

**Method to Assess the Radionuclide Inventory of Irradiated Graphite from Gas-Cooled Reactors –
13072**

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ABSTRACT

About 17,000 t of irradiated graphite waste will be produced from the decommissioning of the six French gas-cooled nuclear reactors. Determining the radionuclide (RN) content of this waste is of relevant importance for safety reasons and in order to determine the best way to manage them. For many reasons the impurity content that gave rise to the RNs in irradiated graphite by neutron activation during operation is not always well known and sometimes actually unknown. So, assessing the RN content by the use of traditional calculation activation, starting from assumed impurity content, leads to a false assessment. Moreover, radiochemical measurements exhibit very wide discrepancies especially on RN corresponding to precursor at the trace level such as natural chlorine corresponding to chlorine 36. This wide discrepancy is unavoidable and is due to very simple reasons. The level of impurity is very low because the uranium fuel used at that very moment was not enriched, so it was a necessity to have very pure nuclear grade graphite and the very low size of radiochemical sample is a simple technical constraint because device size used to get mineralization product for measurement purpose is limited. The assessment of a radionuclide inventory only based on few number of radiochemical measurements lead in most cases, to a gross over or under-estimation that is detrimental for graphite waste management. A method using an identification calculation-measurement process is proposed in order to assess a radiological inventory for disposal sizing purpose as precise as possible while guaranteeing its upper character. This method present a closer approach to the reality of the main phenomenon at the origin of RNs in a reactor, while also incorporating the secondary effects that can alter this result such as RN (or its precursor) release during reactor operation.

INTRODUCTION

Graphite waste management

EDF (Électricité De France) operated in France six gas-cooled reactors, all shutdown now for at least fifteen years. These reactors are of so-called in French, “UNGG” reactor type (Uranium Naturel Graphite Gaz). They were graphite moderated, cooled by carbon dioxide and fuelled with natural metallic uranium. UNGG reactors have to be dismantled as soon as possible and at least by 2022 for the retrieval of the first graphite brick from the Bugey 1 pile. The design of UNGG reactors is, in its general principle, very close to that of the British Magnox reactors, that was developed independently at the same period in United Kingdom. Coming from the lack of uranium enrichment, graphite had a very high level of purity due to the necessity of the highest transparency to neutrons.

The RN inventory of a nuclear waste is a precise quantitative description of all the RNs that it contains. It makes its possible best to anticipate an *a priori* classification of the waste and to develop the best suited management strategies. For the graphite waste producer (the reactors’ operator), assessing the

radionuclide inventory of the graphite of UNGG reactors is essential above all for reasons of safety. During dismantling operations, the knowledge of the RN inventory makes it possible to choose the most suitable deconstruction tools and the health protection means to use for ensuring safety of workers. Identification of the RNs the behavior of which under the dismantling conditions may lead to significant discharges makes it possible to adapt the confinement and purification systems in order to master the impact on the environment.

Concerning final disposal, the inventory knowledge allows to compute the repository sanitary impact during the future centuries and to decide if such a forecasted impact cope with the regulation. The radiological inventory declaration is the result of a rigorous procedure in accordance with the laws of physics, based on results of analysis of samples, on modeling seeking to best reproduce the phenomena explaining the presence of these RNs and sometimes, in the absence of any quantifiable element, on reasoned choices for ensuring the reasonable over-assessment of the radiological inventory declared by the graphite waste producer. With the improvement of techniques of analysis and enhancement of data accessible through the computation of neutron flux, the radiological inventory of graphite can be made precise in order, while guaranteeing its upper character, to be as close as possible to reality.

The radiological inventory based on traditional activation calculations of assumed impurity content in the graphite does not fit at all for the graphite from UNGG reactors. Most of the time and because of a high level of purity, the impurity content of the graphite is not well known or actually unknown. Moreover a simple activation calculation cannot take into account the effect of some phenomena such as radiolytic corrosion, that lead to RNs release from the graphite during operation. This paper describes a methodology coupling modeling tools and radiochemical analysis results. It is fully consistent with IAEA recommendation [1] for the assessment of a radiological inventory that “the result of any theoretical calculations should be compared with the data obtained by experiments to obtain a validation of the calculations”.

Origins of RNs in irradiated graphite

Nuclear graphite is a synthetic material manufactured from basic materials issuing from petroleum and coal, natural products which are full of numerous impurities. Although subjected to thorough purification steps during the production process, some impurities that it is not possible to eliminate completely remains in the nuclear graphite. As it will be shown in this paper, the radioactivity of the graphite in UNGG reactors comes almost exclusively from the activation under neutron flux of these impurities and of the carbon present in the material.

With the production of RNs through impurities activation, out of a principle of exhaustiveness, we have to take into account other phenomena which may also have had an influence on the radiological inventory of the graphite during the reactor operation:

- Radiolytic corrosion induced a loss of mass of the graphite by oxidation of some of the carbon atoms accessible to the gases, which were released as CO₂ or CO in the cooling gas. During this erosion, some of the RNs were able to be released and discharged into the cooling gas.
- Possible contamination of the graphite by the cooling gas, which would be activated when flowing into the fuel channels of the graphite pile, or by corrosion products of the metal internal parts transported by the cooling gas, would also have to be considered for generality purposes.
- Finally, in the particular case of the two fuel cartridges fusion accidents which took place in the reactors at the EDF Saint-Laurent power station in 1969 and 1980, possible contamination of the graphite by fission products released in the cooling gas must also be considered.

