



Original Article

Proposal of a prototype plant based on the exfoliation process for the treatment of irradiated graphite



Silvia Pozzetto ^a, Mauro Capone ^a, Nadia Cherubini ^a, Maria Letizia Cozzella ^{a,*},
Alessandro Dodaro ^a, Giambattista Guidi ^b

^a ENEA Italian National Agency for New Technologies, Energy and Sustainable Economic Development, Nuclear Material Characterization Laboratory and Nuclear Waste Management, Rome, Italy

^b ENEA - Italian National Agency for New Technologies, Energy and Sustainable Economic Development, Energy Technology Department and Guglielmo Marconi University, Rome, Italy

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ABSTRACT

Most of irradiated graphite that should be disposed comes from moderators and reflectors of nuclear power plants. The quantity of irradiated graphite could be higher in the future if high-temperature reactors (HTRs) will be deployed. In this case noteworthy quantities of fuel pebbles containing semi-graphitic carbonaceous material should be added to the already existing 250,000 tons of irradiated graphite. Industry graphite is largely used in industrial applications for its high thermal and electrical conductivity and thermal and chemical resistance, making it a valuable material. Irradiated graphite constitutes a waste management challenge owing to the presence of long-lived radionuclides, such as ¹⁴C and ³⁶Cl.

In the ENEA Nuclear Material Characterization Laboratory it has been successfully designed a procedure based on the exfoliation process organic solvent assisted, with the purpose of investigate the possibility of achieving graphite significantly less toxic that could be recycled for other purpose [1]. The objective of this paper is to evaluate the possibility of the scalability from laboratory to industrial dimensions of the exfoliation process and provide the prototype of a chemical plant for the treatment of irradiated graphite.

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1. Introduction

In the world there are more than 250,000 tons of irradiated graphite, whereas graphite has been used as moderator and reflector of neutrons in more than 120 nuclear power plants worldwide and in several research and plutonium-production reactors (Fig. 1) [2]. Chicago Pile-1, the world's first nuclear reactor, was a graphite moderated one, containing 360 tons of graphite. From that point on, many designs of graphite moderated reactors have been developed. According to IAEA recommendations, after defueling or after dismantling of the peripheral structures, there is the option either to dismantle the moderator immediately or to opt for a “safe enclosure” period, which allows significant decay of the shorter-lived isotopes. Usually the second option is preferred, but

there are some special circumstances where the first option is taken. Most of them are energy-production reactors, others are research and material testing reactors (MTR), a meaningful subgroup was expressly designed for the production of plutonium and, finally, a small number are experimental reactors [3]. Irradiated graphite (i-graphite) constitutes a waste management challenge mainly owing to the presence of long-lived radionuclides such as ¹⁴C (half-life 5,730 years), ³⁶Cl (half-life 308,000 years), but also short-lived ones, such as ⁶⁰Co (half-life 5.3 years), and ³H (tritium, half-life 12.3 years). It requires large volume for its disposal and precautions have to be taken for its specific properties, such as stored Wigner energy, graphite dust explosiveness and the potential release of radioactive gases [4]. Many different solutions to manage the radioactivity associated with the bulk of i-graphite have been investigated during the European Commission project “Carbowaste” which proposed best practices for its retrieval, treatment and disposal [5]. This project selected 24 management options for i-graphite taking into account its lifecycle. Methods of

* Corresponding author.

E-mail addresses: silvia.pozzetto@gmail.com (S. Pozzetto), letizia.cozzella@enea.it (M.L. Cozzella), g.guidi@unimarconi.it (G. Guidi).

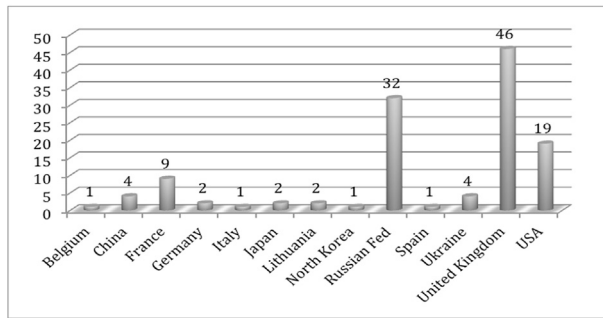


Fig. 1. Graphite moderated reactors in the world.

treatment or conditioning are able to convert i-graphite into physical and chemical forms easier to manage.

