CHLORINE EVALUATION OF GRAPHITE FROM NUCLEAR POWER PLANTS

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ABSTRACT

In France, EDF manages a nuclear fleet of 58 units on 19 sites. The first reactors were built between 1958 and 1966 and belonged to UNGG technology (Untreated Uranium, Graphite, Gas).

All the E.D.F. UNGG reactor (CO_2 coolant gas and graphite moderator) have been shut down permanently and these reactors are now being dismantled.

Since March 2000, French Ministry has given to the new near-surface repository an authorization of a very small quantity of Cl-36 in order to receive last Bugey-1 graphite sleeves [5]. Nowadays, the rest of graphite from the six graphite NPP needs an other disposal.

Cl-36 is one of the radionuclide which safe disposal management represent a challenge for both the producer EDF and the French radioactive waste management agency ANDRA.

An original global approach is proposed to build a reasonable maximization of the initial chlorine content based on fabrication data on nuclear grade graphite.

It is a preliminary and simplified result with approximate input values. More precise calculations need to be performed later.

INTRODUCTION

The context is that of the low-level long-lived waste storage facility planned with ANDRA (French governmental radioactive waste management agency) for graphite from UNGG plants. While pursuing an overall objective of gaining margins on the health impact of Cl-36, in parallel with studies of the conversion factor and the influence of the geological environment, the aim of the proposed method is to determine the inventory of Cl-36 in EDF’s graphite.

The method is based on the effective capture cross-section analyses carried out on the graphite moderators during monitoring of their manufacture. Having first set aside the influences of nitrogen, boron and ashes, the balance enables the chlorine to be assessed and the Cl-36 to be deduced by means of activation calculations. On the basis of feedback from English experience, only part of this calculated Cl-36 needs to be kept, in view of a loss observed in the reactor.

By using this method, it is possible to apply the mean absorption coefficient in millibarn per ppm of ashes obtained by linear regression to statistically representative batches of graphite (excluding so-called “special” graphite, but EDF has not used any).

PRINCIPLES ADOPTED

Monitoring of Graphite Quality during Manufacture

The principle of the method adopted is that of using the neutron irradiation data in CEA Reactor Zoé of graphite samples intended for monitoring the manufacturing quality of the stacks of all EDF’s UNGG power plants as a basis.

These irradiations have served to measure the effective absorption cross-section of the moderator. The other measurements taken during this quality monitoring were the chemical measurement of the boron, enabling the contribution to the effective absorption cross-section per ppm of boron to be quantified and the incineration residue (ashes), consisting above all of metals, to be measured.

The statistical basis for the regression presented below up to “ST-LAURENT II” consists of 1279 measurements.

The method adopted first sets aside the influences of carbon, hydrogen and nitrogen, then the mean millibarn/ppm ratios of boron and ashes, and allocates the balance to chlorine alone. Provided that the contribution to the effective cross-section of the chlorine element is known, the value of the mean coefficient of the ashes enables a statistical upper bound of the chlorine content in ppm in the graphite to be deduced.

The contribution of the “ashes” depends on their chemical composition. This is only known as a mean value originating from statistical regression based on approximately 50% of the graphite, extrapolated to the entire production destined for EDF’s UNGG power plants.

The last points of the regression correspond to lower ash proportions (which explains the grouping of these points around the straight line), but no bias was observed to emerge significantly from the background noise as a result of this reduction on the relative composition of the ashes. This is confirmed by the analysis of the sleeves, which do no not form part of the population that served to adjust the regression.

Furthermore, by using the mean values measured on the various stacks and by weighting them with the corresponding amounts of graphite, the regression equation of references [2] and [3] is recreated.

Direct Calculation of Overall Cl-36 by a Method we will call “Barycentric”

The exposé that follows shows that the graphite masses in question (when sufficient) multiplied by the integrated neutron flux received (flux multiplied by the equivalent number of years at full power) remain to be weighted so as to have Bq/ppm values and thereby obtain the entire chlorine 36 activity.

EFFECTIVE ABSORPTION CROSS-SECTION STATISTIC IN MBARN

Reference Formula

Effective absorption cross-section statistic in mbarn reference formula is taken from reference [2] “Correlation between the neutron capture cross-section and the proportion of impurities”.

During the manufacturing cycle of the graphite intended for EDF reactor 2, more accurate systematic tests were performed to determine the correlation between neutron capture cross-section and impurity content. The effective absorption cross-section of a graphite sample, measured on the Zoé stack, represents the capture of the carbon element increased by the capture cross-section of the impurities of the graphite. However, if a series of samples originating from the same raw materials (coke and pitch) and obtained by the same process are considered, it can be observed that the relative concentrations of the metal impurities vary little but that, in relative terms, the variations in the boron contents are greater.