Anyway, concerning the last two points about deposit phenomenon, we have to admit such a hypothesis as unfit because it would be the exact opposite of the “nugget effect” (see below) clearly observed in graphite measurement.

By definition, this effect is the very negation of a meaningful deposit because it matches with the total lack of any correlation between the same radionuclide measured at two points even being very close.

As it is not realistic to consider all the 144 RNs with a half-life greater than 6 months that are requested by ANDRA¹ in the context of safety studies for both the long-term behavior and the disposal operating management of irradiated graphite, it has been chosen to focus arbitrarily this paper on four RNs considered to be representative of various phenomena that may occur in the reactor or considered to be significant for the management of graphite waste. They are the following:

- H-3 is in term of activity level a major RN in irradiated graphite from UNGG reactors. It is a short-lived (half-life 12.33 years) low energy radionuclide whose potential impact concerns mainly its management during the dismantling period of the reactors and the operating period of a repository. H-3 can be mainly produced through neutron activation of two impurities of the graphite, boron and lithium. The concentrations of lithium and boron impurity in the graphite being equivalent and around 0.1 wppm, the H-3 produced in UNGG graphite is almost exclusively due to the reaction of activation of lithium ${}^6\text{Li} (n, \alpha) {}^3\text{H}$, the neutron effective cross section of which being the highest.
- C-14 is also in term of activity level a major RN in irradiated graphite. It is a long-lived (half-life 5,730 years) pure β emitter. There are two main ways of forming C-14 by neutron activation in graphite: activation of the most abundant isotope of nitrogen N-14 or activation of natural C-13. The origin of C-14 in the graphite between the 2 reactions highly depends on the nitrogen content in the graphite under operating conditions.
- Cl-36 is a long-lived RN (half-life 301,000 years). Such a huge half-life explains that this radionuclide is not taken into account yet in US disposals. In France, it is considered being a sizing factor for disposal of irradiated graphite. This RN is minor in terms of activity level in French irradiated graphite, which is proven by the fact that taking into account isotopic dilution of Cl-36 among natural stable chlorine of irradiated graphite doesn't induce any very significant lowering of its sanitary impact. Cl-36 is assumed to be very mobile in a disposal situation, which makes it the first radionuclide considered by the ANDRA promoted impact studies at the outlet of a disposal. It may be produced in graphite gas-cooled reactors in various ways by direct activation of the isotope Cl-35, of the isotope K-39, and also by indirect pathway neutron activation of the stable isotope S-34. With the sulfur and potassium impurity contents in nuclear graphite, it appears that the reaction with Cl-35 is the by far predominant reaction for the formation of Cl-36 in graphite of a UNGG reactor.
- Cs-137 is a product of uranium fission reactions. This RN makes it possible to attest to the presence or not of fission products that may come from the uranium impurity present naturally in graphite (or possibly the uranium of the fuel elements in case of the proof of geographical auto-correlation which is not the case because of the observed “nugget effect” as seen below).

¹ French governmental agency having a monopoly of radioactive waste disposal in France

ANALYTICAL DATA TO BE USED FOR A RN INVENTORY ASSESSMENT

The issue of impurities measurement in the original graphite

Even if we will show that it is not at all sufficient, the assessment of a radionuclide inventory using activation calculation should begin with the collection and/or the generation of unavoidable data:

- Plant operational history (that means detailed history of each period of power generation)
- Length of the decay period following final shutdown (it is often seen as a fundamental part of operational history)
- Input cross-section data set for given neutron spectra and temperatures (that is usually provided by international libraries)
- Nuclear fuel characteristics (in order to compute the link between fuel neutron flux sources and thermal power generated and to compute the boundary conditions of Boltzmann PDE (Partial Differential Equations))
- Geometry and masses of the components subjected to the neutron flux (in order to solve Boltzmann PDE with their boundary conditions)
- And material composition without needing trace element composition because the effect of trace element composition is negligible to compute neutron flux. It is lucky because at that step of the computation, the values of explaining elements aren't already known (explanations are given below).

If most of these data is accessible to the plant operator especially if the electricity generated data have been saved because feeding the interconnected electricity power net (the problem being different if the reactor has not been operated for such civilian purposes), the last one concerning trace element composition is particularly difficult and even not accessible in some cases for nuclear graphite.

Identification and measurement of the impurities present in the original graphite and liable to have been activated is not a trivial problem. The question of the impurities which may have an impact on the management of the future nuclear waste material was not always considered at the time of reactor building. The graphite from the various manufacturing plants was indeed always characterized from the viewpoint of its transparency to neutron properties (measurement of the capture cross sections) and of the physical properties (density), but not from the viewpoint of the totality of its chemical composition. In addition, another important point that should be emphasized concerns the very low impurity content that gave rise (and it is even worse nowadays than in the past as explained later on) to operational difficulties regarding their measurement with the required accuracy. While for the radioactive elements, it is relatively easy to measure over detection limits (DL) which corresponds to elements that produce no radiation and which measurement by conventional chemical methods is often limited by higher chemical DL.

