# IMPURITIES CHARACTERIZATION to support decommissioning and management of

# irradiated graphite waste

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**Abstract**

Nuclear graphite has been widely used as moderator and reflector in I and II generation reactors and it is being considered for some next generation projects. Several graphite-moderated nuclear reactors have already been permanently shut-down, and others will be in the next years. Therefore, decommissioning of this material is becoming an important issue, given that an ultimate strategy for treatment and disposal has not been found, yet. In fact, the very large use of nuclear graphite is often accompanied by some knowledge gaps, such as activation of impurities in the irradiated material. Experiments reported in the paper aim at obtaining a complete characterization of virgin graphite: an accurate elemental composition of the non-irradiated material is a vital input data for those neutron activation models that are commonly used to estimate radionuclides inventory and to support the radiological characterization before dismantling operations. Inductively coupled plasma mass spectrometry (ICP-MS) analysis can be implemented to quantitatively assess the presence of large numbers of analytes, with high sensitivity. On the other hand, neutron-activation based techniques, as prompt gamma neutron activation analysis (PGAA), can be effectively applied to measure those lighter elements for which mass spectrometer would be ineffective. The proposed experiment considers samples obtained from a virgin graphite rod. ICP-MS results revealed to be mostly consistent with literature history on different types of nuclear-grade graphite, while PGAA confirmed with a good margin the bulk concentrations for most of the nuclides obtained by ICP-MS analysis, and allowed evaluations on the lighter ones. Future works on nuclear graphite could involve analysis on activated samples, in order to compare and validate the already obtained characterization on virgin graphite.

## INTRODUCTION

Retrieval and disposal of irradiated nuclear graphite (i-graphite) represent some of the most challenging issues when it comes to decommission graphite-moderated nuclear reactors, owing to the large quantities of generated waste and its specific properties. Nowadays, it is estimated that more than 250,000 tons of i-graphite have to be properly disposed, with most of them still held *in situ* or in temporary storage. [1]

During an operational lifecycle, nuclear graphite is exposed to neutron activation both of its constituent elements (12C and 13C) and of the dispersed impurities (Li, B, N, Cl, K, Ca, Ti, V, Mn, Fe, Ni, Th, U, etc), the latter ones being originally present in the structural material or introduced during the manufacturing processes. [2,3] A complete radiological characterization of i-graphite is considered an effective preliminary activity before actual dismantling procedures begin, allowing to determine location, nature, and extension of graphite activation. Once collected, these data are of paramount interest for the proper selection of further actions.

Graphite waste management can undergo different strategies, both from a temporal and a treating point of view. On one hand, a *safe enclosure* approach can be adopted, opting for leaving i-graphite on site for a period up to several decades; on the other hand, the moderator can be immediately dismantled. [2] In case of immediate dismantling, the main challenge is represented by short-lived radionuclides, such as 3H and 60Co, while the largest impact on long-term safety of disposed waste is due to the long-lived 14C and 36Cl. [4]

Once i-graphite is removed, the classification of waste streams and the selection of proper processing options (conditioning, packaging, incineration, etc) rely on activation and radioactivity evaluations. [2] As it is impossible to assess an average composition and draw general conclusion for nuclear graphite manufactured with different processes from various producers, and exposed to different environments in the reactor, each representative stock has to be analysed independently. [5,6]

## the role of elemental characterization

Radiochemical procedures followed by radiometric measurements are the most widespread techniques when radiological characterization is intended, since most of the radionuclides of interest are classified as hard-to-measure (HTM) nuclides (3H, 14C, 36Cl, etc) [7]

Neutron activation models can be developed from the determination of elemental impurities in virgin graphite, thus providing an accurate and by far more inexpensive radiological characterization and contributing to fill the knowledge gap on irradiation history and structural composition of the samples. [8] However, historical nuclear-grade graphite may be no longer available in most of the cases, and very few complete studies of non-irradiated samples have been conducted. [9] This lack of information impacts on the assessment of elemental characterization mainly for the lighter elements, such as Li, B, N and Cl, which are important precursors of 3H, 14C and 36Cl neutron-activated radionuclides, and whose adequate and accurate measurement is vital in determining radioactivity of i-graphite.

ICP-MS is a very sensitive analytical method that allows the simultaneous measure of large numbers of analytes at very low concentrations, ranging from ppt to ppb depending on the analyte and the matrix. Nonetheless, this technique reveals quite ineffective when it comes to measure low concentrations of light elements. At this purpose, neutron-activation based techniques – such as NAA and PGAA – can be valuable choices, representing both a complementary method and a benchmark for ICP-MS analysis. [10]

## icp-ms experimental

A preliminary elemental characterization was already performed through ICP-MS analysis on non-irradiated Atcheson Graphite Ordinary Temperature (AGOT) graphite [11]. Samples were obtained from the same stock employed as reflector and moderator at L-54M nuclear research reactor. The nuclear facility was operated between 1959 and 1979 at Politecnico di Milano (Italy) and then was managed according to the deferred dismantling strategy. Recently, a preliminary estimation of radionuclide inventory and volume of radioactive waste, in which the work is set, has begun.

