

New concepts and instruments for ^{14}C and ^{36}Cl measurements in i-graphite

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Abstract

Carbon 14 and Chlorine 36 are key nuclides for the decisions to be taken on irradiated graphite waste management. Being silent with respect to the gamma emission, they are also difficult to measure and assess. This paper will focus on new technical devices and concepts that could be used for their assessment. New measurements capabilities evaluated from numerical models and experimental works will be presented.

Main improvements of these innovations consist in:

- *Nondestructive and in situ measurements conducted on industrial batch, without need of sample collection and radiochemistry,*
- *Characterization and inventories provided by these techniques without need to be related by ratios to gamma emitters and avoiding non homogeneity effects,*
- *Based on reliable and improved techniques used in ores analysis and sensitive material detection as well as well-known calorimetry measurements.*

Introduction

The radioactive graphite coming from nuclear installations is a very special waste form due to its radiological properties. After long irradiation the graphite waste contains a significant amount of long-lived radioisotopes, such as Carbon 14, Chlorine 36 and short-lived isotopes, such as Cobalt 60.

Carbon 14 and Chlorine 36 are key nuclides for the decisions [1,2] to be taken on irradiated graphite waste management. Their activities are key for the choice of methods, tools and means of decommissioning, key for the design of packages and key for means and ways of future storage. Knowledge of their levels of activity thanks to sampling and laboratory measurements by radiochemical techniques correlated to calculations and knowledge of reactor history help to design main lines of decommissioning and give guidance for storage solutions. The difficulty could be to get the right design, generally speaking, matching the right need and avoiding maladjusted precautions by adding "virtual becquerels". This is particularly true for sorting pieces for final storage. So there is a need of good measures, preferably done on the field, with a good credibility and, if not on "real time",

near of that. These measures have to be understood as complementary of reference measures done on laboratory and not as an alternative.

The novelty of what we are proposing for measuring ^{36}Cl and ^{14}C is more on the capability of designing instruments for the field and real time rather than for the laboratory (the goal is not to replace the laboratory expertise). The techniques we are proposed are well known with regards to principles but the technology developed for the instruments take benefit of very recent improvements in electronics (^{36}Cl) and calorimetry (^{14}C).

As of today, due to the quite preliminary technical stage, the use of these new measurement methods with respect to the process of irradiated graphite decommissioning has not been investigated into details. Next step would be for us to demonstrate on the field the relevance of these technical ways. Another interesting further step will be to develop a view of possible i-graphite decommissioning and characterization processes that could take benefit of these innovative measurements, taking into account proven precisions and uncertainties with regards to waste management authorities criteria and according to waste treatment possible scenarios. This is not the goal of this technical paper and could be the purpose of a next one, if technical results are confirmed enough relevant.

What can be done for ^{36}Cl ?

^{36}Cl nuclear characteristics

Chlorine 36 has a half-life of 301,300 years [3]. ^{36}Cl is mostly created by the neutron capture reaction on ^{35}Cl , which is a stable isotope of Chlorine. ^{36}Cl is a beta emitter (probability 98.1%, $E = 710$ keV) and a weak positron emitter (probability 0.014%, $E_{\text{mean}} = 50$ keV). ^{36}Cl does not emit gamma rays (except indirectly those resulting from the annihilation of its positron). The level of activity of the ^{36}Cl in graphite can be estimated in the range from 1 Bq/g to 1000 Bq/g [4,5].

^{36}Cl measurement using its positron

Using the two 511 keV photons resulting from the annihilation of the ^{36}Cl positron is the way we have decided to explore. There are two main drawbacks: first measuring positrons could be not enough as you have to be sure of their ^{36}Cl origin (several isotopes could do it) and second the ^{36}Cl positron is quite rare : 0.014%/Bq.

