Determination of nuclear graphite impurities by prompt gamma activation analysis to support decommissioning operations

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Abstract
Elemental composition of non-irradiated nuclear grade graphite was determined by Prompt Gamma Activation Analysis (PGAA) to quantitively assess some neutron activation precursors. The knowledge of these data is paramount for an accurate radiological characterization of the material before decommissioning of graphite-moderated nuclear reactors. Bulk results of most of the nuclides were consistent with benchmark Inductively Coupled Plasma–Mass Spectrometry (ICP-MS) and literature data. In the case of $^{14}$N and $^{35}$Cl, depth distribution profiles were observed and quantified for the first time. These outcomes could shine a light on $^{14}$C and $^{36}$Cl depth distribution profiles and fractional release during leaching experiments.

Article highlights
- A complete dataset of virgin graphite impurities distribution serves as input data for activation computational codes.
- A complete elemental characterization is achievable by the complementary PGAA and ICP-MS techniques.
- N and Cl depth distribution profiles have been discovered in graphite, untangling $^{14}$C and $^{36}$Cl activation mechanism.

Keywords Decommissioning · Nuclear Graphite · Impurities · Depth distribution · Prompt Gamma activation analysis

Introduction
Irradiated nuclear graphite (i-graphite) represents a challenging issue for the decommissioning of graphite-moderated nuclear reactors, given the large quantities of generated waste and its specific properties.[1] More than 250,000 tons of i-graphite, mainly coming from defence and commercial nuclear power plants developed in UK, USA, Russian Federation and France, still have to be permanently disposed.[2, 3] The main problems concerning the dismantling and treatment of graphite from a reactor after a full operational lifetime involve the handling of large amounts of radioactive graphite stacks, possibly distorted and degraded by neutron damage and radiation-chemical attack, with a variable content of stored Wigner energy.[2, 3] The International Atomic Energy Agency (IAEA) has been promoting research and implementation of processing technologies in the i-graphite management field by supporting the Member States through several coordinated international projects, the last one being Irradiated Graphite Processing Approaches (GRAPA),[3] in which this work is settled. Accurate radiological characterization of i-graphite is an enabling activity for subsequent dismantling and disposal procedures, allowing localization, identification, and quantification of activated radionuclides to be assessed.[4, 5] Owing to their relatively short half-lives, radionuclides such as $^3$H and $^{60}$Co represent the main issue during immediate or deferred dismantling activities, while the long-lived $^{14}$C and $^{36}$Cl impact on long-term safety of disposed waste.[6] Most of these radionuclides are classified as Hard to Measure (HTM), as they decay without emitting easily measurable photons.[7] Consequently, their accurate determination in hundreds of samples would require destructive radiochemical processing and large investment in terms of economic and temporary...
resources, since it is impossible to assess average radionuclide concentrations in the whole nuclear graphite blocks, and each stock needs to be analysed independently.\[8\] In order to acquire an accurate and cost-effective radiological characterization of a large number of specimens, neutron activation models can be developed on the basis of available information about material and structural composition, together with irradiation history of the samples.\[9, 10\] At this aim, elemental composition of the impurities present in virgin graphite must be determined, as they are neutron activation precursors. However, historical nuclear grades are often no longer available and very few complete elemental characterization studies of non-irradiated samples have been carried out, especially for what concerns light and volatile elements such as Li, B, N and Cl, which are important precursors of medium (\(^{11}\)H) and long living (\(^{14}\)C and \(^{36}\)Cl) neutron activation radionuclides.\[11, 12\]

Radiochemical and spectrometric analysis – such as Inductively Coupled Plasma–Mass Spectrometry (ICP-MS), Accelerator Mass Spectrometry (AMS), Thermal Ionization Mass Spectrometry (TIMS), and Secondary Ionization Mass Spectrometry (SIMS) – are the most widespread techniques when elemental characterization is intended. Besides being too time-consuming, expensive or not easily accessible, the mentioned procedures often reveal unadapt in measuring ultralow concentrations of the lighter elements in nuclear graphite, which are the main interest for decommissioning and disposal operations.\[13, 14\] Prompt gamma activation analysis (PGAA) is a valuable non-destructive nuclear analytical method to accurately measure these low-concentration nuclides. It is based on the neutron capture of the atomic nuclei followed by the emission of characteristic gamma radiation. The special strength of PGAA is the analysis of light elements. \[15\] In this work, the bulk assessment of such elements and the study of depth distribution profiles have been attempted by PGAA and compared with ICP-MS benchmark data and literature references, with a view to improve the radiological characterization of i-graphite provided by neutron activation simulation codes thanks to a more accurate input data set. In fact, the already known \(^{14}\)C concentration gradient as a function of depth and its fractional release during leaching experiments could be explained by two main concomitant and concurrent neutron activation mechanisms.\[3, 16, 17\] One is the homogeneous activation of \(^{13}\)C to \(^{14}\)C by (n,\(\gamma\)) reaction, that is not depth dependent as \(^{13}\)C is homogeneously distributed in graphite at natural isotopic abundance; the other one could be the depth dependent activation of \(^{14}\)N to \(^{14}\)C by (n,p) reaction.\[13, 18, 19\] Nitrogen is present as an impurity coming both from graphite manufacturing process and reactor operating environment.\[20\] This concurrent activation path could explain \(^{14}\)C distribution with depth, as the external graphite layers should be more enriched in \(^{14}\)N than the bulk due to manufacturing process and exposure to air.\[13, 17, 21\] Dealing with \(^{36}\)Cl, a depth gradient may similarly arise from activation of \(^{35}\)Cl by (n,\(\gamma\)) reaction, since \(^{35}\)Cl may be more concentrated in the superficial layers of the graphite blocks as well.\[22\] In this case, the purification treatments usually performed during graphitization involve the exposure of carbon blocks to halogen gases, such as fluorinated and chlorinated gases.\[20\] Chlorine diffuses through the porous structure to react with the metallic impurities and forms halides of low boiling point that vaporize from the block: as graphitization process takes places, some gas molecules may remain trapped in the pores of the material, thus originating a depth profile for \(^{35}\)Cl, which, upon activation, generates \(^{36}\)Cl.\[23\] Hence, one of the most ambitious goals of this work is demonstrating the existence of depth distribution profiles of \(^{14}\)N and \(^{35}\)Cl.

