Long history of Cl-36 Assessment of Graphite Waste by EDF Engineering and the Latest Suggested Developments-17043

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ABSTRACT

Prior to 2005, the EDF initial version for the radiological inventory of graphite was based on the maximum values of the measures, namely a very pessimistic way. In 2008, a scientific method was developed by EDF to evaluate the inventory by reverse activation calculation, in order to limit the overestimation.

The radiological inventory computation principles can be compared to those of all engineering studies. First, the calculation is simplified by taking margins, and if the results are not satisfactory enough, some simplifications are suppressed to reduce these margins even if computation becomes more complicated.

On EDF piles, the gain obtained in 2008 represented a factor 50 relative to the initial version of Cl-36, even with a very penalizing multiplicative factor for uncertainty. Today, the accurate calculation of the uncertainty no longer justifies such a factor. A gain of about 150 now occurs compared to the initial version of Cl-36. It is more than 2 orders of magnitude, which is already enough to assess again the necessary type of disposal because Cl-36 is one of the key radionuclides.

After global presentation of graphite waste management in France, the paper focuses on the inventory scientific process of EDF nuclear graphite, the purity of graphite and its consequences, its particular sampling, the lessons learned, the initial method description, the link with the demonstration of the completely random point process of chlorine in nuclear graphite and the last suggested precise uncertainty computation of inventory of Cl-36. The method confirmation for concentration assessment, the history of the EDF method development and its benefits are also emphasized.

INTRODUCTION

Global context

UK (96 000 t), Russia (60 000 t), USA (55 000 t) and France (23 000 t) represent 90% of the total irradiated graphite in the world. Almost 10% of it, French graphite is shared between EDF (17 000 t), CEA (5 000 t) and AREVA (1 000 t).
EDF graphite waste comes from first generation gas-cooled reactors located at Chinon, St. Laurent and Bugey nuclear sites. All permanently shut down

between 1973 and 1994, the six units are: Chinon A1 (70 MW); Chinon A2 (180 MW); Chinon A3 (360 MW); St. Laurent A1 (390 MW); St. Laurent A2 (465 MW) and Bugey 1 (540 MW).
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 (≈88% in weight)
- Sleeves initially containing uranium cartridges, placed in the channels and removed while defueling

Graphite in French dismantling waste typology

<table>
<tr><td>Mass activity (Bq/g)</td><td>Type of waste</td><td>Short life i.e. Long life (>30 years) below CSA (Soulaines) acceptation level</td><td>Long life (>30 years) above CSA acceptation level</td></tr>
<tr><td>≈100</td><td>VLLW</td><td colspan="2">Very Low Level Surface disposal in CIRES (Morvilliers) in operation</td></tr>
<tr><td>1.00E+06</td><td>LLW</td><td rowspan="2">Shallow repository in CSA (Soulaines) in operation and in CSM (Manche) now closed</td><td>Site under investigation</td></tr>
<tr><td>1.00E+09</td><td>ILW</td><td>CIGEO (near Bures in 2030)</td></tr>
<tr><td>From operation</td><td>HLW</td><td colspan="2">CIGEO (opening near Bures in 2030)</td></tr>
</table>

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)

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:

- to indulge in penny-pinching for sampling and measurements,

- to lose confidence in radiochemical measurements in graphite,
- to choose maximum values to quantify inventories and
- 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.

EDF GRAPHITE WASTE INVENTORY AND ENGINEERING

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.
In order to conform with transportation rules and for economical purposes, the most efficient scale is a concrete container for about 2 tons of irradiated graphite. A 9.5 m^3 concrete package has been developed specifically for stacks graphite waste avoiding bricks cutting. The package has been developed to be in accordance with existing shallow disposal specifications. Regarding EDF's progress, packaging is not a priority, even if the company is still interested in improving conditioning.
In the following part of the paper, focus will be on the Cl-36 inventory in Bugey 1 (BUG1). These results could be generalized to other graphite wastes and most radionuclides.