Conventional measurements

The Figure 1 shows the classical measurement of a graphite sleeve with one gamma detector. The 511 keV corresponding channel of the gamma spectra will contain the number of partially detected positrons. After a calibration that will give the detection efficiency, it would be easy to obtain the number of positrons. This number can lead to a first rough estimation of the ^{36}Cl . This estimation could be very good ... if the chlorine 36 was the only isotope emitting β^+ in the sleeve and if there were not any high energy gamma emitter that could create positrons by pair production in the sleeve or, worse, in the detector. Unfortunately this is not the case in irradiated graphite which is our purpose. We found that the most active β^+ emitter in irradiated graphite is ^{152}Eu , which is also like ^{36}Cl a weak emitter with a probability of emitting positron is 0.0256% per disintegration [3]. At the end the

number of positrons of ^{152}Eu is in the same order of magnitude as the ^{36}Cl ones. The good news about it is that the ^{152}Eu isotope can be easily measured by gamma spectrometry, so that its number of positrons can be estimated and subtracted from the total having been measured. But the most harmful noise in irradiated graphite comes from ^{60}Co . Its effects are: creating a Compton background in the spectra, creating positrons in the graphite by pair production (we calculated that each Bq of ^{60}Co created twice more positrons in a typical sleeve (type Bugey 1) than a Bq of ^{36}Cl) and, even worse, creating positrons directly in the detector. In conclusion, a conventional spectral measurement could be done but would give interesting results only with samples where high energy gamma ray emitters have disappeared.

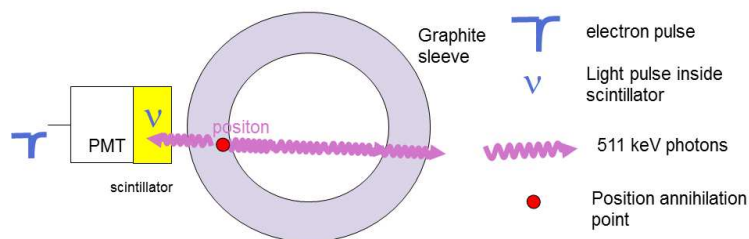


Figure 1. Classical gamma measurement system.

Measurements using photon detection coincidences

A “pet scan” like system

Filtering the noise described above could be reached by using coincidence technique as done in the famous “PET scans” [6]. Figure 2 shows a coincidence detection system using eight 5’’x 3’’ LaBr3 scintillation detectors [7]. In such a system, the same 511 keV photons are used as above but the taken into account events are not single photons but coincidence of single photons having 511 keV energy detected by a pair of detectors each one being placed in front of the other and the object being in between.

The benefit of this configuration is the quite complete suppression of the noise created inside the detectors: Compton effect and positron production effect. The positrons created (pair production effects) inside the scintillator are suppressed by a time of flight criterion: the time delay between the 2 photons detection is higher than those corresponding to a positron created in the graphite. Obviously to do that the resolution of the acquisition electronics must be low enough, not more than 1ns. It is one of the keys of the success of such a system. This benefit in terms of signal over noise ratio has a (quite high) cost: the detection probability has fallen and we have been obliged to put detectors around the sample.

The drawbacks identified above remain nevertheless: we still measure positrons, so to access those due to ^{36}Cl only, we will have to add a new feature to the instrument. This feature is the capability of making also a gamma spectrum of the object in order to:

- Identify and quantify the isotopes that emit $\beta+$ and gammas. This is the case for ^{152}Eu already cited. This will allow to know how many positrons (coincidences) are to be subtracted from the counting result as not originated in the ^{36}Cl .

- Quantify high energy gamma rays flux in order to be able to predict how many positron they will create by pair production effect. This calculation has to be done with regards to the geometry of the object being measured and also with regards to the geometric distribution of the high energy gamma isotopes. The found number of pair production created positrons will be subtracted too from measurement result.

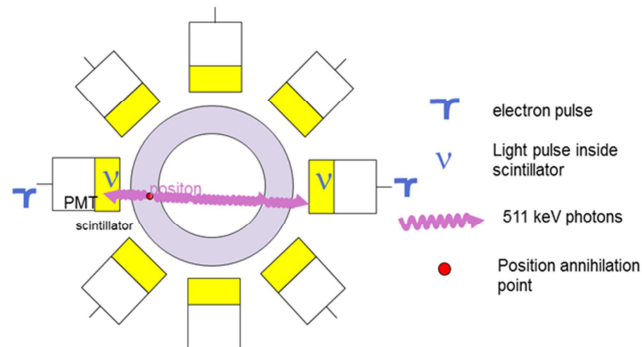


Figure 2. Gamma-Gamma coincidence detection system.