It was even easier formerly to proceed to measurement of RN produced with a calibrated activation flux and these methods are getting nowadays more and more difficult to use because of the increasing constraints of regulations to comply with. Mass spectrometry is easier but less accurate than old activation methods. Moreover, in addition to these difficulties of a technical nature, the case of nitrogen, one of the precursors of C-14, is an example of an impurity for which it is impossible to determine its content in the graphite in operating conditions. In fact the nitrogen can be present in virgin graphite as an impurity

introduced by the raw materials used for its manufacture (mainly including air trapped in the closed pore structure), but it could also have been added or removed during the operating period. The adsorption of nitrogen on the surface of the graphite is known, and nitrogen is an impurity in the coolant gas that can also come from a deliberate entry of air (in maintenance periods) or an unintentional entry (leaks) into the atmosphere of the reactor. Their measurements in the graphite moreover don't make any sense, since it is impossible from the operational viewpoint to avoid its pollution by the nitrogen from the air during the execution of them.

Studies performed on nuclear graphite have only assessed the capacity for adsorption of nitrogen at its surface. However this kind of measurement has always been performed on non-irradiated graphite in conditions (under air or nitrogen) that are very far from the usual operating conditions. Under irradiation with carbon dioxide, it is well known that the carbon surface of the graphite is continuously oxidized: this very certainly leading to the release of a significant part of the nitrogen that could have been adsorbed on it.

Although a "mean" nitrogen content of 30 to 50 wppm is sometimes used in academic studies in order to assess the C-14 inventory by activation calculation, application of such data to the case of the graphite from the EDF UNGG reactors leads to calculated C-14 contents that are greater, by at least 1 order of magnitude, than those actually measured. In addition, certain published measurements on the graphite of UNGG reactors before passage through the reactor give nitrogen levels of the order of 4 wppm [1], which seem to be more compatible with the C-14 activity levels actually measured on graphite after passing through the reactor.

The issue of RN measurement reproducibility

Another way to assess the radiological inventory of the irradiated graphite should be by interpreting radiochemical measurement on irradiated graphite sampled from the core of the reactors. For EDF reactors, according to the dimensions and geometry of the piles, a set of 20 to 30 irradiated graphite samples were in general analyzed by radiochemistry on the 200 cores taken on average per reactor pile.

The radiochemical analyses were performed by CEA according to state of the art methods whose main principles are presented in [1]. In the case of the RNs present in very small quantities such as chlorine 36, the reproducibility of the results is difficult to achieve.

The fundamental physical phenomenon that explains the clear impossibility of the reproducibility of the analyses for the elements present at trace level has nothing to do with the quality of the sampling and neither with the quality of analyses. The variability of the results is well known and completely impossible to avoid because it is inherent to sampling process of finely divided material. The performance of the measuring laboratory is also not at all in question.

If some samples of graphite are shared for comparison purposes between different laboratories, it makes no sense is not possible at all to do it with that material even if it is completely acceptable for example with samples coming from the same casting phase of a metallic alloy. Concerning graphite, it is completely impossible to decide if differences are coming from the laboratories or simply from the sampling.

To compare several laboratories, you need to compare the results coming for example from the sampling of only one unique mineralization liquid solution. If you send different graphite samples to the

laboratories, first of all, you will compare the different samples and you will discover again the “Theory of Sampling” explained below.

It is a case of the variance that affects the measurement of a sample for representing a concentration (chemical content or specific activity) of a given batch, according, among other parameters, to the concentration, the mass of the sample or the mass of the batch. This phenomenon, which it will be attempted to explain briefly below, was in particular theorized by Pierre Gy [2].

We should admit that such demonstration usually begins to upset the chemist, even the best, who is used to aqueous solutions, which obviously never present any sampling variability because of the liquid phase, exactly as what occurs with an alloy which was also a liquid phase during the casting.

If a sample of mass M_e is taken, normally low in relation to the mass M_L of the batch from which it is extracted, the relative variance of the fundamental sampling error can be written, by grouping together in a factor K the other parameters of influence, as a particular expression of the Gy formula:

$$\frac{s^2}{a_L^2} = s_r^2 = \frac{1 - a_L}{a_L} \left(\frac{1}{M_e} - \frac{1}{M_L} \right) K \quad (\text{Eq. 1})$$

where:

- M_e , the mass of the sample is given in grams;
- M_L , the mass of the samples batch is normally much greater than M_e ;
- a_L is the concentration of the component of interest expressed in the form of a weight fraction.

In the case of graphite samples, the mass of the sample is negligible compared with the mass of the batch since it is equal to approximately 0.5 gram for the measurement.

The characteristic of the impurities of nuclear graphite is their very low proportion, for reasons that are fully understandable related to the neutron performances necessary for obtaining criticality despite the use of “non-enriched” uranium (UNGG).

