reverse calculation, with the aim of limiting the overestimation of the initial version.

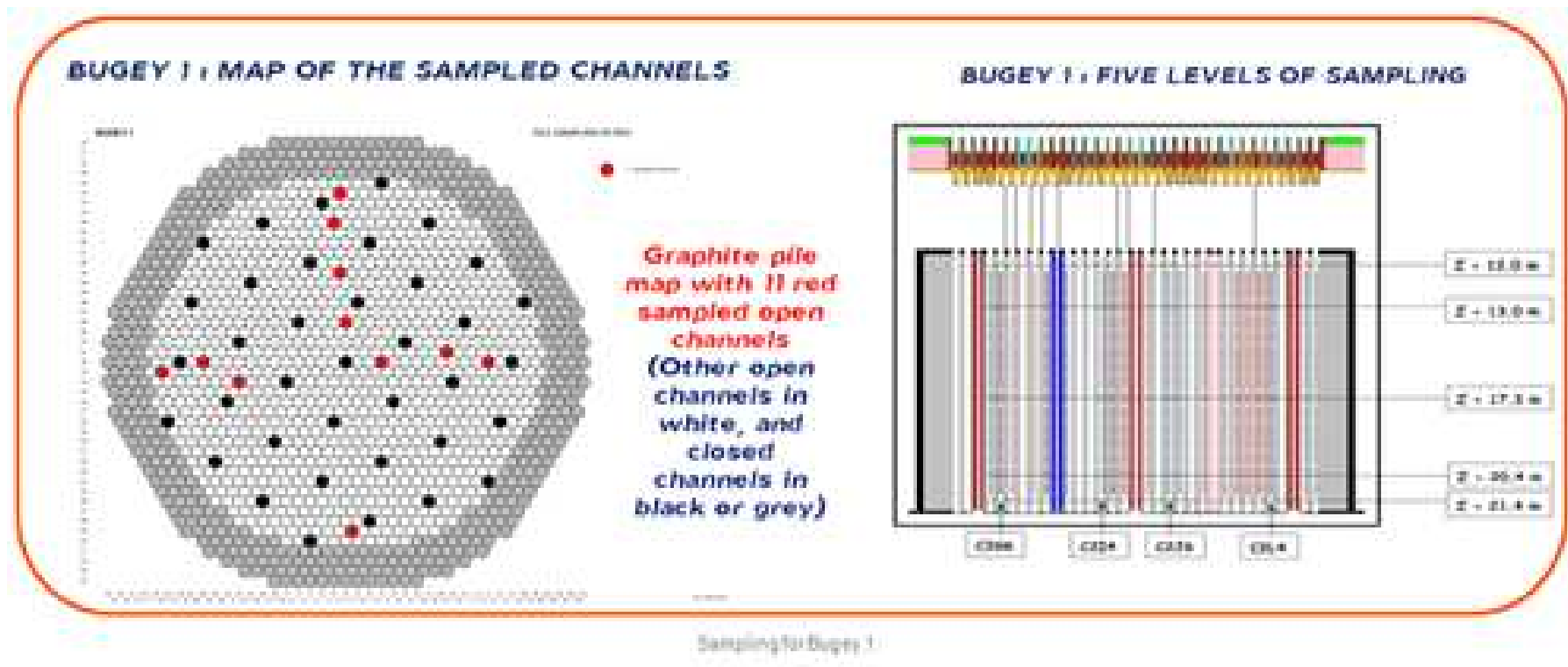
Scientific explanations will now be given on the Cl-36 inventory computation process for Bugey 1 pile.

# GRAPHITE WASTE SAMPLING AND MEASUREMENTS

Statistical purposes require multiple measures ( $\approx 30$  appears to be efficient enough)

Samples are described below (choice of 11 channels and of 5 levels for BUG1)

Samples of 20 to 30 g are crushed to obtain a powder from which 2 or 3 sub-samples of about 1 g are taken to make the final measurements and compute the average for the sample.