Another term of noise is to be taken into account: the number of “false coincidences” due to detection events occurring at the same time but without any physical link between them. This kind of event could be numerous in case of high detector counting rate. The number of “false coincidences” can be nevertheless very well known by a simple statistic algorithm.

Building the measurement result

The result in terms of ^{36}Cl activity is built as follows:

- Counting the total number of coincidences (rejecting those out of time)
- Estimating the number of “false coincidences”
- Estimating the number of coincidences due to positrons coming from β^+, γ emitters identified by gamma spectrometry and quantified thanks to it. This comes from isotopes like ^{152}Eu for instance.
- Estimating the number of coincidences coming from positrons created by pair production by high energy gamma rays. This is done by calculations using as input data the geometry of the object, its density and nature, the distribution of high energy ($E > 1.022 \text{ MeV}$) gamma rays and their intensity obtained by collimated gamma spectrometry. The typical case is due to ^{60}Co which dominates this effect in typical irradiated graphite.
- The number of coincidences due to ^{36}Cl is computed making the subtraction of the 3 estimated number of coincidence not coming from ^{36}Cl and described above from the total measured. This net number is then converted in becquerels of ^{36}Cl . In case of the presence of others and non-identified β^+ emitters (which are very rare in typical irradiated graphite), the activity of ^{36}Cl would be overestimated.

The noise due to ^{60}Co

Calculations made with some typical compositions [8] showed that the biggest source of error is due to the influence of ^{60}Co . So we focused on it to find a better way to estimate its contribution. The Figure 3 illustrates a feature of our instrument that seems very relevant to increase the accuracy in estimating the number of positrons due to ^{60}Co . The idea comes from the fact that the ^{60}Co emits its two gamma rays synchronously. So when one of this two high energy gamma creates a pair electron-positron, the second gamma ray still exists, could be detected (or not) in one of the other detectors, could diffuse and the gamma diffused could be (or not) detected or even could create itself another pair that will annihilate too and creates a new pair of 511 keV gamma-rays. As a result a “Cobalt positron” could be identified by a triple coincidence¹ (511 keV)–(511 keV)–(any energy) scenario that we cannot encounter with a “Chlorine positron”. We calculate that the probability of detecting a triplet when having detected the positron (conditional probability) is about 5% with 8 detectors as shown in Figure 3 that is quite high. The “conditional” character of the probability is very interesting because it has as a consequence that to compute the number of potential “Cobalt positrons” we do not need to measure the activity and cartography of the ^{60}Co but only its *relative* activity and cartography. So that it reduces the uncertainty.

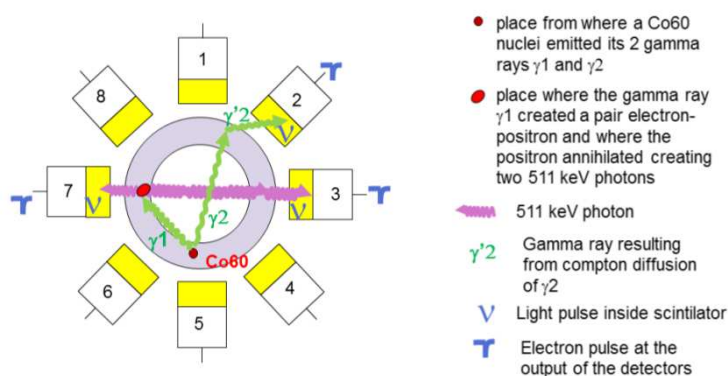


Figure 3. Detection of triplet.

Experimental validation of that principle and more largely speaking of the whole system has been done at Sodern facilities [9]. A ^{36}Cl early designed equipment based on three LaBr3 detectors has been designed, realized and tested at lab.

Estimated performances in the scope of irradiated graphite

The performances of such measurement instrumentation are to be thought in terms of precision i.e. in the relative standard deviation value. Often the goal of such a measurement is to verify that the activity values less than a given threshold. So it is usual to give the result of the measure added by its standard deviation or by twice its standard deviation that is equivalent to say the activity is “below such value with a confidence interval of 97.5%”.

¹ We call it « triplet »

To calculate the expected performances, we evaluated each contribution to the global variance of the ^{36}Cl result. These contributions are : Poissonian variance of the counting result, variance of the estimated number of positrons coming from β^+ , gamma emitters, variance of the “cobalt positron number” (graphite originated or instrument originated) and the variance due to estimated “false coincidences”.