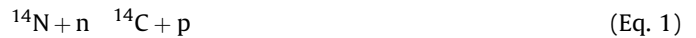
Waste acceptance criteria (WAC) are generally established across the countries, which opted for geological disposal of high-level wastes, and for near-surface disposal. In some cases, they are forced by preconditions set when a facility was authorized. This is particularly true for countries where the amount of i-graphite waste is rather limited (few thousand tons) and therefore the construction of a specific repository is not justified [3]. For countries having larger amounts of i-graphite to deal with, dedicated disposal facilities can be considered but an accurate study is necessary to balance technical, financial, social and safety criteria. Germany is backfilling a previous site at Morsleben and establishing a new site (Konrad) to which i-graphite from AVR and THTR (Thorium High Temperature Reactor) must be stored [2]. Participants to a IAEA Coordinated Research Programme (CRP) to address “Treatment Options of i-graphite to Meet Waste-Acceptance Criteria” explored the following disposal strategies [2]:

- **Geological disposal** (i.e. several hundreds of metres underground), which is probably the least restrictive solution for i-graphite waste in terms of WAC but could also be the most costly one. Furthermore, i-graphite activity does not inevitably demand such an in-depth disposal;
- **Surface or near surface disposal** (chosen by Spain, France, Lithuania) which is the most common solution. However, this generally implies more rigorous constraints in terms of radiological capacities and leach rates due to shorter pathways to external environment and lower residence times;
- **Decommission of graphite waste** if below clearance levels (validated by Switzerland) or to inject it deep underground after previous treatment processes. However, the latter raises strong regulatory constraints and is, at the present, not supported by national management agencies.

2. Materials and methods

Disposal in deep geological formations is one of the most probable ways of final i-graphite management. The large volume of contaminated graphite significantly reduces the cost efficiency of this management route [6]. The aim of treatment processes for i-graphite is to make easier its disposal and to decrease the environmental impact of the chosen pathway [7]. The most used methods to treat i-graphite are: Wigner energy elimination, chemical treatment, thermal treatment, immobilization and gasification. Graphite with a high releasable stored energy can be annealed to unload it. Thermal treatment can eliminate a significant percent of ^{14}C on graphite's surface [7], but this process is highly dependent on the availability of absorbed oxygen

compounds that react with graphite carbon to form carbon oxide gases [8]. While ^{14}C is produced by several routes (Eqns. (1)–(3)) during neutron irradiation of graphite, the reaction of most significance for the surface, labile ^{14}C component, is that involving ^{14}N [8].



Characterization of irradiated reactor graphite has revealed an inhomogeneous distribution of ^{14}C , which is indicative of neutron capture by ^{14}N and ^{17}O rather than ^{13}C , since ^{13}C is homogeneously distributed. The neutron capture section and isotopic abundance of ^{14}N (Table 1) shows that the neutron activation of ^{14}N is the more likely source of this effect. Oxygen and nitrogen adsorption occurs during graphite manufacturing, component assembly and storage: consequently ^{14}N and ^{17}O are found on the graphite surface [9].

For this reason it has been investigated the possibility of exfoliated graphite both to reach the inner ^{14}C , and increase the decontamination level of irradiated graphite obtaining stable graphite layers (graphene) which shows properties that make it useful for potential applications in a wide fields of applications [11,12]. It is well known that solvent-based exfoliation of graphite can produce graphene sheets [13,14]. It has been demonstrated that organic solvents, whose surface energy is close to $70\text{--}80 \text{ mJ m}^{-2}$, enhanced the exfoliation and dispersion of pristine graphite. It has also been demonstrated that mixture of water and organic leads to more stable graphite dispersion: water/acetone; water/acetonitrile and water/pyridine formed highly stable dispersions [15].