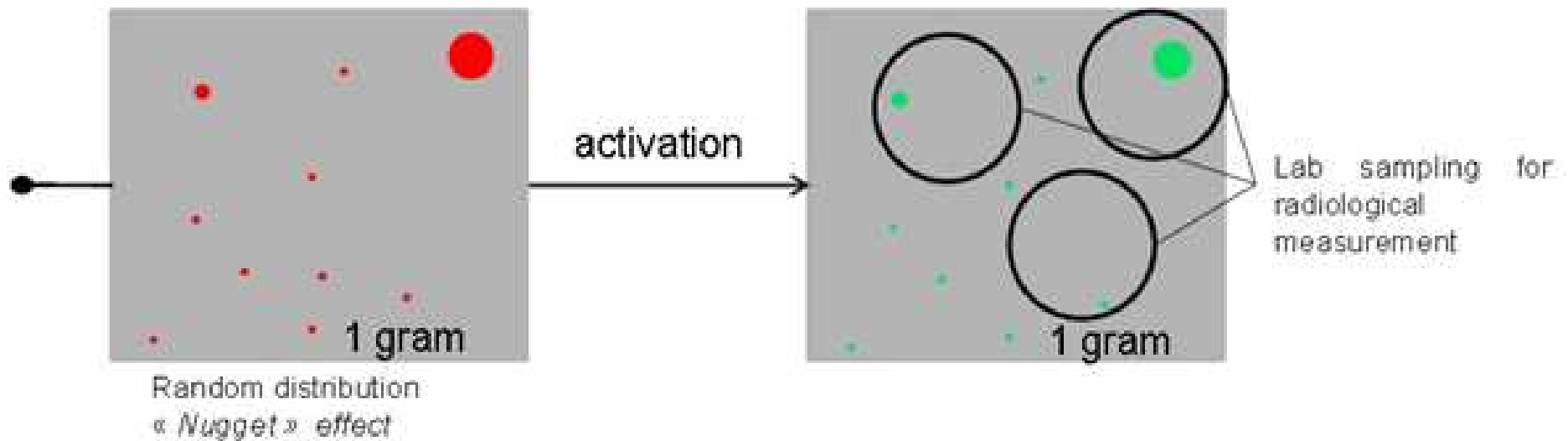
# RESULTS OF THE MEASUREMENTS

3 orders of magnitude of discrepancy between the minimum and the maximum.

2 scientific reasons explaining this discrepancy in connection with Pierre Gy formula:

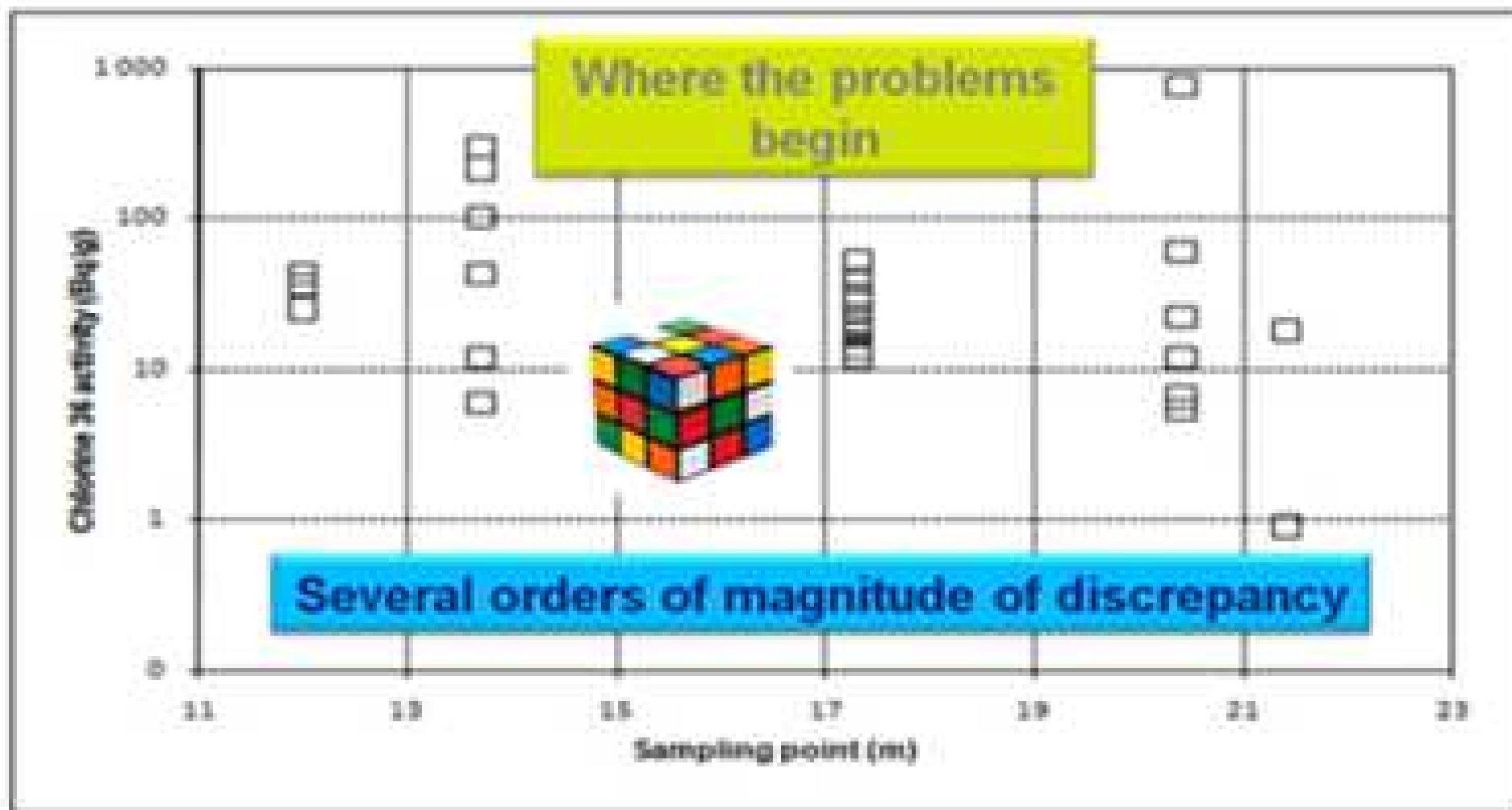
Inevitable purity of nuclear graphite: remember that this type of reactor is moderated by high density graphite but graphite impurities are required to have very low concentrations to allow criticality in spite of a lack of uranium fuel enrichment.

Inevitable tiny size of measured powder graphite sub-samples of less than 1 g which is a requirement because of radiochemistry constraints.





## BUGEY 1 : CL-36 MEASURE HIGH DISCREPANCY



Logarithmic Cl-36 (in Bq/g) in samples from pile: x-axis height of the sampling point.

# LESSONS LEARNED

## **First solution “the choice of the maximum value” is senseless**

As usual with contaminated waste management and a poor number of measures, traditional methods of radioactive waste management lead to simply choose the maximum value because of ignorance of the phenomena. The fallacy of this approach will be demonstrated later.

## **Second solution “direct activation of impurities” is worse**

Direct use of the activation computation classical approach consists of activation computation using impurities in the non-irradiated graphite.

For radioactive elements, detection limits lead to mg/t (ppb), but for non-radioactive elements, their detection is often limited to mg/kg (ppm). Such concentrations are higher than what exists in nuclear graphite (due to the high purity of nuclear graphite in order to allow a nuclear chain reaction as highlighted above).

About 80 ppb of chlorine in both Bugey 1 and St. Laurent A2 were activated to Cl-36 before final shut down.

Chemically detecting chlorine in nuclear graphite is completely impossible and only Cl-36 is measurable. Thus, the 2nd solution that consists in calculating activation of impurities is neither relevant here.



