Proceedings of the 4th International Topical Meeting on High-Temperature Reactor Technology
HTR2008
September 28 - October 1, 2008, Washington D.C., USA

HTR2008-58280

CARBOWASTE: New EURATOM Project on 'Treatment and Disposal of Irradiated Graphite and other Carbonaceous Waste'

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Abstract

A new European Project has been launched in April 2008 under the 7th EURATOM Framework Programme (FP7-211333), with a duration of four years, addressing the 'Treatment and Disposal of Irradiated Graphite and other Carbonaceous Waste (CARBOWASTE)'.

The objective of this project is the development of best practices in the retrieval, treatment and disposal of irradiated graphite & carbonaceous waste-like structural material e.g. non-graphitised carbon bricks and fuel coatings (pyrocarbon, silicon carbide). It addresses both legacy waste as well as waste from future generations of graphite-based nuclear fuel.

After defining the various targets for an integrated waste management, comprehensive analysis of the key stages from in-reactor storage to final disposal will then be undertaken with regard to the most economic, environmental and sustainable options. This will be supported by a characterisation programme to localize the contamination in the microstructure of the irradiated graphite and so more to better understand their origin and the release mechanisms during treatment and disposal.

It has been discovered that a significant part of the contamination (including ^{14}C) can be removed by thermal, chemical or even microbiological treatment. The feasibility of the associated processes will be experimentally investigated to determine and optimise the decontamination factors. Reuse of the purified material will also be addressed to close the 'Graphite Cycle' for future graphite moderated reactors. The disposal behaviour of graphite and carbonaceous wastes and the improvement of suitable waste packages will be another focus of the programme.

The CARBOWASTE project is of major importance for the deployment of HTR as each HTR module generates (during a 60 years operational lifetime) about 5,000 to 10,000 metric tonnes of contaminated graphite containing some Peta-Becquerel of radiocarbon. It is strongly recommended to take decommissioning and waste management issues of graphite-moderated reactors already into account when designing new HTR concepts.

Project Objectives

The objective of this project is the development of best practices in the retrieval, treatment and disposal of irradiated graphite (i-graphite) including other i-carbonaceous waste like structural material made of graphite or non-graphitised carbon bricks and fuel coatings (pyrocarbon, silicon carbide). It addresses both existing legacy waste as well as waste from graphite-based nuclear fuel resulting from a new generation of nuclear reactors (e.g. Very/High-Temperature Reactors (V/HTR)). After defining the various targets (end points) for an integrated waste management approach, analysis of the key stages of the road map (i.e. from in-reactor storage to final disposal) will then be undertaken with regard to the most economic, environmental and sustainable options. This methodological approach will enable users to select the most appropriate options to meet their specific criteria and considerations. Emphasis will therefore be given to legacy i-graphite as this currently represents a significant problem that will have to be addressed in the short and medium term.

Some countries are beginning to evaluate strategies and develop options for the identification, retrieval, treatment and final disposal of this waste. It is important that this project takes account of them and assimilates their considerations against appropriate end points. The project unites organisations from most EU member states being faced with a need for i-carbonaceous waste management and South Africa, which is entering into the deployment of graphite-moderated High-Temperature Reactors.

It has to be recognised that the public perception of nuclear energy is strongly influenced by the issue of long-lived radiotoxic waste. The waste issue is sometimes regarded as “the Achilles Heel for nuclear fission” and has not been well managed in earlier generations of gas-cooled reactors (Magnox, AGR, UNGG, HTR) and in other graphite-moderated reactors such as RBMK or in Materials Test Reactors (MTR) as well as in early production reactors, resulting in a lack of suitable facilities both for any treatment or final disposal of radioactive carbonaceous waste. Irradiated and contaminated graphite from reactor moderators and reflectors or thermal columns, and other related carbonaceous materials, represent the greatest volume of waste materials from these reactors. To date, about 250000 metric tonnes have been accumulated, worldwide.

The specific problem about the group of i-carbonaceous waste stemming from the structures of the core is the varying content of long-lived radioisotopes like radiocarbon (^{14}C), chlorine (^{36}Cl), iodine (^{129}I), technetium (^{99}Tc), selenium (^{79}Se), caesium (^{135}Cs) etc. resulting from activation processes under neutron irradiation. Therefore, this type of waste is handled as Intermediate- or Low Level Waste (ILW or LLW), depending on national classifications. Burning i-graphite might be an alternative to the disposal option but will most probably not be politically accepted due to the radiocarbon releases to the environment if not separated or reduced in the exhaust gas. Recycling or reuse of treated i-graphite in the nuclear industry might be a preferable new option to minimize waste streams for disposal. Irradiated graphite from the fuel element might even contain contamination by fission products and request special treatment.