As already said the main source of error is the cobalt pair production phenomena. The Figure 4 shows calculations done for the eight-detector system with a graphite sleeve type Bugey (600 mm in height, overall diameter 220 mm, 20 kgs of graphite) arranged like illustrated by Figure 3, for an acquisition time of 1200 seconds. The y-axis represents the measured activity added with two standard deviations depending and the x-axis represents the true (real) ^{36}Cl activity. Several curves have been calculated for several activities of ^{60}Co . We can see that the measurement is easy when the quantity of Chlorine is high. But the goal is to reach low values. Typical values of 10 Bq/g can be measured with a standard deviation of 100% if ^{60}Co is enough low, less than 100 Bq/g. If the ^{60}Co is about 1000 Bq/g, the detection limit in ^{36}Cl is about 100 Bq/g.

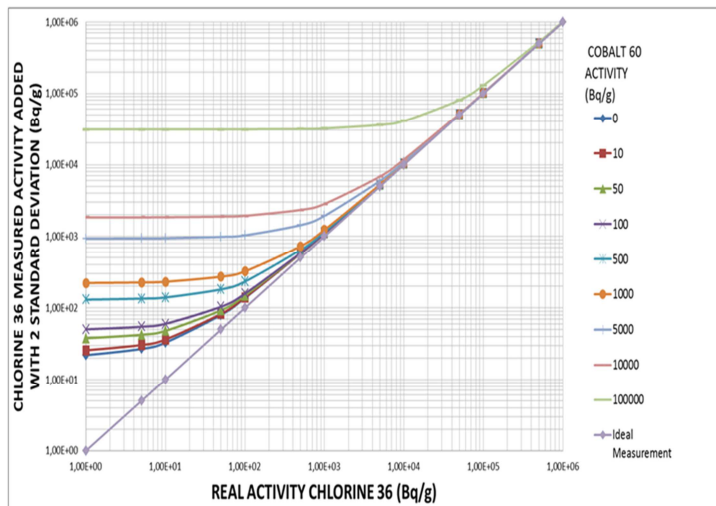


Figure 4. Measurement performances depending on ^{60}Co and ^{36}Cl activities.

What can be done for ^{14}C ?

^{14}C nuclear characteristics

Carbon 14 has a half-life of 5730 years [3]. In irradiated graphite ^{14}C is created by neutron capture on the stable ^{13}C (stable isotope 1.1% part of natural carbon) and (n,p) nuclear reaction on ^{14}N . ^{14}C is a pure beta emitter (probability 100%, $E_{\text{mean}} = 50$ keV). The 21,500 tons of graphite belonging to CEA and EDF are estimated to contain 755 TBq of ^{14}C , i.e. $3.5\text{E}4$ Bq/g in average [5].

^{14}C measurement by calorimetry

Calorimetry is a well-known way of measuring ^{14}C by means of measuring the heat produced by disintegration. Measurements of pieces of graphite by such a technique seem appropriate but there are two difficulties:

- the first one is the sensibility and the relative low energy quantity released by ^{14}C decay: 50 keV in average, i.e. $8\text{E-}15$ W/Bq. It means $8 \mu\text{W}$ per GBq. The calorimeter must have a very low detection limit and a good sensitivity,

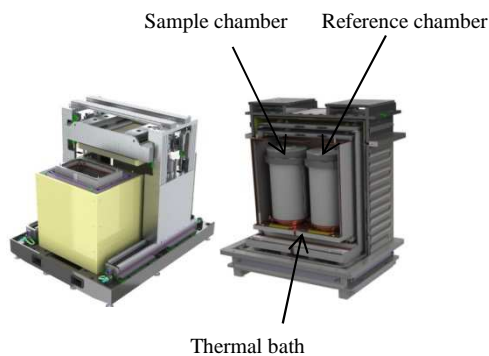
- the second is the fact that irradiated graphite does not contain only ^{14}C . As for the ^{36}Cl we will be obliged to calculate the contribution of other isotopes. Not identified, such as ^3H , will be ignored and thus the ^{14}C activity will be overestimated. The identification of beta emitters will be done by gamma spectrometry. This spectrometry will aid on identifying charged particle emitters and quantifying gamma rays. To do the right estimation of the power brought to the object by the gammas, knowledge of their escaping part will be necessary. This could be estimated thanks to a simulation study.