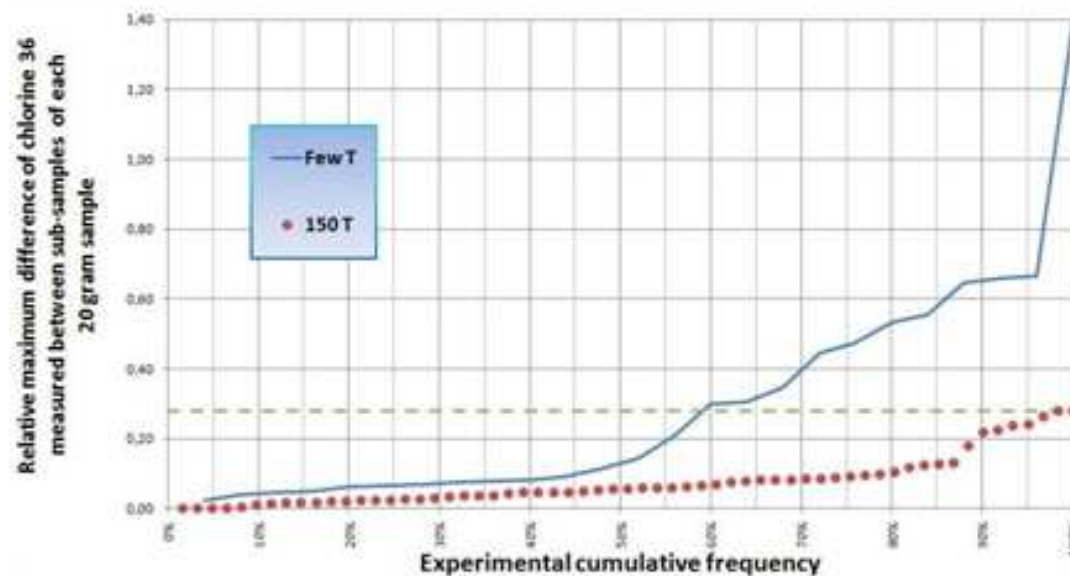
Mass spectrometer (ICPMS)

# FACTUAL SITUATION

There is no correlation between power (and therefore neutron flux) and Cl-36 measures. Nuclear power variability between samples was 1 order of magnitude while Cl-36 variability between the same samples was 3 orders of magnitude.

There is no correlation between Cl-36 measures and any other macroscopic parameters such as temperature.

There is no space correlation between Cl-36, i.e. “nugget effect” according to “geostatistical” vocabulary. This has been confirmed by comparing results from two CEA laboratories. One lab used a press of a few tons and the other a press of 150 ton. The former has a higher discrepancy among sub-samples taken in the powder of crushed graphite than the latter which used a stronger crushing. Chlorine is randomly distributed in graphite with an obvious “nugget effect”.



