

Review

Management of Radioactive Waste Containing Graphite: Overview of Methods

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Abstract: Since the beginning of the nuclear industry, graphite has been widely used as a moderator and reflector of neutrons in nuclear power reactors. Some reactors are relatively old and have already been shut down. As a result, a large amount of irradiated graphite has been generated. Although several thousand papers in the International Nuclear Information Service (INIS) database have discussed the management of radioactive waste containing graphite, knowledge of this problem is not common. The aim of the paper is to present the current status of the methods used in different countries to manage graphite-containing radioactive waste. Attention has been paid to the methods of handling spent TRISO fuel after its discharge from high-temperature gas-cooled reactors (HTGR) reactors.

Keywords: graphite; irradiated graphite; graphite processing; radioactive waste; waste management; waste disposal; spent TRISO fuel

1. Introduction

As of December 31, 2018, 451 nuclear power reactors were in operation and produced 392,779 MWe of electricity. Fifty-five reactors, with a net capacity of 57,441 MWe, were under construction, while 172 reactors were permanently shut down [1]. At the turn of the millennium, scientists from several centers around the world started working on the development of new nuclear energy systems, called Generation IV systems, that will deliver energy at a relatively low cost and will work with a high level of safety. Most of the reactors use moderators and/or reflectors made from graphite.

Like any other industry, nuclear power plants (NPP) generate waste; however, compared with other industries, the mass of this waste is relatively small. According to the recent data published by the International Atomic Energy Agency (IAEA), the global volume of solid radioactive waste is about 35 million m³, of which 28.5 million m³ (82%) has been permanently disposed of, and another 6.3 million m³ (18%) is in storage awaiting final disposal. Over 98% of this is classified as waste with a very low or low radioactivity level, and the majority of the remaining waste is at an intermediate level [2]. Much of the waste comes from the dismantling of nuclear installations, which are the main source of the irradiated graphite (called *i*-graphite) originating from the reactor's structural material, as well as from other irradiated carbonaceous (*i*-carbonaceous) waste, non-graphitized carbon bricks, or fuel coatings (pyrocarbon, silicon carbide). It has been estimated that as a result of the decommissioning of one water-cooled graphite-moderated reactor, about 1500–2000 tons of radioactive graphite waste is produced [3]. According to data published in 2010 by the IAEA, the world resources of *i*-graphite at that time were approximately 250,000 tons (160,000 cubic meters). Handling *i*-graphite and *i*-carbon poses a particularly large problem for Great Britain (containing about 86,000 tons of *i*-carbons), the Russian

Federation (60,000 tons), the USA (55,000 tons), and France (over 23,000 tons) (Figure 1) [4–6]. The resources of several other countries range from 6000 to 2000 tons each.

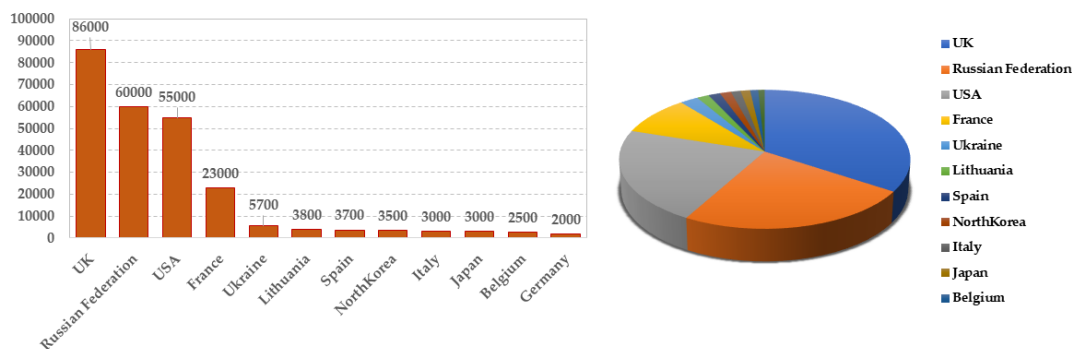


Figure 1. World resources of irradiated graphite waste by country (tons).

The increasing trend of global graphite reserves can also be seen from the data published by Pavlyuk (Figure 2) [7]: in Russia, from 2010–2020, the total amount of radioactive graphite waste increased by about 15,000 tons, and it is expected to reach roughly 60,000 tons in 2030.

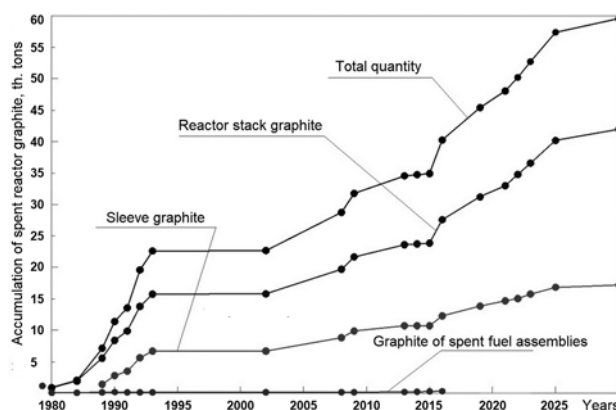


Figure 2. Forecasted dynamics of collecting radioactive graphite waste in Russia. Reproduced from [7] with permission.

According to Smith and Bredell [8], the graphite content in radioactive waste increases mainly due to the increasing number of pebble bed modular reactors [9]. Each 200-MWe pebble bed reactor may produce about 90,000 burned fuel elements with about 17 tons of irradiated carbonaceous waste material per year [10]. Light Water Reactors (LWR) reactors, in turn, work without breakdowns for decades, so they do not currently generate large amounts of graphite. In the future, however, they may generate significant amounts of this material.

A large problem, both in the case of reactor operation and decommissioning, is the management of nuclear graphite that serves as a moderator due to its extreme purity and its ability to withstand extremely high temperatures. A schematic of the location of the graphite moderator and graphite reflector in a nuclear reactor is presented in Figure 1. Graphite waste is highly radioactive, and each ton of this material withdrawn from a stack contains about 50 TBq of tritium (hydrogen-3, a radionuclide with a half-life of 12.3 years), 50 TBq of carbon-14 ($t_{1/2} \approx 5730$ years), and 0.5 TBq of chlorine-36 ($t_{1/2} \approx 300,000$ years).