**Materials and methods**

All analytical grade reagents were purchased from Merck and used without further purification. The certified standard solutions for ICP-MS analyses were purchased from Inorganic Ventures (CMS-x standards). The herein reported experiments have been conducted on non-irradiated AGOT graphite (Atcheson Graphite Ordinary Temperature) coming from the same stock employed as reflector and moderator at L-54 M nuclear research reactor, operated between 1959 and 1979 at Politecnico di Milano, Italy.\[9, 24\] The samples collection and preparation were previously designed in view of conducting the measures under optimal conditions to allow full and homogeneous neutron irradiation of the specimens during PGAA. In order to perform the measures and acquire both N and Cl depth distribution profiles and bulk concentration data for B, N, and Cl and other impurities, a 2 cm diameter cylindrical core-drill was obtained from a virgin AGOT graphite rod by abrasive water jet technique.\[25\] Four cylindrical slices (samples #1 – #4, see Fig. 1) were collected at increasing depth from the surface,\[26\]...
using deuterated water as the sample to simulate the irradiation of the surrounding structural elements by a strong scatterer. This step was performed at atmospheric pressure (960 mbar), and the background nitrogen masses were subtracted according to the chamber pressure. From the intensities of the characteristic peaks, the concentrations of the components were determined.

For what concerns the ICP-MS analysis, the graphite powder was obtained from a virgin AGOT graphite rod by drilling and further grinded in a ceramic mortar. In view of the analysis, a proper matrix destruction protocol has been specifically developed in this work, based on the method applied in a previous study on the same graphite stock, with some modifications. First, the weighed amount of treated graphite was increased from 2.5 to 14 g, in order to obtain a more representative sample. The graphite powder sample was oxidated in a furnace at 650 °C for 24 h and the residues were treated with ultrapure HCl and HNO₃ until complete dissolution. In order to simplify the protocol, dissolution with HF was not performed. The resulting solution was diluted with 1%v ultrapure HNO₃ to comply with the ICP-MS detection limits and optimal ranges in terms of analytes concentrations and acidity of the injected solutions. The Perkin Elmer NexION 2000 single quadrupole ICP-MS instrument was employed upon external calibration by means of standard certified solutions properly diluted with the intention to cover, when possible, the 0.1–100 ppb concentration range.

Fig. 2 Prompt gamma spectrum of sample #5 (bulk sample). Most important characteristic lines are marked with the chemical symbol of the element.
Results and discussion

As an example, the PGAA spectrum of sample #5 is shown in Fig. 2. The measurement was performed in a flux $2 \times 10^{10}$ cm$^{-2}$ s$^{-1}$ for 10 h.

PGAA results were then compared with ICP-MS benchmark data and literature references, revealing to be mostly consistent.[9, 29] In addition to the novel information about B, N, and Cl in AGOT graphite, further data were obtained for other impurities, such as Ca, V, Fe, Ni. These elements were found to be nearly constantly distributed with depth. PGAA bulk results for sample #5 are shown in Table 1 together with literature values and ICP-MS data (this work), while the obtained depth distribution profiles for N and Cl in samples #1 - #5 are reported in Figs. 3 and 4 respectively.