# EDF DEVELOPED REVERSE METHOD (1/2)

## EDF method initial version

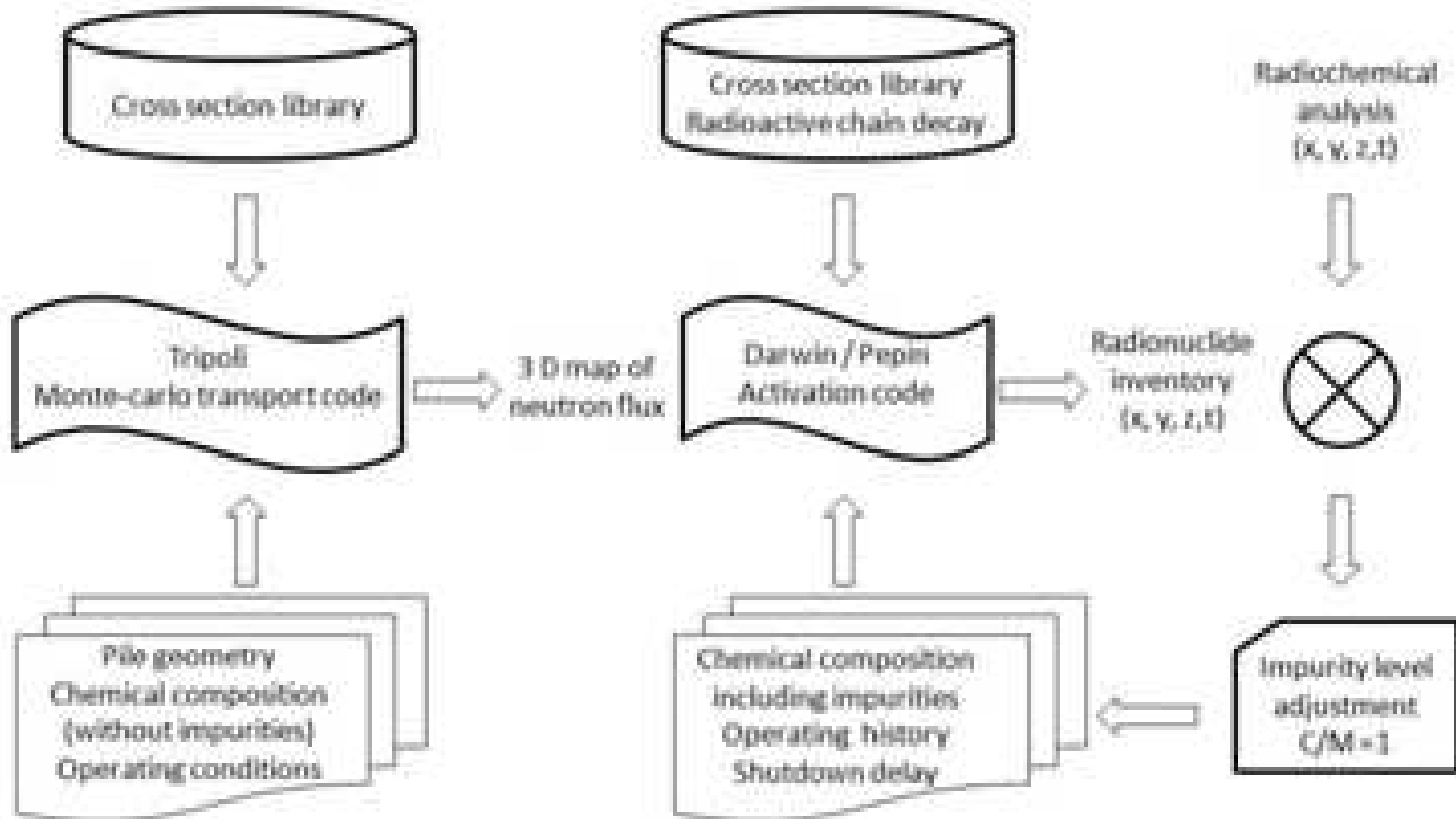
1. “3D” map computation of neutrons of each pile by solving the Boltzmann equations.
2. By solving the Bateman equations, activation is adjusted with the available measures to fit impurities, iterative adjustment process toward the minimization of