Finally, a more general correlation based on all the graphite manufacturing cycles for EDF reactors, and corresponding to more than 10,000 metric tons of graphite, was calculated. For all the manufacturing cycles, the following is obtained:

$$\sigma_{Zoé} = 3.52 + 0.838\left[Boron\right] + 13 \cdot 10^{-4}\left[Ashes\right] \qquad (Eq.1)$$

This formula, expressed in mbarn, is restated in [1], and the values between parentheses are expressed in ppm.

Confirmation of the Reference Formula

The reference formula was confirmed five years later [3] by the points originating from the UNGG power units up to “ST-LAURENT II”. The new points do not cast doubt on the initial correlation. In particular, this shows the robustness of the 13.10^{-4} coefficient of the ash ppm.

Formula for Estimating the Chlorine

Let us detail the twice-confirmed statistical regression by stating its constant term in σ[carbon] + σ[chlorine] + σ[hydrogen]. As seen above, the ash coefficient originates from a statistical regression validated over 1279 points.

$$\sigma = C^{te} + 10.70 \cdot 10^{-3}\left[Cl\right] + 0.838\left[Boron\right] + 13 \cdot 10^{-4}\left[ashes\right] \qquad (Eq.2)$$

Since the [ash] coefficient is derived from the above confirmed regression, the calculation has overall statistical validity. In particular, the [ash] coefficient only has a mean value over a large quantity of graphite, since the other coefficients originate from [1].

The contribution of the pure graphite used had a value of 3.50 mbarn [1]. This value also corresponds to conventional sources and appears to have been cross-referenced with Zoé at the time. Indeed, the current data put it at 3.337 mbarn, as the recent assessments shows:

JEF-2 .2 (EU):	σ_{Carbon} = 3.3370 mb
ENDF/B6 (USA):	σ_{Carbon} = 3.3372 mb
BROND-2 (Russia)	σ_{Carbon} = 3.3370 mb

For hydrogen, a minimum content of 17 ppm is indicated in [1]. Moreover, analysis of the absorption cross-section measurement data shows that the section measured was systematically reduced by a set value of 0.2 mbarn to remove the effect of the nitrogen of the porosity, whereas, the correction value calculated on the basis of the mean density over 15,000 metric tons of graphite (namely 1,686) gives 0.2182 mbarn when applying the formula of reference [2], which uses the apparent density of the graphite.

Under normal temperature and pressure conditions, the correction due to nitrogen can be written:

$$\Delta\sigma_{N2} = 1.445\left(\frac{1}{d} - \frac{1}{2.26}\right) \qquad (Eq.\,3)$$

where d is the apparent density of the graphite, that of single crystal being 2.26.

From which the following can be derived

$$C^{te} = \sigma_C + \Delta\sigma_H + correction_N = 3.422\ mbarn \qquad (Eq.\,4)$$

BARYCENTRIC APPROACH

We shall posit that, for a mass M_i of graphite with (long-lived) Cl-36 activity A_i, expressed in Bq:

$$A_i = \mu_i \cdot [Cl]_i \qquad (Eq.\,5)$$

where μ_i is a chlorine activation coefficient expressed in Bq/ppm. In the first order, μ_i is proportional to the neutron flux and the graphite mass.

By taking, for each mass M_i of graphite, the equation subscripted by i of the effective capture cross-sections and by establishing the barycentre of these equations weighted by the μ_i , the following is obtained:

$$\frac{\sum_i \mu_i \sigma_i}{\sum_i \mu_i} = 3.422 + 10.7 \cdot 10^{-3} \frac{\sum_i \mu_i [Cl]_i}{\sum_i \mu_i} + 0.838 \frac{\sum_i \mu_i [Boron]_i}{\sum_i \mu_i} + 13 \cdot 10^{-4} \frac{\sum_i \mu_i [Ashes]_i}{\sum_i \mu_i} \qquad (Eq.\,6)$$

As barycentre (i.e. general weighted average) is naturally introduced, we called the approach as “barycentric”.