The available literature on this problem proposes many solutions for dealing with graphite-containing radioactive waste. All of them, as a basic principle, assume the absence of (or, at least, a reduction in) both radiological and chemical hazards to humans and the environment. Thus, before being put into practice, each of these procedures should be accepted both by nuclear and

conventional environmental authorities. However, none of the proposed procedures for conditioning radioactively contaminated graphite and/or withdrawing it from nuclear installation have been accepted for common use [6]. Thus, despite significant progress in this area, recycling of irradiated graphite (called *i*-graphite) aiming to re-use either graphite alone or certain radionuclides is the only method for its management and disposal.

Poland currently has no operating nuclear power plant, but there were past plans to construct four 440 MWt Russian VVER-440 units. This project was cancelled due to unfavorable public opinion, and the components already delivered to the site were sold. Recently, the government decided that Poland should immediately introduce nuclear energy, and the first power plant is expected to begin operating shortly after 2033. The current nuclear research reactor at the National Centre for Nuclear Research (NCBJ) is the only unit operating in Poland. Simultaneously, a strategy to implement high-temperature gas-cooled reactors (HTGR) for industrial heat production was proposed by the Polish government in 2018. There are plans to construct an experimental 10 MWt HTGR at the NCBJ, followed by a commercial 200–350 MWt HTGR for generating process heat

The International Atomic Energy Agency (IAEA) and the European Atomic Energy Community (Euratom) have devoted lots of attention to the problems arising from the need for competent and safe disposal of *i*-graphite.

An initiative to select the optimum method for the disposal of radioactive waste graphite started in the frame of the IAEA conference Solutions for Graphite Waste: A Contribution to the Accelerated Decommissioning of Graphite-Moderated Nuclear Reactors (Manchester, UK, 2007) and the presented papers along with records of the discussion sessions may be found in IAEA-TECDOC-1647, published in 2010 [9]. In order to follow up on the activities related to *i*-graphite management, the IAEA has launched two more projects: establishing a repository for data and reports within the IMMONET knowledge network (accessible via the IAEA 'Nucleus' portal) [11] and a new project called Irradiated Graphite Processing Approaches (GRAPA) in which experts from the following countries participate: Belgium, France, Germany, India, Italy, the Democratic People's Republic of Korea, Lithuania, the Netherlands, the Russian Federation, Spain, Switzerland, Ukraine, the United Kingdom, and the United States of America [12]. The common goal of both of these initiatives was to encourage an international debate and collaborative work aimed at optimizing and facilitating the treatment of irradiated graphite.

In turn, the European Commission, under the Seventh Framework Programme (2007 to 2011) of the Euratom has established a network of experts which is designed to ensure the best available and most environmentally acceptable technologies have been identified for the characterization, retrieval, treatment, reuse/recycling and disposal of irradiated graphite [13].

In light of the planned development of nuclear energy in Poland, and probably the earlier installation of HTGR reactors, the problems associated with irradiated graphite management are important not only for Poland but also for all countries introducing this type of energy production method. This paper attempts to briefly describe the theoretical and practical knowledge for managing graphite-containing radioactive waste produced by nuclear reactors.

2. Carbonaceous Components of Nuclear Power Plant Installations

Nuclear Graphite and Radioactive Isotopes in Graphite-Containing Waste

Nuclear graphite (defined as graphite having a purity level < 5 ppm (boron equivalent) and with a density greater than 1.50 g/cm³ [14]) is produced from selected pitch or petroleum coke, which are either natural or industrial products. In traditional nuclear reactors (Generation I, most of them being already excluded from use) and operating commercial power reactors (Generations II and III), graphite is used to produce large-scale reflectors and neutron stream moderators.

Apart from the above, HTGR nuclear fuel (e.g., of the TRISO type) is also fabricated in the form of pyrolytic carbon/porous and carbon/silicon carbide-coated fuel particles with extremely high

mechanical strength that are highly resistant to irradiation. Such fuel particles, like the graphite blocks in which they are packed, can survive high temperatures up to ~1600 °C. In pebble bed reactors, more than 8000 TRISO small fuel pellets are packed inside spherical graphite packages with diameters of 60 mm [15]. The core of the HTR-10 HTGR-type reactor is loaded with more than 25,000 fuel spheres, so this type of HTGR pebble bed reactor may produce large amounts of graphite material.

Graphite for use in nuclear reactors should not contain neutron-absorbing elements, particularly boron, which has a large neutron capture cross-section. The boron content of thermally purified graphite (such as AGOT graphite, known to be a good non-conductor but currently commercially unavailable) is usually smaller than 0.4 ppm [16], but in chemically purified nuclear graphite, this may be lower than 0.06 ppm.

Despite the high chemical and mechanical stability of graphite, during NPP operation, the graphite elements of an installation may be oxidized and/or cracked. These processes determine when the items must be decommissioned. In addition, as a result of neutron irradiation, both the chemical composition and physical properties of graphite elements are significantly altered. For example, if irradiated with a very high radiation dose, the size of the graphite elements increases, which increases their fragility. These changes may lead to the destruction of nuclear installation components and, ultimately, to their removal as radioactive waste.

When graphite is irradiated by a flux of neutrons, defects may form in its crystal lattice in which atoms are displaced from their normal positions, accompanied by energy storage (the Wigner effect). It was found that the amount of this energy stored due to irradiation depends on the neutron energy that crosses a unit area (i.e., neutron fluence) and the temperature of the irradiation process. Thus, the thermal conductivity of graphite decreases upon increasing its stored energy. By increasing the temperature of the irradiated graphite, e.g., by external heating or by the heat supplied by irradiation, dislocated atoms may return to vacancies in the graphite lattice, which induces the release of stored energy in the form of heat. In uncontrolled conditions, the accumulated energy may result in the auto-ignition of graphite-containing waste.

Furthermore, radioactively contaminated *i*-graphite spontaneously emits significant amounts of often radioactive gases and, as a result, reveals significant weight loss. During the reactor's operating life, it can even exceed 20% and occurs fairly uniformly within the whole graphite portion. Moreover, fast neutron irradiated graphite exposes a significant differentiation in the materials' properties, such as the Young's modulus, thermal conductivity, etc. [17]. In the formed methane, carbon dioxide, or hydrogen, a non-radioactive atom is exchanged by its radioactive isotope. The most important radioactive gases that may be released from cemented waste are methane-¹⁴C and tritiated hydrogen (HT) [18]. Additionally, even if a large portion of the formed carbon-¹⁴C dioxide is immobilized within a landfill, a significant part of this gaseous product may be released into the atmosphere.