From these two findings the following simplified formula comes:

$$s_r^2 \approx \frac{1 - a_L}{a_L} \frac{K}{M_e} \approx \frac{K}{a_L M_e} \quad (\text{Eq. 2})$$

The Gy formula was essentially originally elaborated from the hypergeometric discrete distribution law that describes the probability of drawing “m” white balls (“m” fragments of chlorine to give an idea on a practical example, chlorine being the species of interest, the concentration of which is sought) from “n” (“n” fragments of the carbon + chlorine mixture) when the complete batch contains “M” white balls (chlorine) among “N” balls (the chlorine + carbon mixture) in a drawing without putting back in order to model the taking of a sample (of “n” fragments of the mixture).

This hypergeometric law, when N is large², can be approximated by a binomial law and, with the notation $p = M/N$ for the concentration of the batch (here the pile), the expectation and the variance of the random variable m/n can be calculated, which corresponds to the (chlorine) concentration measured.

Using the fact that the law is very close to the binomial law, which makes it possible to write its mathematical expectation: $E\left(\frac{m}{n}\right) = p$ and its variance $\left[\sigma\left(\frac{m}{n}\right)\right]^2 = \frac{p(1-p)}{n}$. The relative variance is a

dimensionless quantity since it is the square of $\sigma\left(\frac{m}{n}\right) / E\left(\frac{m}{n}\right)$. The relative variance of this measured concentration will therefore be written $\left[\sigma\left(\frac{m}{n}\right) / E\left(\frac{m}{n}\right)\right]^2 = \frac{(1-p)}{np}$.

This formula indicates that the concentration “p” of the batch (the pile) and the number of fragments “n” in the sample (the sampling) each fulfills an essential role in the relative sampling variance. The fundamental relative variance of the sampling therefore increases when the number “n” decreases and/or when the number “p” decreases. Thus the lower the concentration the more the relative variance increases. Likewise, the more the number of fragments in the sample decreases, the more the relative variance increases. However, the number of fragments is directly proportional to the mass of the sample.

The relative variance of the measurements of the content on sampling, corresponding to the fundamental relative sampling variance, is therefore inversely proportional to the mass of the sample (corresponding to the number “n” of fragments of the sample) and/or to the true content (corresponding to “p”, the true chlorine 36 concentration of our example) when this is low.

The formula (Eq. 2), $s_r^2 \approx \frac{1-a_L}{a_L} \frac{K}{M_e} \approx \frac{K}{a_L M_e}$, given previously is indeed found again. This formula explains the relative variance of a sample for representing the content of a given batch (here the graphite pile) according to the mass of the sample (corresponding to the mass of the sampling of less than 1 gram) and the content of the constituent of interest (for example chlorine 36 and/or chlorine).

The issue of RN measurement spatial variability

Moreover, to the scale of the pile of a reactor, variability over sometimes two orders of magnitude (or even 3 orders of magnitude if using the sub-sampled analyses instead of average computed at the level of a 20 or 30 gram core given in the following figure 1) is also observable. Figure 1 presents by way of example the distribution of the chlorine 36 measurements obtained on graphite samples taken from graphite cores in the EDF reactors Chinon A3, Saint-Laurent A1 and A2 and Bugey 1.

² 100 Bq of chlorine 36 per g of graphite corresponds referred to an atomic scale to a ratio of 1 atom of chlorine 36 for 36×10^6 atoms of carbon, assuming as a first approximation that the graphite consists solely of carbon atoms.