Engineering study process

The assessment principles of radiological inventory can be compared to those of all engineering studies. 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. It was not possible to converge at once because the demands of the radioactive waste management governmental agency were increasing with their own parallel studies of the proposed disposal.
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. Such simplification is done in the case of radioactive contamination by a fluid, because no global model can explain the deposits in a complicated real geometry.
French law number 739 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.
Considering the calculation of the best estimate multiplied by a factor which included a particularly penalizing assessment of uncertainty, the gain was still a factor 50 on the Cl-36 of EDF stacks compared with the initial version.
Physical and mathematical properties of graphite explain the spatial distribution of chlorine impurity and today, the uncertainty calculation no longer justifies such a penalizing factor.
Using the best estimate, the gain factor is about 150 compared to the initial version. This may confirm that the inventory Cl-36 no longer has the huge inventory that appeared while calculating the initial version built on the largest measured values.
Scientific explanations will now be given on the Cl-36 inventory computation process for Bugey 1 pile.

GRAPHITE WASTE SAMPLING AND MEASUREMENTS

Sampling

- Statistical purposes require multiple measures (≈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.

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.

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 t. 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

Main steps of the 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 $\frac{C}{M}=\frac{Calcul}{Mesure}=1$ adjustment process toward the minimization of $\left|\sum_{i=1}^{i=N_{Rn}}\left(\ln C_{Rn,i}-\ln M_{Rn,i}\right)\right|$ where N_{Rn} is the number of available measurement activity of radionuclide “Rn”. 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

Large over-assessment from initial version

The first version of the method computes the inventory using steps 3 and 4, which lead to:

- a deliberate over-assessment by multiplying 2 upper values of 95% confidence interval which cover a much higher confidence interval (enlargement much higher than 2 standard deviations, the most widespread one).
- and to top it all, the two over-estimating approximations given by the CLT are applied on logarithms and the exponential operation increases the over-estimating.

Impurity in graphite, a completely random point process

In order to not have to use CLT on logarithms and to stay within positive values with exponentiation, 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 the probability distribution of the number of successes in a sequence of *n independent y*es/no experiments, each of which yields success with probability p. The binomial distribution is frequently used to model the number of successes in a sample of size *n* drawn with replacement from a population of size *N.* If the sampling is carried out without replacement, the draws are not independent and so the resulting distribution is a hypergeometric distribution, not a binomial one. However, for *N* much larger than *n*, the binomial distribution is a good approximation, and widely used.

As a model for sampling and counting each Becquerel, corresponding to Cl-36 or not, the comparison of size between a 20 g sample and 2000 t of graphite in the pile shows that "drawing without replacement" is very close to "drawing with replacement" in case of graphite sampling.

Poisson distribution can be used to calculate an approximation of the binomial distribution:

If $n > 30,\ p \le 0.1,\ np(1-p) \le 10\ and\ \lambda = np$ B(n,p), i.e. $P(X = k) \approx \frac{\lambda^k}{k!} e^{-\lambda}$. In all cases, the Poisson point process has the property that each point is stochastically independent to all the other points in the process, which is why it is also known as a "purely or completely random process".

Consequences of the statistical property of the impurity

Considering the result of taking sub-samples from a crushed sample in which the powder has been carefully mixed, this creates a random distribution S. Using the "Pierre Gy formula" on the graphite **Poisson point process** shows:

$$S_{Gy} = E(S) = \frac{E\left(\sqrt{S}\right)}{E\left(\frac{1}{\sqrt{S}}\right)} \text{ and also } \frac{E\left(\sqrt{\frac{S}{S_{Gy}}}\right)}{E\left(\sqrt{\frac{S_{Gy}}{S}}\right)} = 1 \Leftrightarrow E\left(\sqrt{\frac{S_{Gy}}{S}} - \sqrt{\frac{S}{S_{Gy}}}\right) = 0 .$$

With $\sqrt{\frac{C_i}{M_i}} - \sqrt{\frac{M_i}{C_i}} = \sum_{m\geq 0} \frac{1}{(2m+1)!}\frac{1}{2^{2m}}\left[\ln\frac{C_i}{M_i}\right]^{2m+1} = \ln\frac{C_i}{M_i} + o\left(\left[\ln\frac{C_i}{M_i}\right]^2\right)$, $\ln\frac{C_i}{M_i}$ is a second order approximation and step 2 of the EDF method can be slightly altered with $\sqrt{\frac{C_i}{M_i}} - \sqrt{\frac{M_i}{C_i}}$ replacing $\ln\frac{C_i}{M_i}$

Considering the relevant logarithmic properties, S will be seen as a logarithmic average of a random number of drawings of the native Poisson point process X of the graphite. If λ is the parameter of the graphite **Poisson point process** of more significant impurity of the radionuclide of concern, with n measures, it can be shown that this parameter λ is solution of the following equation:

$$\varepsilon = \frac{1}{n}\left(\sum_{i=1}^{i=n}\ln\frac{C_i}{M_i}\right) = \sum_{k=0}^{\infty}\left(e^{-\lambda}\frac{\lambda^k}{k!}\ln\frac{1+\frac{1}{\kappa}}{\frac{k}{\lambda}+\frac{1}{\kappa}}\right)$$ (ε ≤ 10% because the criteria has been slightly altered) and κ being chosen large enough to be close to Poisson distribution.