This new spatial configuration of graphene sheets makes possible to design a strategy to substantially remove the inner ^{14}C . In the ENEA Nuclear Material Characterization Laboratory, it has been verified that the exfoliation ultrasound assisted is more efficient using an organic and inorganic mixtures. NaOH (50 mg/ml) in the mixture seems to actually act on a stable graphene dispersion removing ^{14}C by surface and by inner layers, better than inorganic solvent alone [1]. In order to increase the amount of treated i-graphite overcoming the laboratory scale a prototype of a plant based on the decontamination of i-graphite through the exfoliation method ultrasound assisted has been designed. Due to the huge amount of i-graphite and its high level of radioactivity produced during the decommissioning of a nuclear power plant, it is desirable to have an automatized treatment factory close to the nuclear site in order to minimize the radioactive materials handling and reducing the contamination of exposed workers. Taking into account what has just been said and the results previously obtained in the ENEA Nuclear Material Characterization Laboratory [1], a prototype plant has been designed.

2.1. Dismantling of moderator: the extraction of i-graphite

The removing of graphite blocks from reactor occupies a major

Table 1
Properties of ^{14}C precursors available in reactor-irradiated graphite. Reaction cross-section values refers to thermal neutron energy (0.025 eV) [10].

Reaction	Cross Section (barns)	Natural isotopic abundance (%)
$^{14}\text{N}(n,p)^{14}\text{C}$	1.93	99.63
$^{13}\text{C}(n,\gamma)^{14}\text{C}$	0.0014	1.07
$^{17}\text{O}(n,\alpha)^{14}\text{C}$	0.257	0.04

portion of the work in the reactor dismantling. A reduction of the time period will contribute to reduce the operational cost. Since the procedure can generate hazardous dust for the staff directly involved in decommissioning, it is necessary to filter the indoor air through a powder suppression system equipped with HEPA filters, arranging, for instance, the equipment directly over the reactor core. One option is represented by Tokai-I mechanical arm (Fig. 2) which is a tool capable of extracting seven blocks at a time [16]. After the extraction, the block must be ground by hammer mills to obtain a very fine powdered graphite.

At this step the amount of ^{14}C can be previously determined through a wet Oxidation Acid Digestion ($\text{H}_2\text{SO}_4\text{--HNO}_3\text{--HClO}_4$ 8:3:1 v/v/v), carried out under N_2 flow. Under this condition ^{14}C is trapped as CO_2 in 3-MPA(3-methoxypropylamine) [1].

2.2. The prototype plant

The proposed plant scheme (Fig. 3) has been designed taking into account the laboratory practical experiences: at this stage no structural calculations have been carried out. Details of the proposed process are reported below.

Graphite, finely powdered, is blended in the mixer (A) with exfoliation solvents through an automatic device, following the experimental ratio determined in a previous work (10 g/5 L) [1]. The resulting mixture falls for gravity into inert and transparent tubes, located inside the ultrasonic bath (B), for the exfoliation

reaction. The operational conditions ($P = 1 \text{ atm}$; $T = 60 \text{ }^\circ\text{C}$) have to be constantly monitored. The ultrasonic bath is basically a tank filled with water as vibrational transmission medium. A possible hermetic ultrasonic apparatus is showed in Fig. 4.

After the sonication process, the solvent with the exfoliated graphite must be separated from the residual sludge into a mixer settler (C). A possible choice for the pilot plant can be a vertical peeler centrifuge basket with a speed rotation around 500 rpm, or a horizontal multistage decanter (Fig. 5), which allows a physical separation between the reaction solvent and the residual sludge, containing the unreacted i-graphite, and the treatment of larger volumes of mixture i-graphite/solvents.

The unreacted i-graphite will be collected and, through a conveyor belt (D), directed again towards the exfoliating process; while the dispersed graphene (E) is separated from the solvent by filtration, dried and analysed in order to evaluate the effectiveness of chemical treatment. The solvent is also recovered, analysed to evaluate its level of contamination and, if it is possible, pumped into the recycled solvent mixer (F) to be reused. Graphene will be analysed to verify the strength of the process and dried in vacuum.