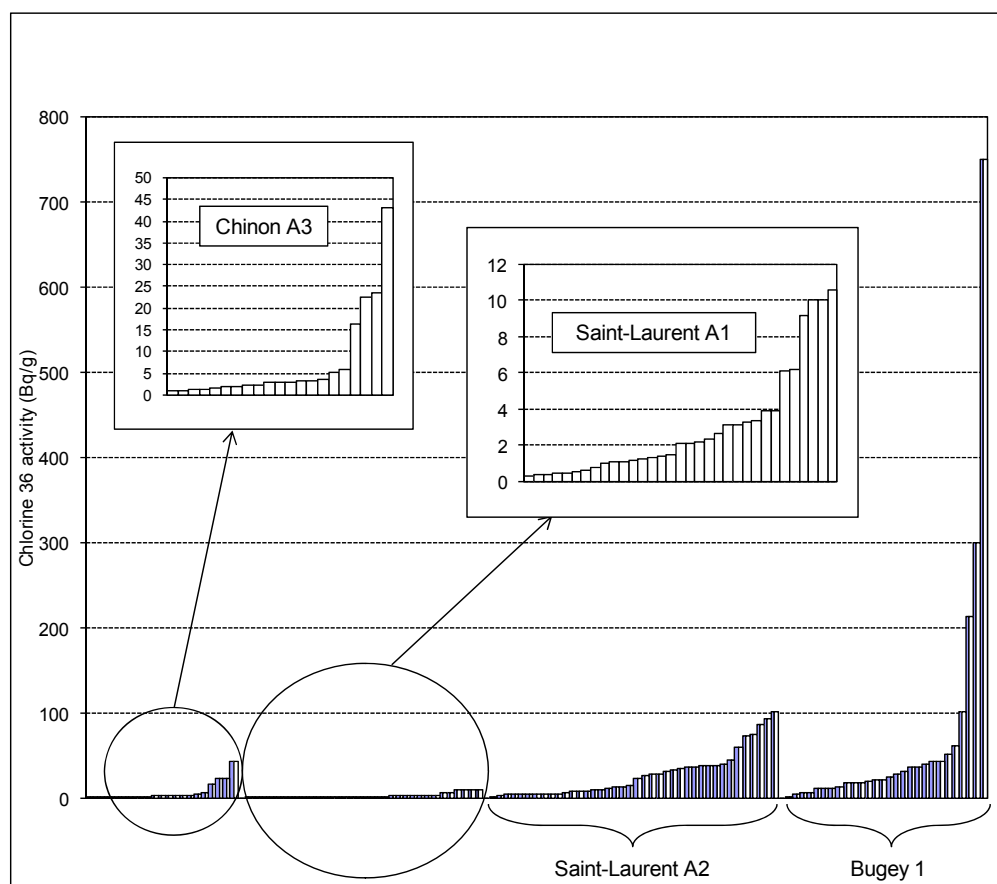


Figure 1: Cl-36 measurements (in Bq/g) on graphite core from EDF UNGG reactors

This very great variability observed to the scale of a pile cannot be explained by the variability of the neutron flux, giving rise to the production of Cl-36, which is not as great (in the graphite moderator the mean transport length of the neutrons is around 60 cm and the activation factor scale doesn't exceed the value of 6 among the Bugey 1 pile samples for example).

Logarithmic Figure 2 squares reproduce the dispersion of the Cl-36 measurements in the samples from the Bugey 1 reactor according to their sampling point in the graphite pile³. The variability of these measurements is correlated neither with the variation in the neutron flux according to the altitude, nor with the other macroscopic operational parameters of the reactor such as the temperature which varies between the top and the bottom of the pile.

This high variability in the measurement (due to the very high purity of nuclear graphite) shows that it is not possible to obtain a representative and reproducible measurement of an object, whether with regard to a 20 or 30 gram graphite core scale and even to a graphite brick, in particular for RNs which precursors

³ For Bugey 1, the heights are given with reference to the top cap of the reactor vessel in metres. The Bugey 1 graphite pile consists of 12 beds of graphite bricks. The bottom of the pile (bed n° 1) is at 21.80 m with respect to the level of the top cap, while the top of the pile (bed n°12) is at 11.60 m.

are present in very small quantities such as Cl-36. The link with the purity and the sampling size is coming from “Theory of Sampling” by P. Gy [2] as explained above.

Without taking into account the fact that a difference of level of activation between the sampled bricks which explains no more than 1 order of magnitude, it appears impossible to get representative and reproducible measurement to the scale of an entire pile.

This finding shows that for establishing the radionuclide inventory of the irradiated graphite in the piles, an approach based on a statistical tool through the calculation of a mean of several measurements is a necessity. The use of a mean value is in fact the only method that makes it possible to divide the variance observed by the number of measurements and is reliable, whereas the extrema (minima and maxima) represent by definition singular measurements very far from average reality because we know the pure random origin of the observed variability.

THE IDENTIFICATION CALCULATION-MEASUREMENT METHOD

General principles

EDF has chosen to develop a method of 3D geographical reconstitution of the inventory of the nuclear piles that is based on an activation calculation which is adjusting the mean value of the several measurements available with the mean value of the calculation corresponding to the measurements (same position and same time). The objective of developing this method is twofold. By using a statistical averaging approach to the measurements, and not an approach based on the maximum measurement, the measured data is made more representative.

Apart from this, the use of an activation calculation results in a closer approach to the reality of the main phenomenon at the origin of RNs in a reactor, while also is incorporating the secondary effects that can alter this result (release during the operation of the reactor). In order to be able to take account of these possible secondary effects, this calculation is performed without prejudging any initial impurity content, or the behavior of this impurity, in the graphite, in conditions of reactor operation, but by prior calculation of its best estimate adjusting measured and computed mean values. It is based upon measurement of the levels of RNs, which are much easier to detect than the non-radioactive impurities, for the very small quantities observed in the nuclear graphite, since the radioactivity is then the only measurable magnitude. This enables to compute explanatory impurity content from the measurements performed on samples by reverse activation calculation.

Specifically designed for disposal sizing purpose, which explains the chosen over-estimation of ratios with respect to Co-60 which will be the only radioactivity measured directly on each container, the method of inventory assessment by identification calculation-measurement consists of using the following process so as:

- In a first stage, to create a 3D map of the flux density of neutrons with 315 intervals for energy in

the reactor pile concerned in the calculation. This map is based on the geometry of each pile, with the TRIPOLI calculation code. This code for the transmission of particles (neutrons) is solving the Boltzmann equations, coupled with nuclear databases (ENDF, JEF-2).