Radioactive contamination of *i*-graphite arises either from the irradiation of impurities within graphite or from contamination by the corrosion products within the operating reactor loop. The former, arising from the activation of atoms within the graphite structure by rapid neutron capture, occurs in naturally occurring ¹³C and also the impurities introduced into graphite during its production (e.g., chlorine, nitrogen, cobalt, and lithium isotopes). The latter generally comes from contact with the reactor cooling water and generates ¹⁴C from nitrogen or oxygen irradiation. The deposited heavy metal radionuclides (uranium, transuranic elements, and fission products) come from inside reactor installations and may contaminate graphite elements due to nuclear fuel crashes that may occur during reactor operation [19].

In terms of *i*-graphite management, short-lived radionuclides are important only immediately after reactor shutdown. If the recovery and treatment are delayed for tens of years after shutdown, their activity significantly decreases due to their decay. About 95% of the radioactivity concentration emitted by *i*-graphite, however, comes from carbon ¹⁴C and can achieve a value of more than 3×10^{11} Bq/m³. This value approaches the upper limit of ¹⁴C permitted for storage as long-lived waste (LLW) waste (i.e., a low-level Class C according to the U.S. Regulatory Commission on Nuclear Safety, NRC) [20–22].

Since this radionuclide has a relatively long half-life (~5730 years), if it is released into the atmosphere, it may produce potentially long-term health risks due to the emitted radiation. Thus, long-living radionuclides (^{14}C , but also ^{36}Cl) are the most important radioisotopes to consider when choosing a management strategy for radioactive waste containing *i*-graphite.

In waste containing radioactive *i*-graphite, one may also find corrosion and activation products (^{57}Co , ^{60}Co , ^{54}Mn , ^{59}Ni , ^{63}Ni , ^{22}Na), fission products (^{134}Cs , ^{137}Cs , ^{90}Sr , ^{152}Eu , ^{154}Eu , ^{155}Eu ; ^{144}Ce) and small amounts of uranium and transuranium radionuclides (^{258}Pu , ^{259}Pu ; ^{241}Am , ^{243}Am) [23,24]. Even if present in small amounts (usually less than 0.01%), 20–30 years after irradiation, the neutron flux in these impurities may still pose a radiological risk to the environment.

3. Management Strategies of Waste Containing Irradiated Graphite

Radioactive waste is defined by the International Atomic Energy Agency, IAEA as “any material that contains or is contaminated by radionuclides at concentrations or radioactivity levels greater than the exempted quantities established by the competent authorities and for which no use is foreseen” [25]. This waste is generated by any human activity that uses radioactive materials, either as part of the process (e.g., nuclear medicine, science, tracking certain industrial processes) or by using radioactive materials as equipment or instruments for the process (defectoscopes, fume detectors, tank fill meters containing closed radioactive sources, etc.).

Several attempts have been made to classify radioactive waste, and some are presented in Figure 3. The left part of the figure contains the categorization proposed by the IAEA [26]. Currently, most countries base their national systems of categorization on this IAEA scheme.

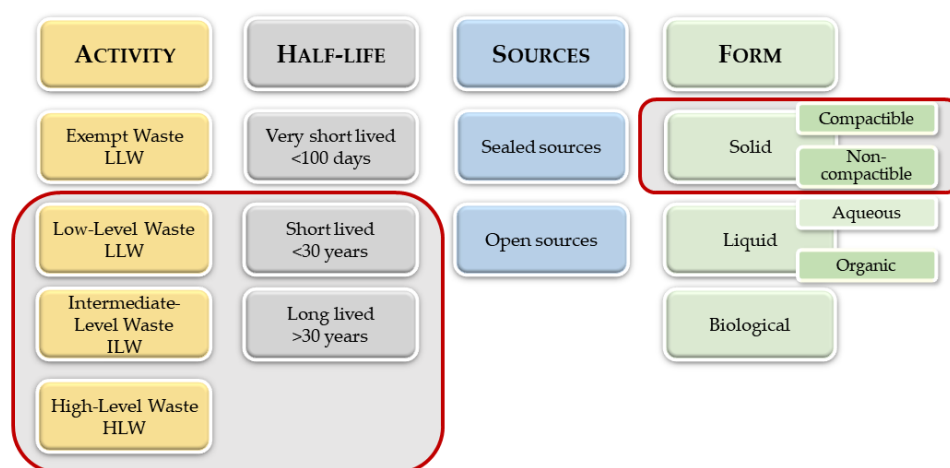


Figure 3. Different categorizations of radioactive waste based on [27]; radioactive waste containing graphite is shown.

3.1. Standard Methods of Radioactive Waste Management

The objective of radioactive waste management is to isolate it from the environment so that the release of radionuclides does not pose a radiological risk to either people or the ecosystem. This management should guarantee negligible negative effects for future generations.

The main stages of radioactive waste management, as proposed in the IAEA Safety Glossary: Terminology used in nuclear safety and radiation protection, 2018 edition [28], are shown in Figure 4. Namely, they are pretreatment, treatment, conditioning, storage and disposal. When designing a management process, a complex approach is necessary because each step affects the others, and decisions made at one stage may affect the others. In addition to this, some waste management operations generate secondary radioactive waste or recyclable materials. Since the stages of radioactive waste management often do not immediately follow one another, in many cases, the optimal variant

must be chosen before starting the full waste management process. In any instance, the environmental effects of radioactive waste management activities should be taken into account.