Barycentres of the measurements of effective cross-section, boron and ash :

$$\sigma_{barycentre} = \frac{\sum_i \mu_i \sigma_i}{\sum_i \mu_i} = 3.746\ mbarn,$$

$$[Boron]_{barycentre} = \frac{\sum_i \mu_i [Boron]_i}{\sum_i \mu_i} = 0.1163\ ppm \quad and$$

$$[Ashes]_{barycentre} = \frac{\sum_i \mu_i [Ashes]_i}{\sum_i \mu_i} = 97.82\ ppm$$

ACTIVITY OF OVERALL STATISTICAL VALIDITY

From calculation of neutron activation of chlorine for each plant, we get the result:

$$\sum_i \mu_i = 1.655.10^{12}\ Bq\ /\ ppm\left[Cl\right] \qquad (Eq.\,7)$$

On the basis of:

$$\sigma_{barycentre} = 3.422 + 10.7\cdot 10^{-3}\,\frac{\sum_i A_i}{\sum_i \mu_i} + 0{,}838\left[Boron\right]_{barycentre} + 13\cdot 10^{-4}\left[Ashes\right]_{barycentre} \qquad (Eq.\,8)$$

it follows that:

$$\sum_i A_i = \frac{\sum_i \mu_i}{10.7\cdot 10^{-3}}\left(\sigma_{barycentre} - 3.422 - 0.838\left[Boron\right]_{barycentre} - 13\cdot 10^{-4}\left[Ashes\right]_{barycentre}\right) \qquad (Eq.\,9)$$

A rough inventory of **15.4 TBq** is obtained for EDF's Cl-36.

N.B.: Chlorine barycentre weighted by the μ_i :

$$\left[Cl\right]_{barycentre} = \frac{\sum_i \mu_i\left[Cl\right]_i}{\sum_i \mu_i} = \frac{\sum_i A_i}{\sum_i \mu_i} = 9.276\ ppm$$

The latter value is to be compared with the mean "chlorine" originating from the overall regression.

$$\sigma_{Zoé} = 3.52 + 0.838\left[Boron\right] + 13\cdot 10^{-4}\left[Ashes\right] \qquad (Eq.10)$$

and which has the value

$$\left[Cl\right]_{statistical\ mean} = \frac{3.52 - 3.422}{10.7.10^{-3}} = 9.16\ ppm$$

VALUE OF THE STATISTICAL ESTIMATE

Robustness of the Method

Since the conservatisms of the calculation are set aside, the method provides the best estimate (in the mathematical sense of the "maximum likelihood") of EDF's Cl-36 production as a whole.

An Overall Assessment

By virtue of its overall independent approach, this method provides freedom from results that have too little real statistical value, because they are obtained from the small number of analyses of irradiated graphite core samples from the reactors, and consequently decreases dependency on their high degree of scatter [5].

Were new analyses to be undertaken, they would take a very long time to obtain a result as statistically sound as that of the present method and could never be carried out at a scale as representative as that of the many inspections performed during the initial manufacture of the graphite.

The method is derived from experiments and systematic measurements during the manufacturing phase, performed for entirely different purposes than the assessment of Cl-36.

A Reduction of the Upper Bound of the Overall Inventory

The use of an overall statistical estimate (even penalizing) naturally reduces the resulting Cl-36 inventory relative to the initial, particularly penalizing, assessment.

This assessment was based on sporadic increases vitiated by the fluctuations in the spatial distribution of the graphite samples. Also because of the small size of the graphite samples used for mineralization, a very high degree of scatter is apparent, similar to that observed on the cobalt present in the sleeve graphite as shown in [5].

Assuming mutually independent errors reaching 20% of the μ_i weights, conventional quadratic calculation shows that the relative uncertainty on the activity would only reach 10%. It still remains possible to fine-tune calculation of the Bq/ppm, but this would not make any significant change.

THE EFFECT OF IN-CORE CHLORINE LOSS

Reference document [4] brings to light a systematic shift, on a significant statistic, between the distribution function of the initial chlorine measurements and the distribution function of the initial chlorine values recalculated on the basis of the Cl-36 measurements taken at the end of irradiation.

Such a systematic shift can only be explained by a disappearance of the chlorine atoms during irradiation, whether said atoms are irradiated or otherwise, and thus document [4] allows the conclusion to be reached that the mean fraction of chlorine lost is 0.33 for the sleeves and 0.7 for the stack.

CONCLUSION

The computation of all what has been explained gives only a global final figure.

Tacking into account all the elements presented above and taking the chlorine loss described above as 33% for the sleeves and 70% for the stacks, on the basis of a penalizing overall gross value, every computation being made for each UNGG NPP, EDF's Cl-36 inventory is then preliminary estimated at **5.22 TBq**.

This preliminary global result comes from approximate input values of NPP characteristics and more precise calculations of these input values are in progress.

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