- In a second stage, from this map of the flux, and incorporating the history of reactor operation, to reconstruct a global inventory of the radioactivity produced by this flux throughout the geometry of the reactor pile. The inventory is then created by using the impurity levels, which are adjusted to their explanatory values, from the result of the activation calculation with the available measurements of the same RNs. These activation calculations are performed by EDF, using the DARWIN/PEPIN code which is used to integrate all of the phenomena that lead to the production of RNs (activation, fission, radioactive decay, etc.) by solving the Bateman equations.
- In a third stage, use is made of the fact that each RN measurement is characterized by a specific standard deviation that is dependent on the number of measurement points available. This standard deviation, which corresponds to each measured radionuclide, is used to calculate a confidence interval for its mean calculated value. For an overall determination of the inventory, we consider the upper value of the confidence interval (which corresponds to a 2.5% risk of under-evaluating the result) of the ratio with respect to the cobalt 60 gamma tracer, in order to remain consistent with the usual choices because of the ratio robustness.
- In a fourth stage, in order to determine the value of activity to be declared for each radionuclide, we consider the upper value of the confidence interval of the cobalt 60 tracer, which thus corresponds to a radioactivity to which is added a 2.5% risk of under evaluation, and we multiply this upper value by the upper value of the ratio previously calculated for the radionuclide concerned.

The relevance of the method for inventory calculation by adjustment calculation-measurement is based upon the availability of a sufficient number of measurements of the wanted RNs carried out on samples of irradiated graphite. These data, in sufficient number, are processed using the Central Limit Theorem (CLT), which is employed in order to determine the uncertainty in the activity (which follows a Gaussian distribution by application of the CLT).

The acquisition of measurements is a long and costly process that should have been justified with respect to an accepted uncertainty. Since the variance of a mean is obtained by dividing the variance of the population of measurement by the number of points, then the larger this number of measurement points the smaller the standard deviation and confidence interval on the mean value of the activity of a given RN.

This is used to directly obtain the uncertainty calculated from:

- Statistical measurement data and the associated adjusted calculations,
- Number of points used, and
- Under-assessment risk selected.

In practice, for each reactor, EDF has arranged for the all possible analysis of RNs on some thirty samples of graphite taken from the reactor. It is from an order of magnitude of about 30 points that the number of points can be seen as always being sufficient since the withdrawal of any of them does not significantly change, neither the estimate of the mean, nor its confidence interval. On the other hand, below 15 points, the calculation that employs the Student Law introduces a penalty in terms of increasing the size of the confidence interval.

Generally speaking, by taking account of the measurements below the detection limit, about 900

measured, of which about 350 are at the detection limit, have been included for each reactor, for the 4 piles of the Saint-Laurent A1, Saint-Laurent A2, Chinon A3 and Bugey 1 reactors.

Main results

All the results presented relate to an activity calculated for the date of 01/01/2017, this being the initial reference date for withdrawal of the first graphite elements from the Bugey 1 reactor.

Table 1 presents the calculated inventory (in TBq) with the respective graphite masses expressed in metric ton, calculated in the case of the covered RNs of interest.

Table 1: Radiological inventory (in TBq) of irradiated graphite from EDF UNGG reactors as determined according to the identification calculation-measurement method.

	10^{12}Bq	^3H	^{14}C	^{36}Cl	^{137}Cs
0.000	Chinon A3 (2,530 t)	82	101	0.018	0.07
	Saint-Laurent A1 (2,570 t)	70	102	0.007	0.15
	Saint-Laurent A2 (2,440 t)	217	187	0.092	0.12
	Bugey 1 (2,060 t)	192	260	0.170	0.18

The calculation results in averages that lead to a distribution of RNs subjected to the neutron flux. As illustrated in figure 2 in the case of chlorine 36, by calculation an activity greater in the central zones of the pile where the neutron stream has been the most intense, is logically obtained.

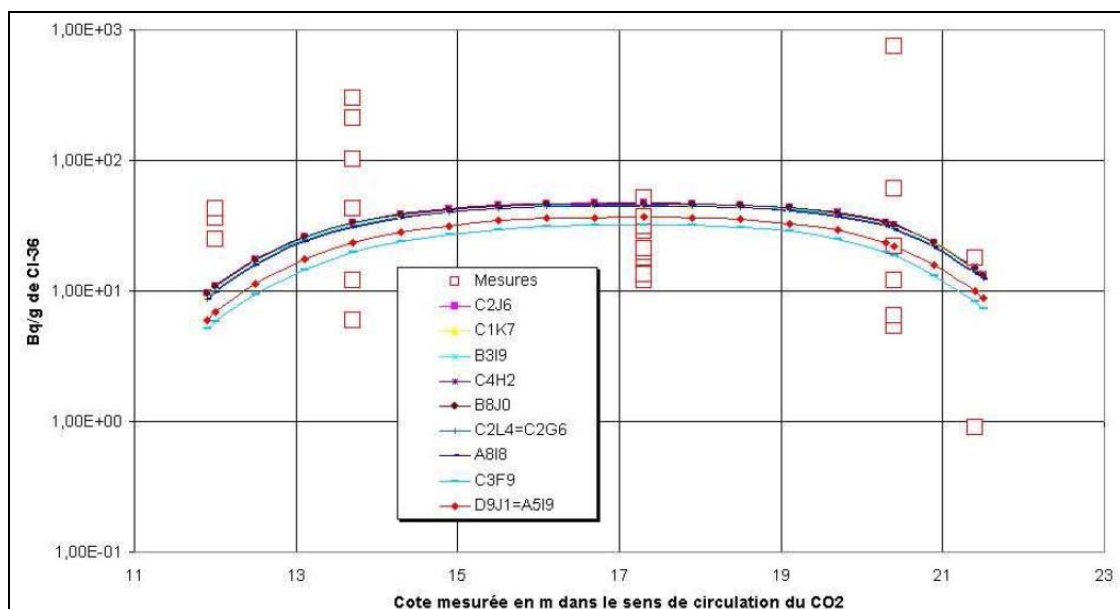


Figure 2: Average calculated values (in Bq/g) of chlorine 36 for the graphite of some fuel channels in the Bugey 1 graphite pile (squares represent measurements - x-axis: height of the pile)

DISCUSSION

RNs and impurities release

For the RNs for which there may have been a release by the graphite, adjustment of the value of the explanatory impurity allows taking account this phenomenon. This is the case for Cl-36, C-14 and H-3.