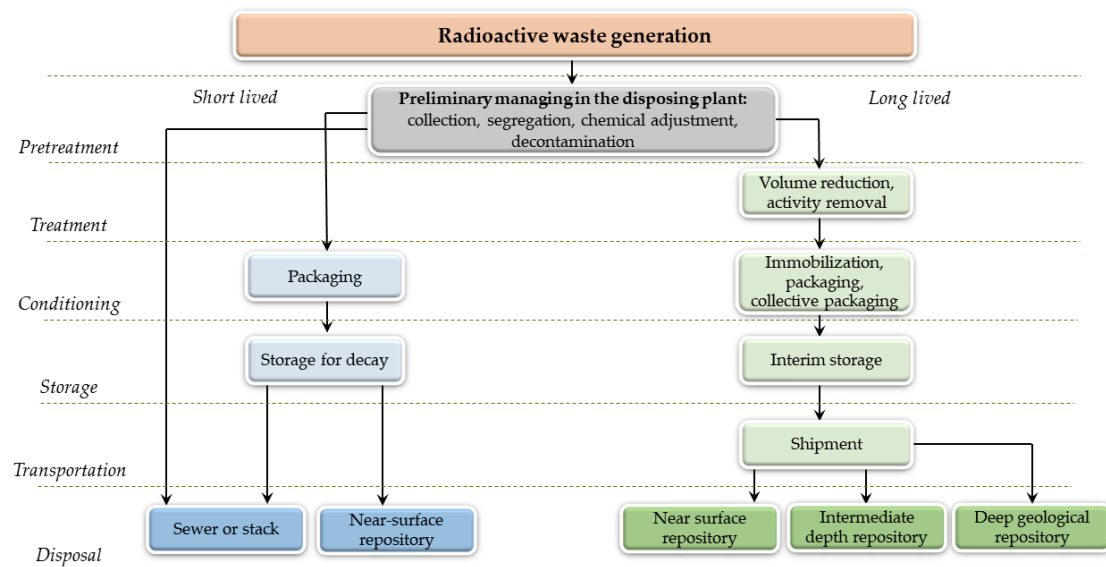


Figure 4. Main administrative and operational activities involved in radioactive waste management.

In more detail:

- ✓ waste pre-treatment and treatment involve waste collection, segregation, characterization, mass (or volume) reduction, drying (of wet or liquid waste), the separation of high-activity waste from waste with lower activity, combustion (e.g., of *i*-graphite-containing waste), solidification of liquid radioactive waste, etc.
- ✓ conditioning operations include cementation, bituminization, immobilization using synthetic resins and polymers, vitrification or inclusion in SynRoc materials, followed by packaging.
- ✓ temporary storage, sending some parts of the waste for recycling, transportation to a repository, and final disposal are often considered a single operation.

An advanced overview of the immobilization methods can be found in numerous publications, e.g., in a book by Ojovan and Lee [29].

Radioactive graphite constitutes a major waste stream which arises during the decommissioning of certain types of nuclear installations. As shown in the following text, problems in the radioactive waste management of graphite arise mainly because of the large volumes requiring disposal, the long half-lives of the main radionuclides which contaminate this waste and from the specific properties of graphite, e.g., the stored Wigner energy, graphite dust explosibility and the potential for radioactive gases to be released. Different methods for the management of radioactive graphite have already been studied but, until now, a generally accepted approach has not been elaborated. Thus, different solutions may be proposed for various cases and our main ideas for the management of radioactive graphite performed worldwide will be presented in the following sections.

3.2. Management of Radioactive Waste Containing Graphite

As mentioned above, graphite-containing radioactive waste releases Wigner thermal energy. For this reason, management of this type of waste must consider the possibility of overheating, and thus ignition. In this respect, this type of waste requires special handling.

Put simply, the management of radioactive waste containing *i*-graphite may be realized in two ways:

- a. **Long-term storage**, e.g., removing *i*-graphite by breaking it up in situ and storing outside the reactor core for a sufficiently long time in special containers filled with a binder. The unit cost when a radiation-resistant polymeric matrix is used is approximately USD 2600 per ton of graphite. [3]. In turn, the cost of immobilizing graphite in an inorganic binder (e.g., cement) is only USD 1400 per ton. In the Russian Federation, piles of decommissioned reactors are planned to be decommissioned in reactor chambers [3].
- b. **Disposal** of *i*-graphite by thermochemical treatment, i.e., by combustion or incineration. In the UK, graphite is gasified to carbon dioxide to manage the resulting gas and residual secondary solid waste, which diminishes the graphite volume by 95% and saves up to GBP 2.4 bn in graphite management costs [30].

A detailed inspection of the existing literature allows us to state that the most popular method for managing radioactive waste containing *i*-graphite seems to be the combustion method. This method can be used at both large and small scales and has a significant advantage over other methods because:

- ✓ it considerably reduces the volume of the waste to be stored. Graphite, like any carbonaceous material, may be completely gasified. For example, according to Sugikawa, 99% or more of the graphite matrix can be gasified by soaking the graphite in a catalyst solution and gasifying the catalyst-impregnated graphite at temperatures below 900 °C [31]. The resulting residual solid secondary waste containing mainly ^{60}Co , ^{137}Cs and ^{55}Fe and residual gamma particles have only about 1–2% of their initial volumes. Radioactive contaminants in the form of carbonates may be trapped in filters or in the scrubber solutions.
- ✓ the gaseous radioactive products (beta emitters: ^{14}C in the form of carbon dioxide and tritium in the form of water vapor), if their concentrations are not very high, may be diluted many times and dispersed in the atmosphere. If the concentrations of gaseous beta emitters are too high to be diluted, existing technologies offer their solidification as carbonates with the aim of protecting the environment.

On the contrary, the total processing time of radioactive waste containing *i*-graphite due to the dismantling of nuclear installations (including the conditioning of graphite, transport of waste drums, and disposal) is much shorter using the first technology.

Thus, choosing a method for the management of waste containing *i*-graphite must be preceded by studies on the decommissioning of nuclear installations, which take into account a strategy for further management of the resulting radioactive waste. A flow diagram presenting the main stages of the long-term storage and disposal of graphite-containing waste is shown in Figure 5.

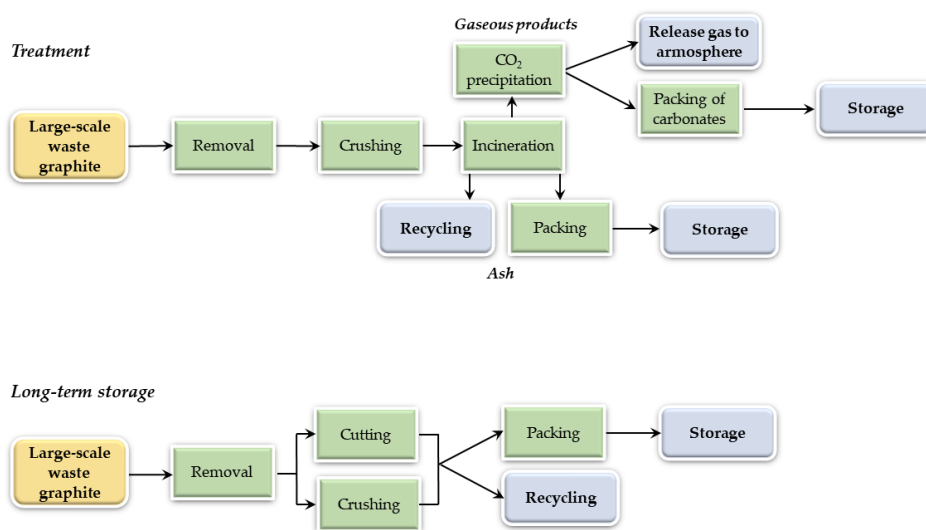


Figure 5. Long-term storage and treatment of graphite-containing waste; based on [32].