$$\left| \sum_{i=1}^{i=N_{Rn}} (\ln C_{Rn,i} - \ln M_{Rn,i}) \right|$$

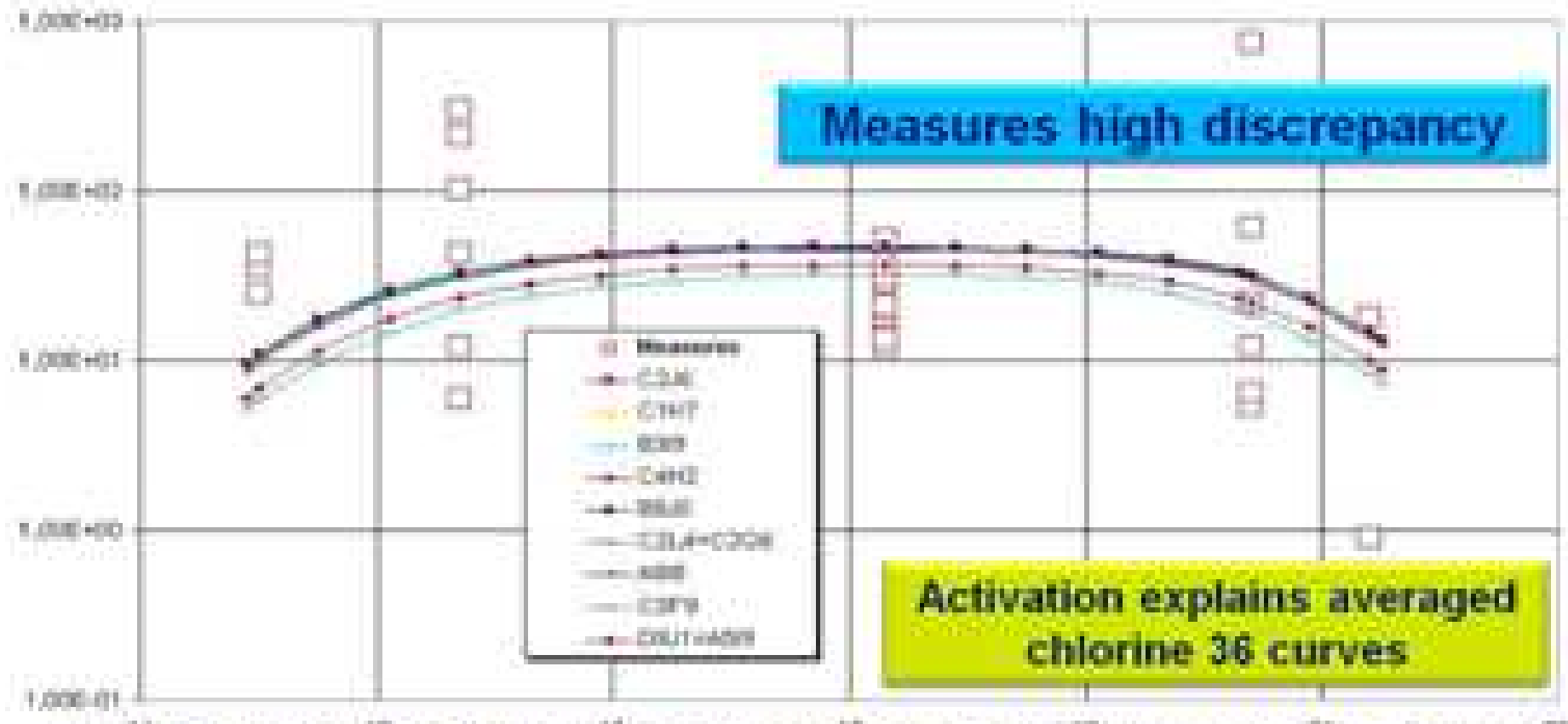
A logarithm is used here to let low measurement values participate to the adjustment process but as seen later on, it is also close to a “completely random point process” for impurities distribution.

3. Computing upper value of the CLT (Central Limit Theorem) 95% confidence interval of the ratio with respect to Co-60.
4. Upper value of the CLT 95% confidence interval of Co-60 multiplied by the upper value of its' ratio previously calculated to compute inventory

# EDF DEVELOPED REVERSE METHOD (2/2)



# BUGEY 1: CHLORINE 36 MEASURED AND ADJUSTED CORRESPONDING COMPUTED CHANNELS



y-axis: Bq/g of chlorine 36 versus x-axis: the height of the Bugey 1 graphite pile - Squares represent sample measurements compared to average calculated curves for the 11 corresponding sampled channels.



# IMPURITY IN GRAPHITE, A COMPLETELY RANDOM POINT PROCESS

The assimilation method may be considered to give a good approximation of the mathematical expectation of a **Poisson point process**, as known as “**completely random process**”. It represents, with an adequate multiplicative factor, the counting of Bq in a sample of a given volume of graphite.

Considering the classical filiations Hyper geometric, Binomial and Poisson, sampling graphite is compared to random drawing of several balls in an urn.