For C-14, application of the method also allows to study the C-14 inventory with this same phenomenon of release in the reactor, probably due to radiolytic corrosion. The calculation results thus show that, in the case of the EDF UNGG reactors, the explanatory nitrogen of the C-14 inventory is much lower than the 50 wppm usually taken as a reference in the literature. For the EDF UNGG reactors, the C-14 that remains in the graphite at the end of the operating comes also from C-13 activation.

In the case of Cl-36, it has thus been shown that the explanatory chlorine content of Cl-36 measured in various samples only corresponds in reality to about $1/100^{\text{th}}$ of the initial chlorine content in the graphite before irradiation. The chlorine impurity consistent with the Cl-36 inventory is of the order of a few hundred mg/t (wppb) against initial chlorine content in the non-irradiated graphite of the order of a few tens of mg/kg (wppm).

This result indicates a significant phenomenon of release of the chlorine initially present in the graphite under the effect of temperature alone, and before the appearance of most of its measurable activation in Cl-36 in the graphite. This phenomenon had been confirmed in academic studies. Chlorine released by the graphite pile in the reactor in operation has been observed through the measurements performed on the deposits observed at the surface of the metal insides and on the lagging inside the reactor vessel. Measurement campaigns performed on similar industrial reactors also highlight the presence of Cl-36 in the traps used to de-humidify the coolant.

This phenomenon of the deposition of Cl-36 observed on some of the cold parts of the reactor does not exist to an extent that is measurable for the graphite moderator as indicated by the absence of spatial correlation of the Cl-36 measured in the moderator (see figure 2). In fact, the regionalized variables resulting from pollution or deposition would appear to represent a continuity that is characterized by a random irregularity which would always lead to envisage a spatial interpolation. In the vocabulary of “geostatistics”, the non-applicability of such a hypothesis to the available measurements corresponds to a pure “nugget effect” (also called 100% “nugget effect”). By definition, this effect is the very negation of a meaningful deposit since it matches with the total absence of any correlation between the same radionuclide measured at two points even being very close.

Concerning the carbon dioxide coolant circulating in a UNGG channel, nothing of the type of “variogram” liable to take account of a deposit of RNs or of pollution carried by the coolant is detectable by measurement, while the pure nugget effect describes perfectly what can be observed on the graphite of the piles through very many available measurements of RNs.

This comment on the absence of any significant deposit of RNs on the pile graphite is not in contradiction with what has been described as hydrogen-carbonated deposits observed in the reactors, for which low methane content has been added in the coolant. In this case, it is a deposit resulting from a chemical phenomenon that is similar to a polymerization which has been produced under the effect of temperature and of the radiation in the reactor in operation, but that is without any significant effect on the inventory of the RNs measured in the waste, according to the high difference of magnitude between stable and

radioactive nuclei numbers.

Fission products contamination

The results obtained for Cs-137, a trace element for the fission reactions, show that the decontamination operations adopted following the two accidents involving the fusion of fuel elements that occurred in the Saint-Laurent A1 and Saint-Laurent A2 reactors, have been effective. In fact, these accidents have no detectable effects in terms of contamination of the graphite in the piles. The levels of Cs-137 are more or less equivalent in all the EDF reactors whether fusion of fuel elements has occurred or not. The presence of Cs-137 in very low quantities and the heavy nuclei produced, are also explained by the fission of traces of uranium present in the original graphite. These traces were identified in the analyses performed on the graphite at the time of their manufacture and now evidenced by the identification calculation-measurement method.

Graphite origin parameter

Another result particularly significant in the case of Cl-36 concerns exposing the differentiated behavior of the different natures of graphite used in the reactors. Depending on the nature of the original coke used in the manufacture of the different graphite, inventories of different magnitudes are observed. Thus the radiological inventory is higher in the graphite produced from Lima coke (Saint-Laurent A2 and Bugey 1). This result is particularly striking when the results obtained on the Saint-Laurent A1 and Saint-Laurent A2 reactors whose designs are identical and that have been operated in very similar conditions in terms of temperature, flux and duration, are compared. For Saint-Laurent A1, whose pile is made of graphite produced from Lockport M coke, the radiological inventory is significantly lower with an order of magnitude less in chlorine 36, than in Saint-Laurent A2 whose pile is made of graphite produced from Lima coke.

This result can be due either to an impurity content that is dependent on the coke, or to behavior of the graphite in relation to the release of the RNs, which are also dependent on the coke. These two reasons are not necessarily mutually exclusive but the same behavior of chlorine for Saint-Laurent A2 and Bugey 1 shows that the coke effect is the main one because they have clearly different conditions of operation but the same Lima coke. The experimental results from previous work tend to show, in studies relating to the release of tritium produced by activation in the experimental reactor that the release seems to be lower in the case of the graphite produced from Lima coke than for those produced from Lockport coke but in close operation conditions.