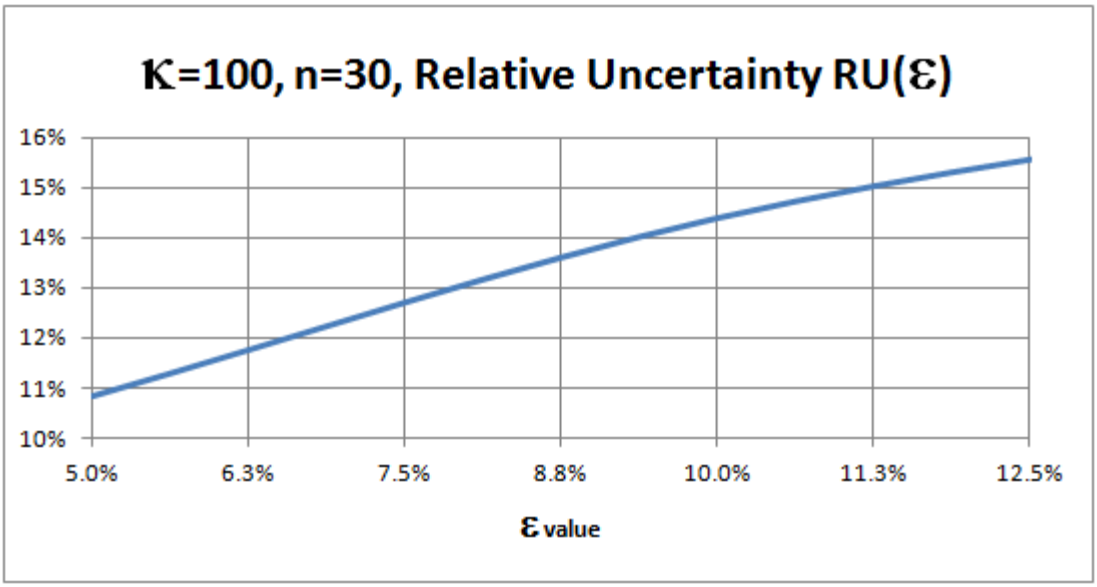
Poisson confidence interval with n samples

Calculation gives: $\left[\frac{\lambda_{\inf}}{\lambda};\frac{\lambda_{\sup}}{\lambda}\right] = \left[\frac{\chi^2_{2N;p_{\sup}}}{2(N+1)};\frac{\chi^2_{2(N+1);p_{\inf}}}{2N}\right]$ with $N = Int(n\lambda)$, integer part of nλ.

$$\Phi(x) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{x} e^{-\frac{t^2}{2}}dt \quad and \quad N \geq 50 \Rightarrow \left[\frac{\lambda_{\inf}}{\lambda};\frac{\lambda_{\sup}}{\lambda}\right] \cong \left[1+\frac{\Phi^{-1}(p_{\inf})}{\sqrt{N}};1+\frac{\Phi^{-1}(p_{\sup})}{\sqrt{N+1}}\right].$$

It gives $\left[1-\frac{1.96}{\sqrt{N}};1+\frac{1.96}{\sqrt{N+1}}\right]$ as 95% confidence interval (usual enlargement factor of 1.96).

With the Relative Uncertainty $RU(\varepsilon)=\frac{1}{1+\frac{1}{\kappa}}\frac{1.96}{\sqrt{N}}$, with a $\kappa=100$ (1% difference with Poisson distribution) and with n=30, the following result can be computed:



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.
Reminder: 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.

History of the reverse calculation method of EDF

- 2008: Development of the reverse method by Bernard Poncet
- 2012: ANDRA (French Radioactive Waste Management governmental agency) validated it and noted that the 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.

CONCLUSIONS

Gains

For Cl-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 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. It was the subject of a WM2016 presentation by the same author.

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.

REFERENCES

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