The key : a new highly performing calorimeter

KEP Nuclear developed a new highly performing calorimeter, called μLVC , to measure low level of energy between $10 \mu\text{W}$ and 100mW . The calorimeter operates according to the differential isothermal heat flow calorimetric principle. The principle of the μLVC involves the complete surrounding of the sample under measurement with a vacuum chamber so that any heat emanating from the sample is measured by sensors. The differential design (see the Figure 5) provides significant benefits against perturbations [10,11].

The instrument has two cavities adapted to the sample's shape, the sample chamber is loaded with the active product to be analyzed, and the reference chamber is loaded with an inactive product. The heat produced by the sample is directly compared to the reference to ensure that any environmental perturbations are not included in the measurement.

One μLVC calorimeter prototype has been manufactured and characterized (see results in figure 5).



	Specification
Sample volume capacity	40 liters
Measurement Chamber internal dimensions	Height 660 mm Diameter 280 mm
Effective power range	$50 \mu\text{W} - 100 \text{mW}$
Mean Random Uncertainty (72 hours time measurement)	<p><u>Objective</u></p> <p>$\pm 10\%$ between $10 \mu\text{W}$ and $100 \mu\text{W}$</p> <p>$\pm 1\%$ between $100 \mu\text{W}$ and 1mW</p> <p>$\pm 0.2\%$ between 1mW and 100mW</p> <p><u>Measured on the prototype</u></p> <p>$\pm 20\%$ between $50 \mu\text{W}$ and $250 \mu\text{W}$</p> <p>$\pm 5\%$ between $250 \mu\text{W}$ and 1mW</p> <p>$\pm 1\%$ between 1mW and 100mW</p>
External calorimeter dimensions	Depth : 3000 mm Length : 2400 mm Height : 2600 mm
Calorimeter weight	9 tones

Figure 5. μLVC views and specifications.

Gamma response of the calorimeter

The energy deposit in graphite and calorimeter due to gamma photons is estimated using MCNPX code [12]. F6 tally in MCNPX gives the energy deposit in medium. It was used to estimate heat due to gamma-rays energy deposit.

In worst case, the gamma-heating of the two regulation blocs was calculated at $20\ \mu\text{W}$ and $50\ \mu\text{W}$. The heating of these parts is not measure during the assay, and so does not disturb the calorimeter working. Figure 6 shows the gamma-heating of the graphite sleeve and the measurement chamber according the gamma rays source position inside the sleeve and gamma rays energy.

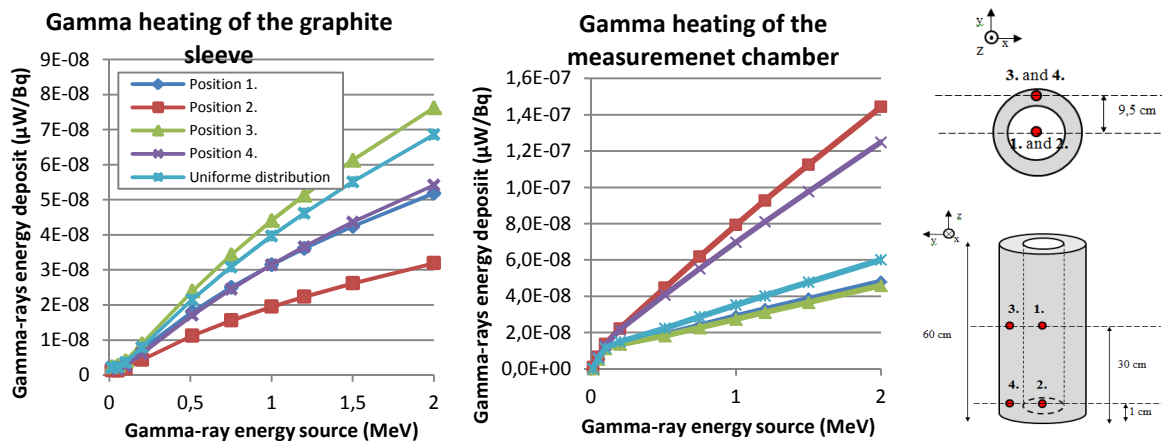


Figure 6. Heating induced by gamma-rays inside the graphite sleeve.