The rediscovery of the influence of the nature of the coke (see figure 3) is a particularly notable result of the method by identification calculation–measurement including averaging process (so called assimilation method or melting). In fact, no account has been taken of this information in developing the method that does not favor any arbitrary assumption but is only based on measurements of RNs and on reverse activation calculation by knowledge of the flux. The influence of the coke of origin parameter is indeed a fact that is tangible, simple and natural, resulting from the method for inventory calculation by identification calculation–measurement, and that confirms its relevance and efficiency by the actual explanation that comes out of it.

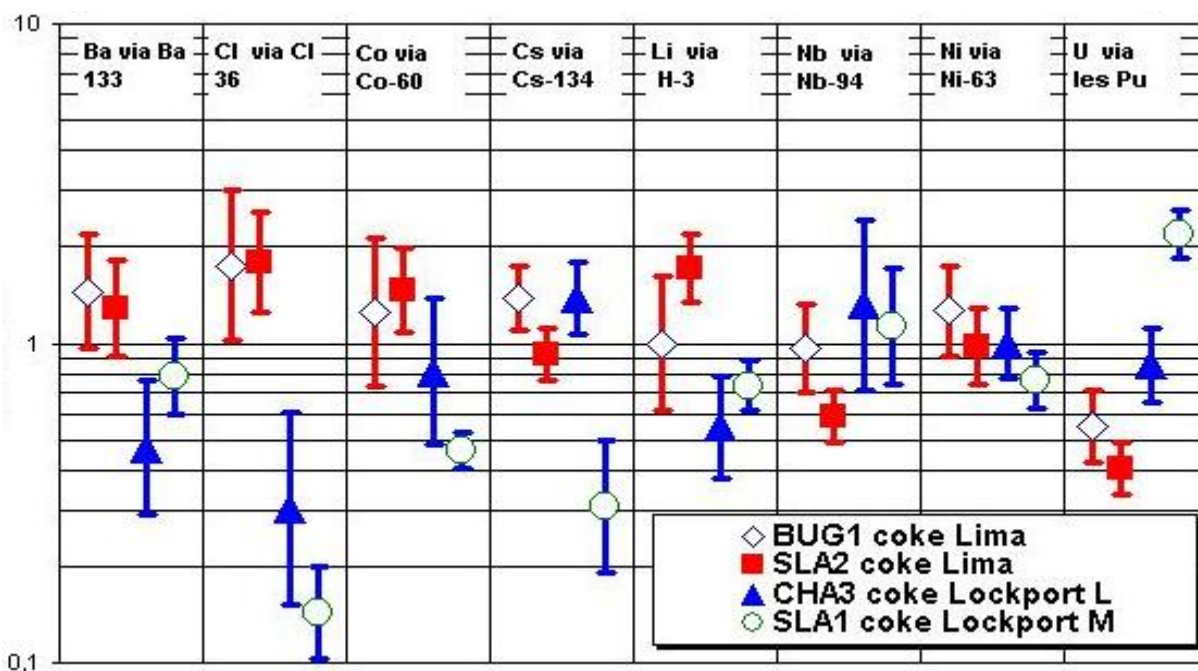


Figure 3: Confidence intervals of impurities adjusted with RN identification calculation/measurement for 4 piles coming from LIMA and LOCKPORT cokes

CONCLUSION

About 17,000 t of irradiated graphite wastes will be produced from the decommissioning of the six French gas-cooled nuclear reactors. Determining the radionuclide content of these wastes is of relevant importance for safety reasons and in order to determine the best way to manage them.

It is not possible to assess the radionuclide inventory by using a conventional activation calculation method alone as for a well known simple activated metallic alloy. As shown through the examples of Cl-36 and C-14, some significant RNs and their precursors are subjected to release from the graphite during reactor operation due to well known phenomena occurring in graphite (radiolytic corrosion, thermal release). A conventional activation calculation is not able to take into account these phenomena. Moreover, the content of some precursors giving rise to RNs in graphite, such as nitrogen, cannot be determined.

Another way to assess the radiological inventory of the irradiated graphite should be by interpreting radiochemical measurement on irradiated graphite sampled from the pile of the reactors. As shown through sampling and measuring campaigns carried out on EDF UNGG reactors, RNs content at the trace level such as Cl-36 exhibits a wide spatial variability. This is explained by the purity of graphite and a “nuggets effect”, very well explained by Pierre Gy theory of sampling (ToS).

EDF has chosen to develop a method of 3D geographical reconstitution of the inventory of the nuclear piles that is based on an activation calculation which is adjusted with the several measurements available from an averaging point of view. By using such a statistical averaging approach and not an approach based on a limited number of values, the measured data is recovering the representativeness in spite of the

high variability of trace measurements coming from required little sampling of very pure graphite. Apart from this, the use of such results is a closer approach to the reality of the main phenomenon at the origin of RNs in a pile, while also incorporating the release effects occurring during operation which are not possible to compute efficiently by any direct way.

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