![Fig. 3 $^{14}$N concentration measured by PGAA as a function of AGOT graphite rod depth. The red dotted line is the Detection Limit (DL).](image1)

![Fig. 4 $^{35}$Cl concentration measured by PGAA as a function of AGOT graphite rod depth. The red dotted line is the DL. Uncertainties bars are within the marker size.](image2)
In both cases, the measured values are above detection limits (DL). A decreasing trend of concentration within the first 3 mm depth is clearly present: reduction factors of about 1.8 ± 0.2 and 4.7 ± 1.0 are calculated for $^{14}$N and $^{35}$Cl respectively as the ratio between the value of the near-surface sample and those of the bottom ones. The values of deeper samples keep nearly constant within the measuring uncertainty, confirming literature data and reflecting the stabilisation of $^{14}$N and $^{35}$Cl concentrations just few mm from the graphite rod surface.[28, 29] According to these outcomes, as a first approximation, the concentration of these precursors in the activation model could be assumed to be equal to the just determined bulk values. This simple and reasonable assumption would be useful during preliminary radiological characterization campaigns since it would allow obtaining sufficiently accurate values of $^{14}$C and $^{35}$Cl activity concentrations with low computational costs. Once more accurate values will be required, the model should just be implemented with the complete impurities’ concentration data set. Moreover, for those i-graphite stacks that have experienced just a very low activation during reactor operation, like in nuclear research reactors, these outcomes may be exploited to demonstrate the applicability of surface decontamination processes with the purpose to declassify most of the waste inventory.[20, 30] This decontamination practice would result in the loosening of regulatory control on a material otherwise considered a radioactive waste. Hence, both management costs and environmental footprint would be reduced, since a smaller amount of material would have to be disposed as a radioactive waste. On the contrary, for highly activated i-graphite stacks, the surface layers could be retrieved and segregated from the less activated bulk material, that could hence be downgraded and disposed in a safer and cheaper way. The same approach could be applied to other situations and activated materials, like biological shield concrete, to optimize their decommissioning and waste management.

A comparison between ICP-MS and PGAA results obtained for bulk sample, together with literature data benchmarks, are provided in Table 1.[9, 28, 29]

The new ICP-MS results appear to be in good agreement with the analogue previous analysis considered.[9] Moreover, both for ICP-MS and PGAA, overall obtained results often fall within the literature references values collected through several elemental characterizations of different nuclear grade graphite stocks.[9, 28, 29] Consequently, it is possible to confirm that AGOT graphite is highly pure, as it contains low amounts of impurities such as other analogue nuclear graphite types. In particular, for most of the considered elements, the measured values are closer to the lower limit of the literature range. In addition, for some other elements – above all U, Th – the herein measured concentrations are orders of magnitude lower than literature values. As undesired losses of these elements due to the treatment steps should not be envisaged – since their solubility in the employed solvents is sufficiently high – such low measured concentrations should rather be ascribed to the lower detection limits ensured by the treatment method and ICP-MS equipment employed in this work. However, in some cases, e.g. Co, the obtained PGAA values are higher – even more than one order of magnitude higher – than ICP-MS results. This could be explained by a not effective background...
subtraction in PGAA data, since these elements are largely present as constituents of the metallic construction material of the measuring chamber.

Furthermore, the complementarity of ICP-MS and PGAA approaches has been demonstrated as well. While metallic impurities are measured more accurately and with lower detection limits by ICP-MS, light elements are best measured by PGAA. In fact, N and Cl are not measurable by ICP-MS at all, also due to the treatment of ashes with HNO$_3$ and HCl mixtures. In addition, boron, another relevant activation precursor, was not measurable by ICP-MS at this ultralow concentration: on the other hand, PGAA proved to be an effective complementary method in measuring these light elements at such low concentrations. The obtained data on elemental impurities of the virgin material could be proficiently fed into computational codes for neutron activation assessment.[9, 32].

Conclusions

An important outcome of this work is the discovery and demonstration of N and Cl depth distribution profiles in virgin graphite. These data could be employed to more accurately simulate radionuclides distribution by activation codes, thus obtaining a more reliable radiological characterization in view of the decommissioning of graphite-moderated nuclear reactor. From this evidence, some literature results such as $^{14}$C depth distribution and fractional release during leaching experiments could be explained. Furthermore, the evidence of these distribution profiles could pave the way to dedicated surface decontamination processes aimed at downgrading or declassifying most of the i-graphite waste inventory, thus reducing both waste management costs and environmental footprint.

Moreover, the obtained results are in good agreement with the literature data and ICP-MS benchmarks, confirming PGAA as an effective technique for completing elemental composition analysis of pure materials, such as virgin graphite, whenever activation codes are used to reduce costs and time. In fact, compared to a full radiochemical analysis in which irradiated samples undergo a complete and expensive radiological characterization, no preparation nor treatment of the sample is needed in this approach. The best performance can be reached by conducting PGAA in a complementary way with ICP-MS: on the one hand, ICP-MS allows for the determination of most of the analytes with great accuracy and sensitivity; on the other hand, PGAA capability in measuring the lighter and most volatile elements at ppm levels can compensate for the lack of information on the remaining ones. The obtained results provide a complete and accurate elemental characterization of the virgin graphite sample, which can be fed into activation codes as input data. Then, radionuclide distribution in real samples can be simulated with accuracy, thus supporting experimental characterization campaigns.

This study opens to further work in the field of radiological characterization in support of decommissioning activities, since it is a generic method to complete input database for accurate and reliable activation codes.

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Author contributions All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by Eros Mossini, Zsolt Revay and Andrea Camerini. The first draft of the manuscript was written by Andrea Camerini and Eros Mossini, all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Declarations

Declaration of competing interest The authors declare that they have no competing financial interests or personal relationships with people or organizations that could have inappropriately influenced the work presented in this paper.

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