The gamma-heating is dependent on the source distribution inside the sleeve. Inside the graphite, if the source is closed to the outside, gamma rays can easily leak and not induce heating. If the source is close to the lateral wall of the measurement chamber gamma rays mainly go through the thin copper wall. If the source is in the low part, gamma rays are absorbed by the thick back part of the chamber. The contribution of beta emitters, such as ^{60}Co , cannot be neglected [13] and can be corrected by modelling the graphite sleeve inside the calorimeter and calculate the gamma heating or using abacus to know gamma-heating according to source energy and distribution. New designs of measurement chambers could be designed in order to reduce the source distribution dependence effect. This can be obtained with an “infinite” thick wall. But in this case, all gamma rays are absorbed and too much gamma-heating could be a hindrance for low activity measurement.

Anyway the calorimeter should be associated to a gamma spectrometer having a certain spatial resolution in case of inhomogeneous distribution of the gamma isotopes in the graphite in order to correct and interpret properly the calorimeter result.

Estimated performances in the scope of irradiated graphite

The estimated performances of ^{14}C measurement in a typical Bugey-1 sleeve (20 kgs of i-graphite) are presented in the figure 7. They are based on the characterization data collected during the test of the first calorimeter prototype (figure 5). They show what would be the result of the measurement increased by its error, as usually practiced when one wants to be sure that the real value of the activity

is not above the indicated value. The error indicated here is the error resulting only from the heating power measurement. Error due to gamma response corrections, which are smaller (except if the sample gamma activity is very high) is not taken into account.

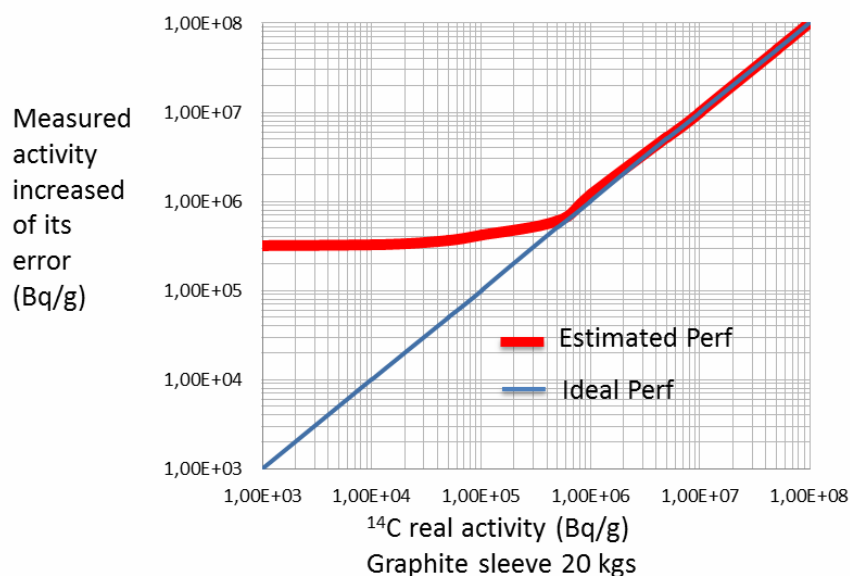


Figure 6. Estimated performances for ^{14}C measurement based on calorimeter test data.

We see that for typical values below 10^5 Bq/g the error measurement is large and leads to consider the maximum possible value of the activity largely above the real one.

Future improvements of the μLVC calorimeters could probably reduce this drawback. Reaching the initial objective of accuracy (figure 5 data) would allow to push the detection limit below 10^5 Bq/g.

Conclusion and perspectives.

Both concepts of measuring ^{14}C and ^{36}Cl have been demonstrated by pieces of hardware (KEP Nuclear calorimeter and Airbus ^{36}Cl acquisition system) tested in lab. An experience done on the field on real pieces of graphite (for instance extracted from reactor as they are) would be of interest to show the capability of such measurements, if the ^{60}Co level is a priori considered to be acceptable. It may be thought also to validate these measurements by a posteriori radiochemical analysis.

Improvements remain probably necessary to demonstrate the interest of such measurement concepts integrated in waste management scenarios and processes with relevant limits of detection and accuracy performance in coherence with activities thresholds and waste institutional authorities criteria.

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