3. Discussion

Currently, the majority of i-graphite is held in situ within reactors or in vault/silo storage [5]. I-graphite is classified in LLW and ILW depending on its position into the core and the neutron flux,

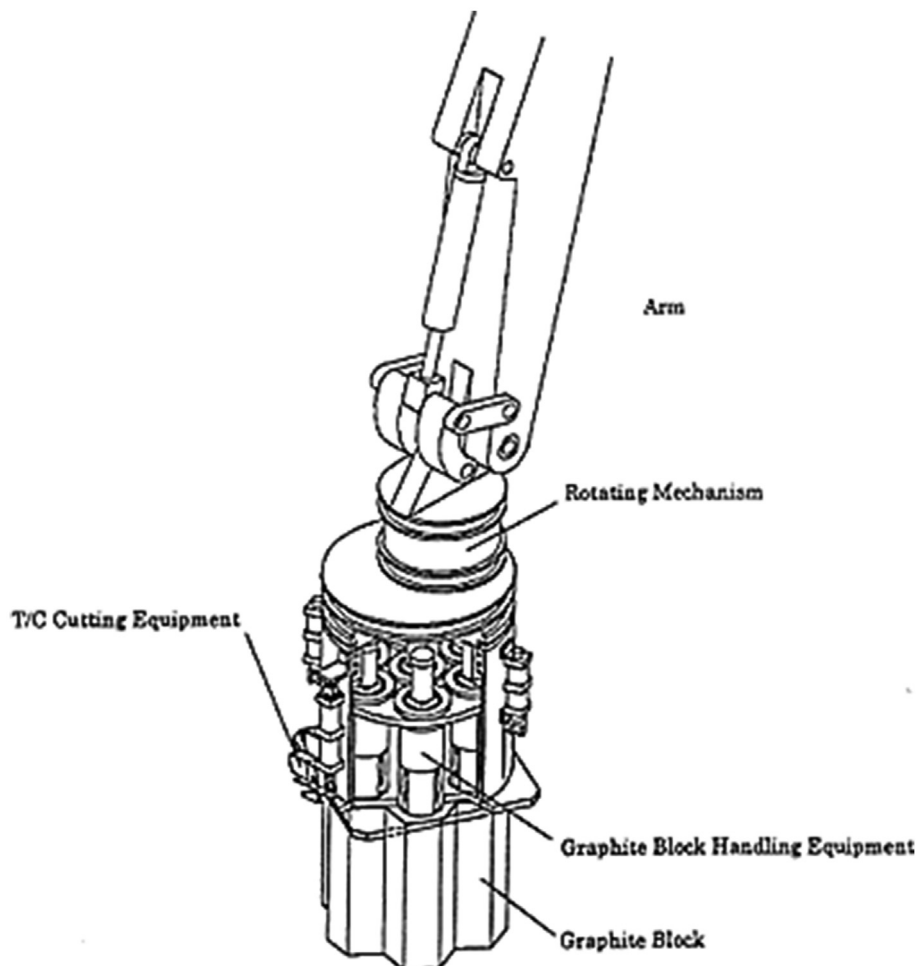


Fig. 2. Graphite blocks extractor Tokai I.