4. Management of Graphite-Containing Waste—Special Cases

As stated above, the generally accepted methods of irradiated graphite disposal may be categorized into one of the following groups:

- (1). Removal of large elements from nuclear installations as solid graphite and prolonged (or permanent) storage with or without crushing.
- (2). Decomposition of graphite elements, e.g., by thermochemical methods (incineration).
- (3). Recovery of graphite (regeneration) for reuse, e.g., by decontamination.

In principle, these categories are in line with the commonly used methods of managing normal radioactive waste. In the following text, we will try to describe the methods of handling such a special waste as radioactive graphite.

4.1. Handling Large, Highly Radioactive Elements of Decommissioned Nuclear Installations Made of Graphite: Long-Term Storage

In many cases, fragmentation or destruction of the large-scale elements of nuclear installations made from graphite that are expected to be decommissioned do not seem to be the optimum actions. Taking into account both the usefulness of these methods and the necessary financial contribution, in some cases, the preferred method of dealing with large-scale radioactively contaminated graphite is its temporary storage. Such a method has been proposed in Great Britain for the Magnox reactors constructed there from the 1950s to the 1970s. The British procedure consisted of three consecutive stages [21]:

- (1). Immediately after dismantling, entire graphite items are carefully washed, roughly decontaminated, and securely placed for temporary storage. This first stage continues for 5–10 years, and during this period, all short-lived radionuclides decay.
- (2). After this phase, the resulting non-radioactive parts of the waste may be withdrawn and, if possible, re-used. The other remaining radioactive components remain stored in special “safes” for an additional thirty years. If needed, this phase is prolonged for 100 years. During this period, only routine radiometric inspections are carried out.
- (3). When the end of the second period arrives, i.e., after about 135 years, the stored graphite elements may be dismantled when their radioactivity is reduced to a relatively low and stable level.

Furthermore, the ‘Moata’ reactor (a 100-kW reactor operated by the Australian Nuclear Science and Technology Organisation from 1961 to 1995 and decommissioned in 1998 [33]) declares that long-term storage may last from several years to 140 years, depending on the characterization results of the radioactive inventories at the time of shutdown.

In France, the storage period of *i*-graphite elements is significantly shorter: only about 50 years. Similarly, in Italy, a period of 40–50 is used for graphite elements of reactors shutdown in 1987 (the Latina NPP Magnox reactor) [34].

Lastly, in the Russian Federation, graphite piles obtained from Units 1 and 2 of the Beloyarsk NPP are planned to be initially cooled for 50–100 years in reactor chambers (not in the specially constructed ‘safes’) and, therefore, effectively isolated from the environment [3].

Typical radiation dose rates over time following reactor shutdown are shown in Figure 6. All periods of isolation from the environment shown in the background of the radioactivity decay curve may be found in the above.

The advantage of long-term storage is that it gives extra time for further studies on the development of cost-effective technologies for the safe handling of *i*-graphite. Currently, many countries have proposed the use of thermochemical methods to handle large components of graphite-containing waste; however, the generally accepted industrial-scale *i*-graphite technology has not been widely approved. The main features of the long-term storage of radioactive waste containing *i*-graphite are summarized in Table 1.

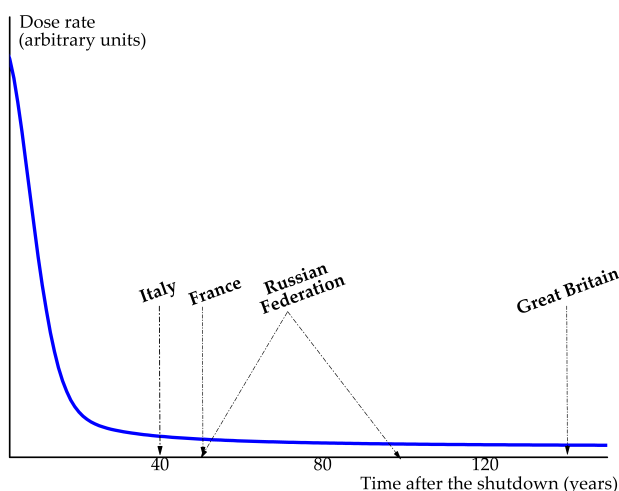


Figure 6. Dose rates resulting from reactor graphite after reactor shutdown.

Table 1. Main features of the long-term storage of radioactive waste containing *i*-graphite.

Advantages	Disadvantages
Waste disposal cost is low.	Maintenance and surveillance must be regularly carried out to prevent environmental accidents.
More efficient and cost-effective dismantling techniques may be developed in the future.	The site cannot be re-used until the waste is dismantled.
Waste from dismantling can be handled safely due to lower activity levels.	Staff with first-hand knowledge of the reactor will not be available in the future.
Volume of highly radioactive waste is low.	Care and maintenance costs may accumulate.
Sufficiently long radioactive decay period decreases radiation exposure to operators during dismantling.	The reactor owner will be liable for its safety for a long time.

4.2. Management of Low and Medium Level Radioactive Graphite-Containing Waste

If reactor owners do not store the graphite components for a long time, one of the other two methods may be applied: decomposition of graphite elements or graphite recovery. For this purpose, several innovative techniques have been proposed, e.g., radionuclide transmutation, ultra- and nanofiltration of the liquid waste or the inclusion of solid waste into a matrix by the sol-gel method. All these methods may change the physical, mechanical, and/or chemical properties of radioactive graphite. Instead, during long-term storage, no significant changes in the aforementioned characteristics are observed [35].

Due to the limited number of deep storage sites, there is a need to reduce the amount of radioactive waste for disposal; therefore, carbon and graphite resources present in the waste should be recycled and reused. Currently, one of the following three methods of treatment are used for irradiated graphite:

- ✓ graphite gasification,
- ✓ direct removal without chemical processing,
- ✓ decontamination of the carbon/graphite matrix with graphite recycling.

The most suitable method for the treatment and disposal of waste containing radioactive graphite must, therefore, be chosen based on the results of its chemical and radiometric analyses.