The CARBOWASTE consortium regards the present unsatisfactory status in this waste disposal area as an opportunity to build upon previous work, to review technological advances and innovative ideas which have arisen in more recent years, and thus to identify the most technologically appropriate, environmentally sustainable, and cost-effective procedures, at all stages in the treatment and disposal of all types of carbonaceous wastes.

The previously employed procedures are not necessarily appropriate for the future. The special character of i-graphite wastes can lead to problems such as electrochemical corrosion and the potential leaching of long-lived isotopes if they are handled by the standard methods thought appropriate for other wastes. A special issue arises from the fact that radiocarbon (^{14}C) has to be safely isolated from the biosphere due to its biocompatibility. Stored Wigner-Energy is another concern which has to be addressed.

Within this project, five principal investigations will ensure that the best-available and most environmentally acceptable technologies are identified in the following areas:

- An integrated waste management approach being compatible with ecological, economic and socio-political requirements to be elaborated in Work Package 1 (WP1),
- retrieval procedures which might affect the nature of the waste (e.g. wet or dry) as well as the radiological and core integrity effects of retrieval over a range of time horizons. Methodologies for separation of coated particles from the fuel matrix, in the special case of V/HTR spent fuel (WP2), will also be considered,
- characterising and then identifying suitable treatments for the carbonaceous wastes for removal of volatile and long-lived radioactive contamination (WP 3 & 4) associated with in-depth scientific investigations on microstructures and localisation of contamination including related analytical modelling,
- elaboration of appropriate options for re-use and recycling of the graphitic materials, together with assessment of alternative options to bulk disposal in repositories (WP 5),
- investigations and further research and analysis on the disposal behaviour of i-carbonaceous wastes (WP 6).

These activities will be accompanied by a qualitative economic analysis and an assessment of environmental impact via Multiple Criteria Decision Analysis (MCDA) for all selected processes and comparison against actual best practices taken as reference cases. Representative legacy waste samples will be selected from different countries and different reactor types (MAGNOX, UNGG, AGR, RBMK, MTR, HTR) to enhance the relevance of the project for those countries having already accumulated significant amounts of i-carbonaceous waste.

The project is expected to assist in the identification of safe and economical waste management practices. It will also provide a better physico-chemical understanding of the structure and structural changes of i-graphite as well as the location of radioactive contamination before and after treatment. This will allow to optimisation of the treatment and conditioning procedures, in a laboratory scale and to provide a knowledge base for entering into a scale-up for pilot plants and subsequent commercial application.

This project is truly 'cross-cutting' as it addresses different types of former and existing reactors whilst also considering future reactor designs of V/HTR and MSR (Molten-Salt Reactors). This consideration concentrates on the waste management issues surrounding the decommissioning of graphite-moderated reactors and the disposal of redundant i-graphite. In addressing the decommissioning and disposal issues due regard to radiation protection is necessary, too.

Progress beyond the state-of-the-art

Recent discoveries on the nature of contamination in i-graphite point to the possibility of a leap in scientific knowledge and i-graphite treatment and/or disposal. CARBOWASTE takes this forward into a new approach by integrating leading edge science, technology and engineering with economic, environmental and social considerations. This approach has not been employed in previous i-graphite waste management activities and may explain why a significant quantity of legacy graphite from various reactors is still residing in reactor buildings or intermediate storage of Magnox, UNGG, RBMK, HTR and MTR.

It must be noted that graphite-moderated reactors belong to the very first generation of nuclear reactors which consequently are facing decommissioning, together with other early reactor types. Therefore, a high priority and acceleration must be given to the adequate management of associated legacy waste and the related research.

Recent reviews of the world status pertinent to i-graphite have been published by IAEA and EPRI [Refs 1-6]. A general challenge is to find common denominators due to:

- Lack of commonality of design and graphite grades between different reactors and types;
- Different operational characteristics of individual reactors;
- Diverse status of policy, strategy and regulation between member states;
- Local specifics for waste management systems and repositories.

In Europe, the industry's experiences to date mainly cover the decommissioning of small-scale reactors (e.g. GLEEP, WAGR) that are a fraction of the size of commercial reactors. However, the experience gained from these activities will be of value in this project as they will provide some in-sight to the problems that need to be addressed. In addition, future reactors should learn lessons from legacy wastes management.