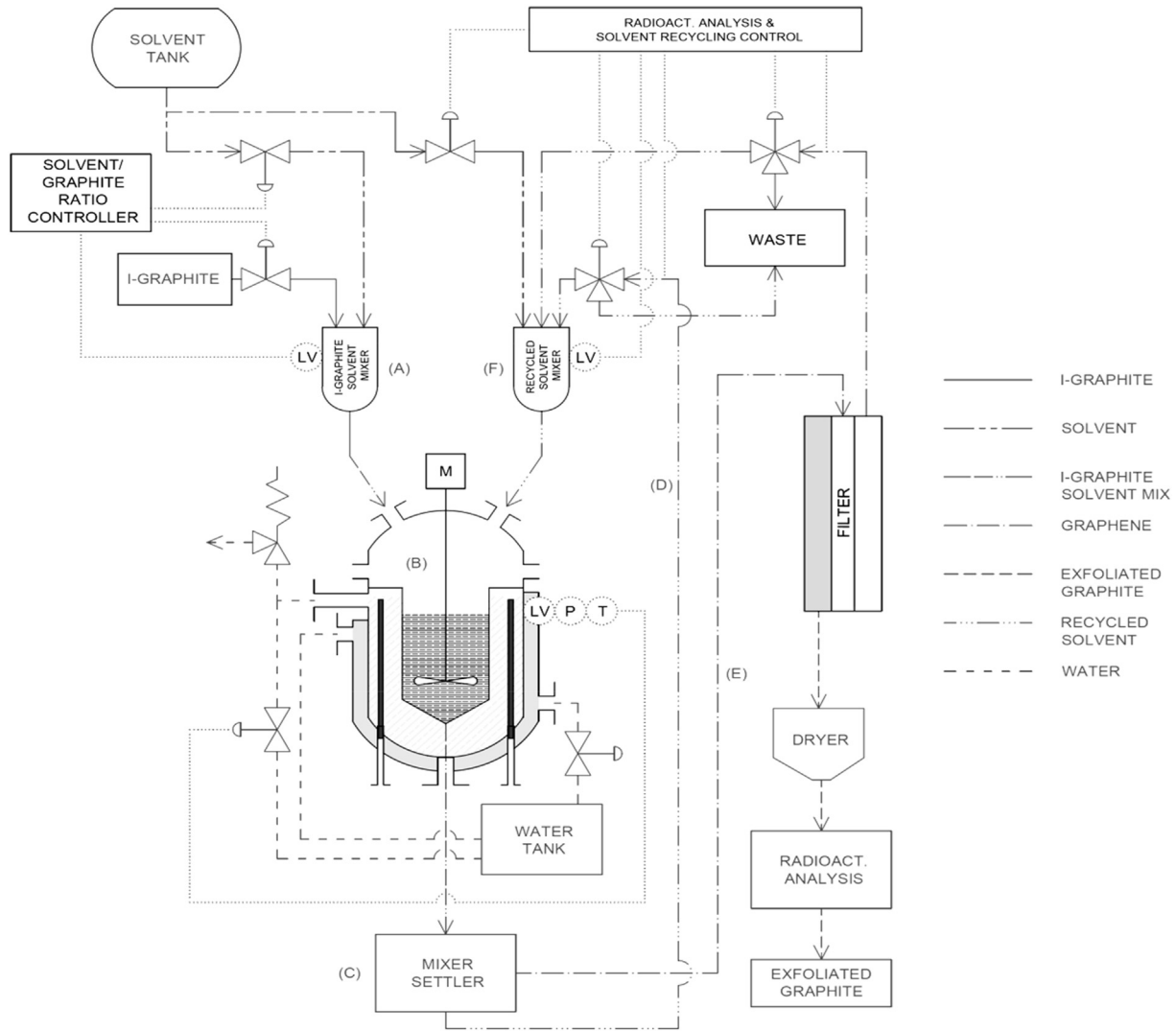


Fig. 3. The prototype plant.



Fig. 4. NPL frequency driven reference ultrasonic vessel (25 l; 25 kHz) [17].

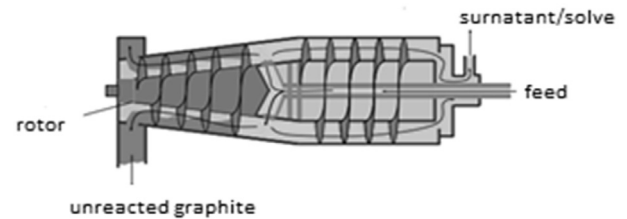


Fig. 5. Horizontal multilayer decanter.

remote activated, might be placed above the reactor core, taking into account all conceivable structural modifications due to the radiation damage.