4.2.1. Conditioning/Disposal Associated with the Gasification of Graphite and Carbon Waste Constituents

Conditioning by graphite gasification is usually performed in one of two ways (Figure 7): combustion in an oxygen atmosphere or pyrolysis in a water vapor atmosphere [36,37].

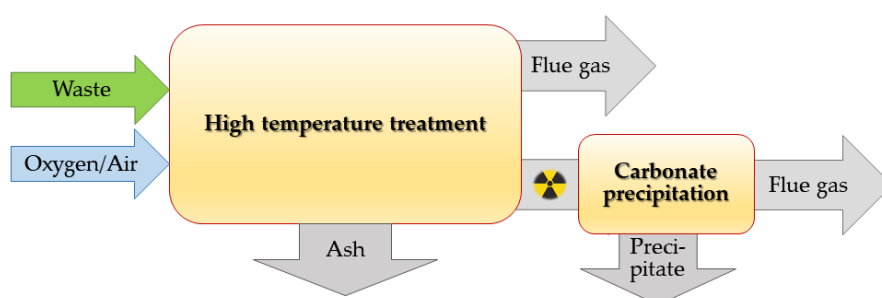


Figure 7. High temperature treatment of graphite and carbonaceous items.

Combustion of flammable radioactive waste in an oxygen atmosphere has the following advantages [38]:

- ✓ it significantly reduces the amount of waste because only a small amount of solid ash is formed, along with some gaseous products,
- ✓ it reduces issues with ensuring the safe storage of waste because inorganic ash formed is extremely resistant when in contact with the environment,
- ✓ it also enables the recovery of many valuable heavy and rare metals, including uranium and plutonium.

Flue gases that do not contain radioactive carbon dioxide may be directly released into the atmosphere; however, aerosols present in the exhaust gas must be separated. In most cases, flue gas also contains radioactive $^{14}\text{C-CO}_2$, which must be removed before being released into the atmosphere. For this purpose, carbon dioxide is immobilized by transforming it into the carbonate form by gas flow through scrubbers filled with Ca(OH)_2 or Ba(OH)_2 aqueous solutions [39].

Graphite waste that is highly contaminated by radionuclides—such as graphite crucibles, molds, or castings contaminated with uranium, plutonium radionuclides, and/or fission products—must be conditioned by a hybrid combustion/precipitation procedure, followed by the separation of radioactive aerosols. This method should also be applied to graphite waste from the reactor core. In such a case, the final mass of ashes containing calcium or barium carbonates may be greater than six times the initial solid waste [40]; therefore, more containers and larger storage chambers should be planned for long-term storage.

The thermal decomposition of waste in an inert atmosphere (e.g., pyrolysis in water vapor) changes the chemical composition of waste and provides an alternative graphite gasification method. The process avoids the Wigner effect in accumulated graphite and permits the separation of graphite from radionuclides under strictly controlled conditions. However, if the process involves reactor core graphite, gases containing volatile ^{14}C compounds may be accidentally released into the atmosphere; therefore, similar to graphite combustion in an oxygen stream, this may limit the applicability of the pyrolysis method.

Many laboratories have attempted to modernize methods for solidifying gaseous products. As a result, we expect a reduction in volatile radioactive emissions, which reduces their potential impacts on human health and the environment. Such improved procedures, however, require complicated and expensive devices, which are currently unavailable [41].

The main features of the gasification of radioactive waste containing *i*-graphite are summarized in Table 2.

Table 2. Main features of the gasification of radioactive waste containing *i*-graphite.

Advantages	Disadvantages
Simple operation	Carbonate precipitation is required for gases containing ^{14}C -CO ₂
Small amount of solid waste (ash)	Large volumes of solid waste containing radioactive corrosion products, actinides, and fission products are produced
Direct removal of non-radioactive gaseous products	Expensive installations are required for current gasification and solidification procedures

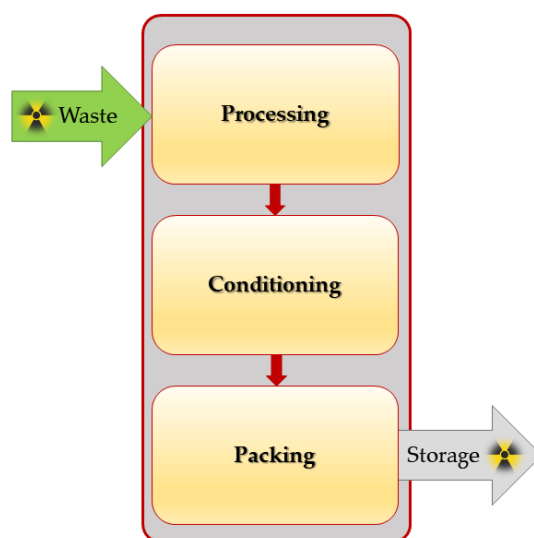
4.2.2. Direct Disposal of Small Graphite Waste

To prepare reactor graphite for treatment and disposal, it is necessary to dismantle the reactor. It has been shown that total dismantling of reactor graphite within about 20 years of the reactor's shutdown may be done with the available technology. However, due to the high radiation activity associated with the material, most of this work must be done with remote-controlled equipment.

Further experiments have shown that it is useful to dismantle reactors later, because the radioactivity decay radiation dose rates of the waste decrease. In addition, in the case of graphite-moderated reactors, doses inside the reactor will decrease over time to a level that permits people entering the reactor, making the use of complex remotely operated equipment unnecessary.

Modern techniques of dismantling nuclear reactors, e.g., of graphite cutting, crushing or simply withdrawing the whole elements are, in principle, the same regardless of the time at which the dismantling is undertaken. They differ only by the extent to which automatization and remote operations have to be used. In the case of reactor graphite, the cores consist of a stack of graphite blocks, and their dismantling should be carried out inversely to their construction. If the use of specialized techniques is not foreseen, channels formed by the holes passing through the blocks, specially prepared for this purpose, are helpful for the extraction of the graphite blocks.

Both whole blocks and small pieces of graphite waste from end-of-life graphite-moderated reactor cores are often highly radioactive. Thus, the resulting parts containing graphite should be grouped based on the emitted radioactivity type and contamination levels. Many countries prefer the method of simple storage of graphite-containing waste packed into properly covered and sealed special casks (called also type B drum packages) [42–45]. To allow for the safe and long-term isolation of graphite-containing vessels from the environment, they should be filled with special hardening mixtures, which are predominantly polymeric conservation agents [46,47]; however, any filling material used for ordinary radioactive waste may also be applied. A diagram of the process is shown in Figure 8.