The CARBOWASTE methodical approach to tackling i-graphite waste starts with the development of a road map that will raise major questions/issues at key stages of the map. These questions will not only identify gaps in i-graphite knowledge, but will also highlight the information that is needed to allow sustainable decisions to be made. This road map and critical decision analysis is crucial to the success of this project and has not been used in this arena, previously. The two key major stages of the road map are the current disposition of i-graphite, i.e. in the redundant reactor under decommissioning, and its final disposal. To address the retrieval scenarios modelling of a specific graphite-moderated reactor core will be undertaken and simulated retrieval will be considered using these models. The approach will allow for physical, chemical, radiological and mechanical properties to be changed identifying the potential impact on the retrieval process.

Some Regulators expressed the concern that graphite somehow presents a fire hazard if reactors are dismantled in air; that graphite dust explosibility and the release of adsorbed radioactivity may present a potential problem. Therefore, some utilities (e.g. EDF CIDEN) have taken decisions to retrieve i-graphite, under water, following the Fort StVrain HTR, USA, precedent that also benefited from shielding of gamma-radiation doses from structural materials and dust control opportunities. On the other hand, not all reactor designs are suitable for underwater dismantling and recent EPRI research has added confidence to the un-reactive nature of graphite [Ref. 7].

For similar reasons, graphite structures of the German AVR are currently grouted, in-situ, and placed disposed together with the pressure vessel in a special interim storage until more appropriate conditioning and disposal methods are available.

It is self-evident that the retrieval processes have a strong impact upon the physical & chemical state of the material (e.g., wet, dry or grouted). Thus, retrieval methods need to be chosen in conjunction to the treatment and disposal methods to find optimal solutions. In addition, the retrieval options need to be engineered into future reactor designs (e.g. weight of water filled into the pressure vessel).

I-Graphite Management Options

Graphite wastes normally contain the long-lived isotope ^{14}C and frequently also the very long-lived isotope ^{36}Cl arising e.g. from processes designed to remove heavy metal impurities during manufacture and/or residuals in the virgin material. Other radioisotopes arise from the activation of the impurities and also through the transport of material such as metal oxides from other parts of the reactor circuit. Activation calculations are often poorly predictive for several radioisotopes (e.g. ^{3}H, ^{14}C, ^{36}Cl etc.). Therefore, better characterisation of virgin and irradiated graphite needs to be made by microscopic examination. The resulting experimental data will contribute to the validation of new codes describing the origin and location of the contamination for various graphite grades.

More recent scientific studies give evidence that there could be two mechanisms for the creation, adsorption and retention of ^{14}C on/into the graphite matrix. Most ^{14}C (except of the fraction being formed from ^{13}C) does not appear to be integrated into the graphite crystal lattice but only bound on the surface of graphite crystallites and pores after neutron activation of ^{14}N and ^{17}O. The position for ^{36}Cl requires clarification. Better understanding of the 'contamination cycle' will have a strong impact on the development of innovative purification processes for i-carbonaceous wastes. It will also support improved graphite manufacturing and operational practice for future V/HTR to minimize the creation of long-lived contaminants.

First experiments at FZJ [Ref 8] and with GLEEP graphite in UK show that it seems to be possible to selectively remove loosely bound ^{14}C from the ^{12}C matrix to a large extent either by thermal treatment or by partial chemical or microbiological corrosion of graphite where the inner graphite surface is attacked.

These results strongly support the need to test different decontamination processes to extract mobile fractions of contamination thereby transforming ILW into LLW and enhancing the safety of a final repository for i-graphite. Thermal processing will also contribute to the removal of any Wigner energy present. Best practice i-graphite management options need to take account of achievable decontamination factors.

If the treatment/purification processes are effective, improved processes for i-graphite waste management may become available, i.e. recycling and reuse of i-graphite for nuclear purposes. To date, several possibilities have been identified ranging from manufacture of new graphite for use in future V/HTR and MSR to new products like electrodes for vitrification or fully ceramic waste packages (e.g. made of SiC). Benefits include better resistance to corrosion and leaching than present matrices and less generation of hydrogen, in a repository. It is evident that i-graphite could be a perfect base material for new nuclear graphite because neutron poisons have more or less completely been 'transmuted'. In general, there is the potential of developing a set of new products from i-graphite in different fields. Even extraction of ^{14}C could find a market for e.g., medical purposes etc., if separation techniques like PSA and centrifuges are applied.