The **binomial distribution** (with parameters  $n$  and  $p$ ) is frequently used to model the number of successes in a sample of size  $n$  drawn with replacement from a population of size  $N$ .

Using the “Pierre Gy formula” on the graphite **Poisson point process** shows that step 2 of the EDF method can be slightly altered with

$$\sqrt{\frac{C_i}{M_i}} - \sqrt{\frac{M_i}{C_i}} \text{ replacing } \ln C_i - \ln M_i$$

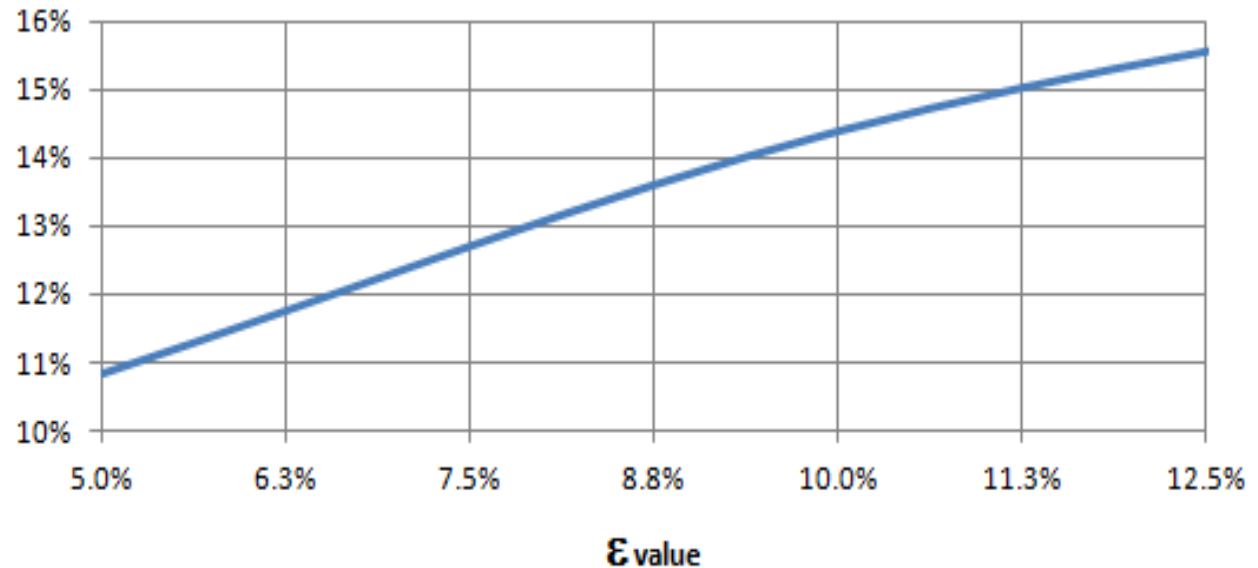
# POISSON CONFIDENCE INTERVAL WITH N SAMPLES

With  $n=30$ , the following result can be computed:  $N = \text{Integer}(n\lambda)$

$$RU(\varepsilon) \approx \frac{1.96}{\sqrt{N}}$$

$$\varepsilon = \frac{1}{n} \left( \sum_{i=1}^{i=n} \ln \frac{C_i}{M_i} \right)$$