**Figure 8.** Direct disposal of small graphite waste.

The principles of the disposal of graphite-containing radioactive waste are not significantly different from those used to store non-radioactive carbonic waste. Low-level radioactive waste (whose decay heat is undetectable and whose radioactivity emitted from the isotopes contained therein is 4 GBq/t of alpha activity or 12 GBq/t beta-gamma activity) and intermediate-level waste (being more radioactive than and the heat generated is smaller than 2 kW/m^3) may be disposed of in near-surface landfills. In turn, high-level radioactive waste (sufficiently radioactive to produce $>2 \text{ kW/m}^3$ decay heat and heat its surroundings) requires long-term disposal in deep geological repositories to prevent environmental contamination [48].

In contrast to the gasification of graphite waste, no reduction in volume/weight can be expected during its packaging for storage. In turn, a small increase in mass is often observed, similar to gasification combined with carbonate precipitation.

However, direct disposal methods have a serious disadvantage: if the waste contains a large amount of highly radioactive graphite, it is necessary to prepare large-capacity storage sites to prevent overheating due to the Wigner effect.

With the anticipated disposal of waste containing irradiated graphite such as LLW, it is important to continuously inspect the graphite elements in currently operating nuclear installations to prevent their contamination, since the disposal of contaminated waste is much more difficult and expensive than non-radioactive waste [49].

The main features of the direct disposal of small graphite waste containing *i*-graphite are summarized in Table 3.

Table 3. Main features of the direct disposal of small graphite waste.

Advantages	Disadvantages
Simple method	Requires large-capacity storage sites to prevent overheating due to the Wigner effect
Resistance to leakage	Continuous inspection of graphite elements in nuclear installations to prevent their contamination
Near-surface landfill	

5. Disposal of Spent Graphite-Containing HTGR Fuel

There are currently many methods available for preparing spent HTGR fuel into a form suitable for long-term storage. The method selection should be based on the criteria used for waste storage, ease of removal from the nuclear installation, and efficiency of reducing the mass of carbon in the waste. In such cases, processing the waste into a form acceptable for repositories should also be accompanied by the lowest cost and minimal risk.

5.1. Storage of the Entire Graphite Blocks of Spent Fuel

If one intends to store a whole block of spent HTGR fuel, the most important problem is to use adequate storage. To select the proper storage method, the following issues must be solved:

- (1) what material the protective packaging should be made from,
- (2) the length of the preliminary storage time required before packing the waste into specially designed capsules,
- (3) whether the use of maxi packages is permitted, or the maximum mass of waste in each package.

The volume of the storage containers used for graphite-containing waste must take into account the release of Wigner energy, and the accompanying *i*-graphite temperature increase. On the other hand, if larger containers are used, the unitary price of storage may be expected to be more economical. The answer to the aforementioned questions, based on radioanalytical analyses, allows the determination of whether the storage of blocks of spent HTGR fuel with no pre-treatment is sufficiently environmentally safe and if the storage methods for spent LWR fuel may be applied. If, however, simple waste disposal

is impossible, the waste blocks of spent HTGR fuel may be repacked, placed behind an additional shield, or encapsulated to improve their storage safety.

5.2. Storage of Spent Fuel Blocks with Preceding Removal of Graphite

Sometimes, it is not possible to store entire burnt-fuel blocks in a radioactive waste repository. In such cases, the waste intended for storage should be separated into a fraction coming from the graphite block and the graphite matrix material obtained from the fuel. Then, the processing of spent fuel and the processing of graphite should be considered as separate processes.

For more than 20 years, both in France and the USA, large blocks of spent HTGR fuel have been successively pulled out from reactors using mechanical methods. Since this technique does not damage the fuel coating, it is a promising technology [6,50].

On the other hand, in the case of small HTGR fuel spheres, graphite-containing pellets are generally removed by applying an electric field to the fluids that fill the reactor [51]. Because fuel particles are known as the most robust nuclear fuel, because they cannot melt in a reactor and can withstand extremely high temperatures [52], generally, they are not damaged in the process of removal. Thus, this method seems to be useful; however, it will require more time and work before it is more widely used [53].

Once spent HTGR fuel is withdrawn from the reactor, it may be processed by combustion. As a result, the fissile materials and/or actinide fission products are obtained as solid wastes. Thus, by burning the carbonic shell of fuel spheres, reusable metals and fission products may be either reprocessed or stored in a repository.

As for any graphite-containing waste, HTGR fuel combustion generates graphite (mechanically separated before pyrolysis) and gaseous carbon dioxide. Under unfavorable conditions, they may be contaminated by fission products due to fuel burn-up. If the contamination level is low enough, carbonic waste can be treated as ordinary LLW. On the other hand, if a significant number of long-living radionuclides are found, the carbon dioxide stream should not be released into the environment. After carbonate precipitation, such solid waste may be directed to a high-level radioactive waste (HLW) repository. However, these calcium (barium) carbonates, from a technological point of view, are significantly different from spent nuclear fuel. Since they have much lower heat removal indices when placed in storage drums, carbonate waste does not require additional heat shields; thus, much larger barrels can be used.

In summary, the storage method for radioactively contaminated nuclear HTGR fuel must be separated into carbonaceous and metallic fractions by mechanical or incineration methods. In both methods, storage of the removed graphite or solidified ^{14}C -carbon dioxide requires techniques specific to the type of radioactive waste. Thus, storage with preceding graphite removal is more expensive and riskier from an ecological point of view than storing entire graphite blocks.

5.3. Disposal of Fuel Combined with Actinides Recovery

The term chemical utilization of spent fuel matrix is often used to describe a set of conventional methods leading to the recovery of uranium, plutonium, and/or thorium from spent nuclear fuel. Spent HTGR fuel, after removing the carbonaceous core, may then be separated into non-reusable fission material and material containing minor actinides (Pu, Np, Am, and Cm), which can be separated and reused. To do this, any method known in the nuclear fuel cycle may be applied.

In summary, this method may be used only when waste is expected to contain a significant mass of recyclable components. It also requires significant developmental work to be used successfully. For example, many laboratories are working on adapting novel, effective extractants or modifying existing ones.

5.4. Decomposition of Spent Spherical Nuclear Fuels

The first stage of any process for spherical spent HTGR fuel is the decomposition of its graphite matrix and withdrawing carbon-coated fuel microspheres. Graphite crushing or combustion are commonly used for this purpose.