This new information will require other interrogative systems and more sensitive techniques such as High-Resolution Transmission Electron Microscopy (HRTEM), Electron Energy Loss Spectroscopy (EELS) etc. to probe both at the macro and micro scale. New laboratory procedures/experiments need to be developed. The FIB (Focused Ion Beam) is e.g. a very convenient technique of preparation of thin sections (< 100 nm) for HRTEM, EELS. There is a strong requirement to understand the spatial arrangement of ^{14}C and ^{36}Cl in the graphite matrix as this information will contribute to explaining both kinetic and thermodynamic affects associated with treatment options.

Controlled disposal is the preferred option for most radioactivity materials generated in the nuclear fuel cycle. There are examples where material has undergone recycle, the recycle melting of contaminated steel for producing waste containers or of reactor depleted U is well known. At the time, economics was a major argument for U recycle. This argument could be made for recycling graphite as disposal costs could be off-setting. This project will probe the current accepted disposal option by evaluating recycle options and/or potential uses of i-graphite treated or otherwise conditioned. The radiological implications will need to be carefully balanced whilst the information from the characterisation and treatment studies will be crucial in considering re-use/recycle options.

Even if purification methods will not be applied, data will be provided for long-term behaviour of disposed i-graphite waste as the processes represent quasi accelerated attack of leachants, microbes etc. This gives evidence that contaminants withstanding the purification processes will also not be readily released, during the long period till ultimate decay. Therefore, the project has a dual benefit of both decontamination process validation and disposal behaviour prediction for i-graphite.

In the investigations on the disposal behaviour, the release mechanisms will also be studied in depth as it is important whether it will be via CO_2, CO, complex oxides or organic compounds like hydrocarbons (e.g. methane). Formation of stable metal carbonyls can also occur when CO is contacted with appropriate metals. The transfer into the biosphere will depend on these geochemical phenomena and have to be determined precisely.

Relevance for V/HTR

For V/HTR, specific additional considerations have to be undertaken due to the fact that the moderator is an integral part of the fuel element and because the coated-particles (CP) are directly embedded into the graphite matrix. Figure 1 shows the volume ratios of graphite matrix, coatings and UO_2 kernel, for a pebble fuel element. The situation for block type fuel is not much different.

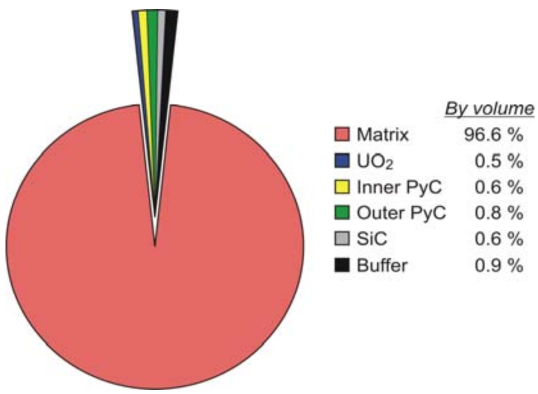

Fig. 1: Volume ratio for HTR Pebble fuel element

These ratios show the principal difference to spent LWR fuel, where the bulk of the High-Level Waste (HLW) for direct disposal are the UO_2 pellets, themselves. Therefore, different disposal and treatment strategies need to be analysed for V/HTR. Figure 2 illustrates the different choices for HTR spent fuel management (e.g. for block type fuel):

- Direct disposal (Path A),
- Separation of moderator and fuel compacts or coated particles (Path B),
- Separation of graphite, coatings and kernels with reprocessing of the UO_2 fuel (Path C).

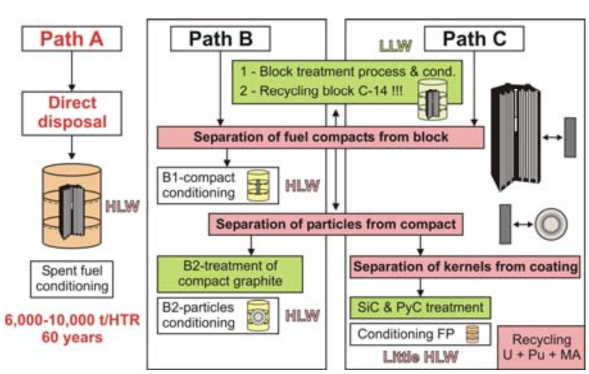

Fig.2: Spent fuel management options for V/HTR

Considerable amounts of spent HTR fuel exist in Germany (~1 Mio. Pebbles) and UK (Dragon) as legacy waste. Direct disposal of the complete HTR spent fuel elements leads to rather high masses of about 6000-10000 metric tonnes over a 60 years operational lifetime of a single 400 – 600 MWth HTR module. This amount of i-graphite can be seen as the 'price' for the large heat capacities of V/HTR cores and the resulting inherent safety of this reactor type.