The grinding of i-graphite blocks can be carried out in two steps: a coarse crumble made by grinded hammer with titanium teeth and a fine milling made by ceramic blades, which are chemically inactive. Titanium shows great mechanical performance and a very high stress resistance is really suitable for the treatment of contaminated materials. To keep the temperature constant, the ultrasonic bath has been surrounded by a perimeter cladding filled with water. The water of the cooling system can also be used as a

which has been submitted. To reduce as much as possible the exposure of the workers and considering the huge amount of moderator, it is preferable that the graphite blocks extractor,

refilling tank in case of evaporation of sonication water. The vessel shape will be designed to avoid sedimentation, to improve the mixing of i-graphite and exfoliation solvents and equipped with a mechanical stirrer. It is possible to obtain graphene with less than five layers and decontamination yield around 15% using the sonication bath at 30 W. Because of the cavitation, pressurization or depressurization processes can occur inside the transmission media. It is possible to calculate the theoretical P_{\min} and P_{\max} [18] with:

$$P_{\max} = P_{\text{atm}} + \sqrt{\rho a I} \quad (\text{Eq. 4})$$

$$P_{\min} = P_{\text{atm}} - \sqrt{\rho a I} \quad (\text{Eq. 5})$$

where P is the pressure in Pascal, $\rho = 0.9832 \text{ g/cm}^3$ (water density at 60°C); a = speed of sound into the medium (m/sec); I = acoustic intensity (W/m^2).

Having already tested the 30 W exfoliation in the laboratory, the scalability factor could be calculated taking into account the volume of the bath used in the experimental tests and calculate the sonication power for the prototype plant. Inside the system, the transducer will be powered by a generator high frequency alternating current, which is converted, by a piezoelectric element, into mechanical vibrations. The vibration thus generated is then amplified by a booster or sonotrode. The variable electric field induced by the electric current varies the thickness of the ceramic elements or of the crystal in the element piezoelectric. This creates a pressure wave, which is propagated through the solid material, in which the molecules are elastically connected to each other. At the output a vibration of a few microns is amplified by a special booster or by the sonotrode itself. The ultrasonic intensity is related to the working frequency and the amplitude of the vibration through the following relationship [19]:

$$I = \frac{1}{2} \rho a (2\pi A f)^2 \quad (\text{Eq. 6})$$

where f = ultrasonic frequency; A = wave width. The water of the cooling system could be used also as refilling tank for the sonication fluid.

This dependency raises concern because the frequency of the equipment on the market is usually fixed and only the wave width can be managed. However, increasing the wave width, its propagation capacity through the liquid decreases, affecting the homogeneity of the bath conditions. It will result a more intense sonication close to the sonotrode that gradually will lessen by moving away from it. In the dimensioning of the bath, this aspect must also be taken into account, especially if high quantities are involved.

In a previous work [1] the ^{14}C removal efficiency of several solvents and mixtures has been tested. It seems clear that mixture of organic solvents in water/alkali are more efficient than several dipolar aprotic solvents in removing ^{14}C . These evidences can guide the choice of materials in the constructions of a first prototype.

4. Conclusion

The quantity of irradiated graphite could be higher in the future if high-temperature reactors (HTRs) will be deployed. In this case noteworthy quantities of fuel pebbles containing semi-graphitic carbonaceous material should be added to the already existing 250,000 tons of irradiated graphite. This makes particular urgent to find a solution for the i-graphite management. Thermal treatment [9] and micro-oxidation process [20] have been suggested as

decontamination methods to remove ^{14}C but only at laboratory scale. Technologies are based mostly on isolation (packaging) of radioactive graphite from the environment and they are not able to provide for a significant volume reduction.

Italy has not yet identified a National Repository for the storage of radioactive materials coming from the decommissioning of Italian nuclear power and fuel cycle plants: the construction of a i-graphite recycling plant would help to overcome the lack of suitable spaces for its storage and in the near future could generate recycled material for nuclear industry and, achieving a level of decontamination below radiological relevance, provide “clean” graphene for industrial use.

Declaration of competing interest

The authors have been approved the final version of the manuscript submitted. There is no financial or personal interest in the subject matter or materials discussed in the manuscript.

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