**K=100, n=30, Relative Uncertainty RU(ε)**



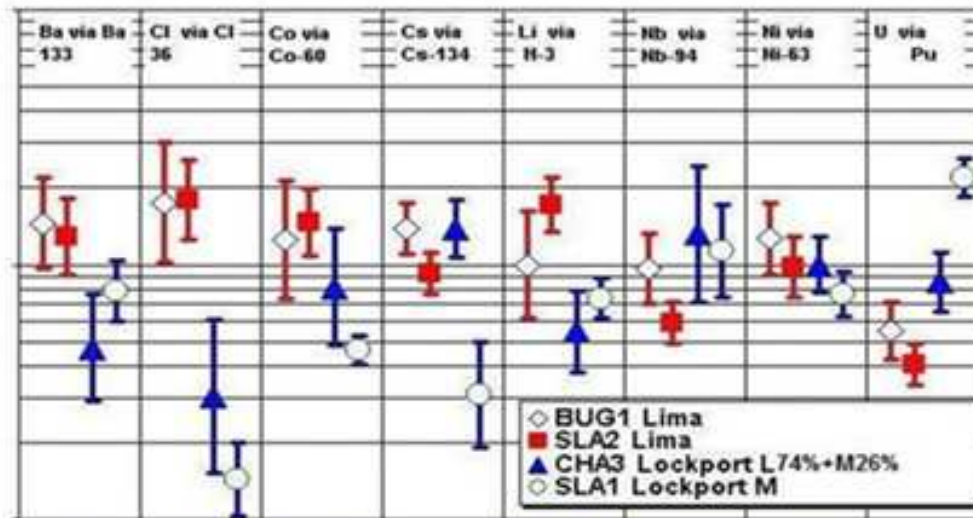
This result represents a low level of uncertainty for radiological inventories produced from activation of impurity close to a “**completely random process**” distribution.

# METHOD CONFIRMATION FOR CONCENTRATION ASSESSMENT

From “3D” neutron flux map and sample measurements for Bugey 1 and St-Laurent A2 (rather different plants), were both calculated to have about 80 ppb of chlorine activated to Cl-36 during operation. This was not the case between St-Laurent A1 and St-Laurent A2 which are nevertheless very similar. The only explanation is that the two piles used the same LIMA coke as raw material for their graphite.

In the calculation, there is no consideration of the parameter « coke ». Nevertheless, only by measures and calculation, LIMA (Bugey 1, St. Laurent A2) and variants of LOCKPORT (Chinon A3, St. Laurent A1) can be recognized.

## METHOD CONFIRMATION: REDISCOVERY OF THE COKES USED FOR GRAPHITE OF THE 4 PILES



With arbitrary units, 95% confidence interval of Ba, Cl, Co, Cs, Li, Nb, Ni and U, impurities adjusted with Ba-133, Cl-36, Co-60, Cs-134, H-3, Nb-94, Ni-63 and (FP+Pu's) for 4 piles

# HISTORY OF THE REVERSE CALCULATION METHOD OF EDF

**2012:** ANDRA (French Radioactive Waste Management governmental agency) validated it and noted that the 2008 EDF radiological inventory method is particularly relevant because it is based on graphite sample measurements.

**2013:** Springer publication. “Method to assess the radionuclide inventory of irradiated graphite waste from gas-cooled reactors” by B. Poncet & L. Petit. Journal of Radioanalytical and Nuclear Chemistry (2013) 298:941-953.

2013: First presentation to the National Assessment Board (Commission Nationale d’Evaluation - CNE) attached to the Parliament's Scientific and Technological Options.

**2014:** Second presentation and validation by the National Assessment Board (CNE).

**2015:** Validation by IRSN, the scientific support of French Safety Authority.

2015: Validation by the Permanent Group of experts mandated by the French Nuclear Authority for the management of EDF nuclear waste.

**2016:** “A reverse method for the determination of the radiological inventory of irradiated graphite “ by Gregory Nicaise & Bernard Poncet - DOI 10.3139/124.110732 KERNTECHNIK - 81 (2016) 5; page 1–6 - Carl Hanser Verlag GmbH & Co. KG - ISSN 0932-3902

# CONCLUSIONS

## Gains

For CI-36 in 15 000 t of stacks, even when considering two times a 2.5% risk of under estimating value (initial method steps 3 and 4), the gain factor is 50 compared to the 2005 simplified evaluation.

## Broadening scope to sleeves

The method is broadening its scope to graphite sleeves that are fitted with stainless steel for fuel support (also known as saddle wires). Measurement of these wires will replace the lost historical knowledge of the sleeves.

## A precise and simple 95% confidence interval computation

The methodology is improving with a better computation of confidence interval which allows a gain factor of about 150 compared to 50 using “best estimate” order of magnitude because of a low level of uncertainty for these inventories.