A significant reduction of disposal volume can be achieved if the spent fuel (coated particles or compacts) can be separated from the matrix and these waste streams being treated either as HLW concerning the CP or as Long-Lived Low-Level or Intermediate Waste (LLW or ILW) with regard to bulk of the moderator graphite. If the UO_2 fuel will be reprocessed another waste stream of carbonaceous waste would arise from the pyrocarbon and SiC coatings.

Reprocessing of spent HTR fuel has formerly been developed in US and Germany based on incineration and mechanical technologies. These combustion processes to extract the coated particles from the HTR fuel element matrix cannot be used anymore in particular due to the release of ^{14}C to the environment. In addition, the mechanical methods like grinding and crushing, which have been investigated and used in the 1970's, lead to a cross-contamination of the moderator graphite with the HLW from the spent fuel particles.

Therefore, future processes have to separate graphite from coated particles without damaging them and without significant contamination transfer. For block-type fuel, methods have to be developed and demonstrated for extracting the fuel compacts from the fuel matrix block. The Idaho National Laboratory (INL, USA) has conducted reprocessing of similar graphite as well as removal of fuel compacts from Fort St. Vrain fuel blocks by remote facilities.

Different processes will be evaluated to perform the separation of coated particles from pebble or compact as ultrasonic pulses, chemical degradation, thermal degradation or pulsed current [see Figure 3]. Exploratory experiments and literature compilations will be carried out to get data allowing to make a first assessment for an industrial deployment and to focus on R&D with the most promising processes.

Several technical options for the removal of coating layers are under investigation which mainly build upon the above-mentioned methods but still have to be adopted for this application. The removal of the coating layers by a Nd-YAG laser was recently demonstrated by the Laser Group in South Africa and are currently repeated in the laboratories of NECSA on PBMR TRISO particles. Experiments will be made with surrogate and irradiated particles to determine the contamination of the fuel coating with regards to further treatment and conditioning.

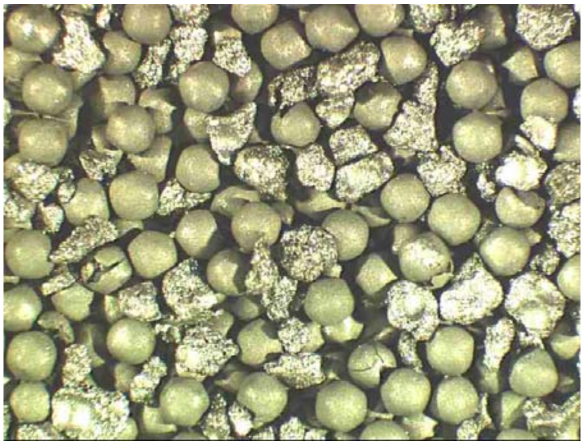

Fig.3: Preliminary segregation tests at CEA

The separated compacts or coated-particles can either be conditioned for direct disposal or further treated to recover the LEU fuel kernels for being fed into existing reprocessing facilities. In that case, the residual coating material needs to be treated and conditioned for disposal or reuse, too.

Conclusions

It is expected that the CARBOWASTE project will provide significant scientific and technical advances also due synergies by multi-disciplinary collaboration within the project and by close communication with potential users of the results. In conclusion, CARBOWASTE is an innovative approach beyond the state-of-the-art on i-graphite treatment and disposal that:

- Develops a solution for integrated waste management;
- Leads to closing of the 'graphite cycle' (recycling) for future reactors;
- Understands in detail the 'contamination cycle', why it arises, how it is contained within the graphite, what are its release mechanisms;
- Understands in detail the interaction of the graphite and its contamination;
- Clarifies mobility and immobility of the various species within the graphite;
- Views graphite as a series of states from initial to final condition so that opportunities can be taken to manage the waste hierarchy;
- Seeks opportunities for safe and fit for purpose disposal solutions;
- Assists predictability of long-term disposal performance by analytical models;
- Develops opportunities for more economic solutions for legacy waste and future use of the material.

Such a rigorous integrated assessment of recycling waste nuclear materials has not been undertaken elsewhere in one single project. Thus, the idea of a 'closed graphite cycle' is a fundamental innovation and may be essential for future graphite-moderated reactors like V/HTR.

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