5.4.1. Mechanical Graphite Crushing

This is one of the most important methods for treating spent HTGR spherical nuclear fuel. Various crushing or milling techniques can be used to destroy fuel coatings and separate graphite. For this purpose, jaw and impact crushers, abrasive and ball mills, and many others have been tested. Some have already been used on a pilot scale, but it is difficult to obtain a high crushing/grinding efficiency, and large amounts of dust are generated [25].

It is proposed that the obtained crushed graphite is subsequently subjected to thermal treatments, and the fuel cores are stored as obtained.

5.4.2. Combustion of Graphite

Both the USA and Germany have tested combined grinding and combustion methods, followed by the dissolution of the crushed residues in aqueous acidic solutions and then the separation of uranium and thorium via the tri-n-butyl phosphate-based THOREX process process. In 1980, in an experiment carried out as a part of the solvent extraction studies under control of the SEPHIS-MOD4 simulation program (Oak Ridge National Laboratory, USA), the THOREX process achieved a plutonium recovery efficiency of 91% (extraction), 96% (partitioning), and 82% (scrubbing) [54]. Uranium recovery, however, appeared to be unsatisfactory, but this method was considerably developed later.

After that, in the Forschungs Zentrum Jülich (Germany), combustion in an oxygen stream was tested in a fluidized bed installation. No special care for the release of $^{14}\text{C-CO}_2$ was taken during combustion. An acceptable result was obtained and about 11,000 spheres of fresh fuel (about 2.2 Mt) were processed by milling and burning at a rate of about 14 kg/h [10].

Considering the potential radiotoxicity of waste obtained by this method, work is still ongoing to improve the actinide recovery. At the same time, due to additional limitations of the method due to the release of waste flue gases, it barely meets the criteria required for its approval [10].

5.4.3. Electrochemical Methods

Each of the aforementioned methods has its own shortcomings. Mechanical crushing methods may destroy the graphite matrix, and subsequent contamination by highly radioactive bare spent fuel microspheres. In contrast, combustion methods may release large amounts of waste gas (containing $^{14}\text{C-CO}_2$), which must be, in addition to the combustion process, absorbed in scrubbers filled with alkaline solutions [55].

To overcome these problems, a group from the Institute of Nuclear Energy and New Technologies (INET, Tsinghua, China) has proposed the use of a pulsed current with a nitrate solution as an electrolyte. The reaction conditions are mild, and the coated particles are not damaged [56,57]. The proposed process requires exposing the processed elements to short-lived, high voltage, high-intensity pulses (from 200 to 500 kV), and/or discharge currents from 10 to 20 kA. In the presence of water, each impulse (several kJ), creates an electric arc on the material's surface. This penetrates the material exposed to electricity and, due to its high energy transfer and short time, forms pores with diameters $<10\ \mu\text{m}$ and heats them to about 10,000 K. Under such extreme conditions, large items exposed to electrical impulses are crushed into smaller fragments. If the electric arc does not penetrate deeply enough, the electric energy is converted into mechanical energy, which spreads in the bulk water in the form of a shockwave, resulting in a similar grinding effect. The impulse method is expensive, requires difficult process conditions, and advanced equipment [58]. In addition, if the pulse method is applied to TRISO

fuel, due to corrosion, such pulses may damage the carbonic coating and form secondary radioactive waste [59].

It was found that ammonium nitrate was the most promising electrolyte [60].

6. Decontamination of Graphite Elements

There are three types of elements made from graphite in high-temperature reactors that, if contaminated, should be cleaned:

- ✓ fuel blocks,
- ✓ solid neutron reflectors,
- ✓ neutron moderators.

All decontamination procedures must be carried out to retain the functionality of the graphite elements and allow their reuse. The choice of decontamination method and decontaminants should take into account the porosity of the graphite surface and the increased penetration of the contaminants inside the material resulting from the erosion of the graphite surface during decontamination.

Graphite elements can be decontaminated several times, but the frequency of maintenance operations should be carefully controlled and defined based on radiometric analyses and computer simulations. The most effective decontamination methods are electrokinetic processes, which allow the removal of mobile radionuclides from pores using an electric field. These methods are well known in civil engineering, e.g., for dechlorinating metal structures (such as bridges).

Decontamination also reduces the mass of graphite-containing radioactive waste, as only a part of the items remain radioactive.

In turn, decontaminating the graphite forming the HTGR fuel and activated in the neutron stream does not appear to be beneficial.

7. Conclusions

Irradiated nuclear graphite, as well as radioactive waste containing graphite components, are difficult to handle. Graphite blocks from Magnox or AGR reactors are huge and heavy, and therefore represent a serious problem for operations typically used to treat radioactive waste. In many cases, nuclear graphite is combined with other materials—metallic or ceramic—which make it significantly difficult to recycle. The greatest challenge is related to the contamination of irradiated graphite by long-lived radioisotopes such as ^{14}C , ^{36}Cl , and ^{60}Co , and the possible emission of radioactive gases. As in the case of other radioactive waste containing long-living isotopes, this is associated with the public fear of processing and long-term disposal of these materials. Hence, there is a lack of social acceptance for facilities such as deep geological repositories.

While there is no uniform approach to graphite waste treatment, many countries have implemented treatment and disposal methods and established practices to deal with this waste. Researchers have devoted significant attention to graphite waste and graphite-containing fuel elements. Our analysis of the existing literature on irradiated graphite generated during the fuel cycle and spent HTGR fuel led to some specific conclusions:

- ✓ Currently, there is no universally accepted procedure that meets the criteria imposed for storing radioactive waste and for handling waste gases generated during graphite processing.
- ✓ The most accepted, perhaps the most satisfying, and certainly the cheapest method is to withdraw entire blocks of spent fuel and store them for a sufficiently long time.
- ✓ To obtain graphite that can be stored as LLW waste, the main task is to separate it from fuel elements.
- ✓ To separate fuel from graphite by physical methods or the combustion of radioactive contaminated graphite, e.g., by ^{14}C , the main problem is its precipitation as carbonates.
- ✓ Waste treatment in connection with the dissolution of fuel elements may be performed when the recovery of some of the fuel components is expected.

- ✓ Special attention should be given to the release of Wigner energy in the form of heat by graphite. This effect, if it is too intense, may cause the self-ignition of the waste.

Solving the problems related to irradiated graphite is important both for countries facing the decommissioning of old reactors containing graphite components and for those who decide to implement new graphite-based technologies, such as HTGR.

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