In the present work, a more complete elemental analysis involved a graphite pre-treatment procedure, which consistently followed the steps set by the mentioned previous experiment conducted on the same graphite stock [11]. Some variations were applied on the considered benchmark method. In particular, the weighed amount of treated graphite powder was brought from 2.5 g to 14 g with multiple additions, in order to increase overall amounts of analytes in the analysed solutions and so enhancing the probability of obtaining valid results, *i.e.* above detection limit (DL). At each addition, samples were collected in ceramic crucibles, pre-heated at 120 °C and then thermally treated in a muffle furnace at 650 °C for 24 h, to grant a complete oxidation. Resulting ashes were treated with ultrapure mixtures of HCl and HNO3 on a hot plate until reaching a complete dissolution of the residues. In this step, HF dissolution reported in the previous method was not performed, aiming at avoiding subsequent fluorine-removal treatments, which could introduce analytes losses by volatilization or precipitation due to the multiple dry-outs. Solutions at different concentrations were then obtained for analysis, by dilution with 1% ultrapure HNO3. A PerkinElmer NexION 2000 ICP Mass Spectrometer was utilized.

Results appear to be comparable with those obtained in the previous work and also with other nuclear graphite available in literature. [11,12] In particular, 31 elements were identified in the graphite sample by ICP-MS method: none of them resulted to be below DL. Vanadium concentration was quantified in the order of tens of ppm. Ca, Fe, and K resulted in the order of ppm. Al, B, Ba, Cr, Cu, Li, Mg, Mn, Mo, Ni, Pb, Sr, Ti, and Zn were found in concentrations of fractions of ppm. Ce, Co, Cs, and La appeared in the range of ppb, while Eu, Gd, Nd, Sm, Th, and U resulted in fractions of ppb.

## pgaa experimental

Further experimental results could be obtained through PGAA, performed on a sample collected from the same virgin AGOT graphite stock considered for ICP-MS analysis. The sample was prepared and shaped with a view to allowing full and homogeneous neutron irradiation of the specimen during PGAA. For this reason, a thickness of about 1.2 cm and mass of about 6 g were selected: the large dimension was meant to improve the minimum detectable concentrations obtained.

Abrasive water jet cutting procedures were conducted aiming at limiting graphite heat exposure and so preventing the release of gaseous and volatile nuclides. The sample was analysed for several hours in vacuum conditions, in order to reduce atmospheric nitrogen interference in the measurements, which could have a serious impact on nitrogen determination in the sample. [13] Moreover, a background measurement was performed by replacing the sample with deuterated water, being it characterized by a neutron scattering cross section similar to graphite. The measurements were performed at Heinz Maier-Leibnitz Zentrum, using a thermal neutron fluence rate of 2×1010 cm–2s–1 from a 20-MW water-cooled heavy-water moderated reactor. For gamma detection, a Compton-suppression spectrometer was used (60% high-purity germanium detector surrounded by a bismuth germanate scintillator and connected in anticoincidence mode). [13]

PGAA results appeared to be in good agreement with ICP-MS, especially for what concerned K, Ti, V, Cr, Fe, Ni, Cu and Zn. In particular, this technique allowed to quantitatively determine some light elements of interest, which could not be measured by ICP-MS (because they were artificially added through solvents during pre-treatment of graphite, or as they suffer from interferences during measurements in the spectrometer). The most important result was the determination of N and Cl, which represent two of the most relevant contributors to long-term activity of i-graphite, being precursors for 14C and 36Cl. Their concentrations appeared to be consistent with those in literature [13] and showed values slightly lower than the benchmark: the reason may be found in the different grade of nuclear graphite and in a probably better vacuum condition reached during measurements. For what concerns other nuclides, such as lanthanides, a NAA might be more proficient in confirming ICP-MS results.

## CONCLUSIONS

A complete elemental characterization was performed, allowing to determine impurities in nuclear graphite from L-54M research reactor. Obtained data represent vital information for the optimization of those neutron activation models that are commonly used to estimate radionuclides inventory and to support the radiological characterization before dismantling operations begin, as at Politecnico di Milano’s nuclear facility. ICP-MS and PGAA techniques were applied, returning results mostly consistent with each other and the literature. In particular, ICP-MS revealed to be an extremely valid approach for measuring most of the nuclides, despite its lower sensitivity for other ones with respect to neutron activation techniques. On the other hand, PGAA was able provide information on the lighter and most volatile elements.

It will be extremely useful to update the currently applied simulation models with the new data provided, in order to improve the overall accuracy. It may also be interesting to repeat the set of measurements on other samples, in order to verify the homogeneity of the results, providing a further validation.

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