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Document Title

HTR-N1

Technical Summary Report of WP4- Treatment and Conditioning of HTR-specific Waste

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1 Introduction

The wastes streams arising from the operations and decommissioning of nuclear power stations have been identified. The methods of treating the different types of waste have been reviewed and the advantages and disadvantages assessed. The assessments are primarily presented from the UK waste treatment and disposal perspective, although the approaches proposed internationally are reviewed. In contrast to most of the world where LWR are the mainstream reactor design, the majority of UK experience to date relates to gas cooled, graphite moderated reactors.

The waste streams from HTR reactors are essentially no difference from those from the current generation of LWR nuclear power plants; the main exception being the graphite, in the form of moderator, reactor block and fuel assembly structures. The UK experience with the operation and decommissioning of graphite moderated, gas cooled reactors is particularly important in this regard.

Traditional treatments are considered separately for operational and decommissioning wastes. Emphasis will be placed on those aspects of proposed HTR designs that could result in waste issues that are particular to this reactor type.

The HTR-N1 project compliments the activities recently completed under the HTR-N project. Within HTR-N, WP4 the quantities and characteristics of the waste arising from the whole lifetime of a future HTR project have already been compared with that arising from LWR activities on the basis of the same generated output (Ref. 1). In general the level of activity and volumes of active waste were found to be no more onerous for future HTR designs, the main exception being the additional graphite waste stream for HTR compared with LWR.

2 Deliverables and Documents of HTR-N1, WP4

Deliverable	Title	Document No.
4.0.0	Summary report	HTR-N1-05/02-D-4.0.1
4.1.1	Review of traditional treatments of operational wastes	HTR-N1-04/07-D-4.1.1
4.2.1	Review of traditional treatments of decommissioning wastes	HTR-N1-04/07-D-4.2.1
4.3.1	Conditioning and thermal treatment tests on irradiated HTR graphite	Draft issue received.
4.4.1	Assessment of advantages of conditioning & thermal treatment in each country of WP4	In progress

3 Operational Wastes (Task 4.1)

Operational wastes from typical UK nuclear power stations can be considered to arise from the three sets of activities listed below:

Ongoing power operations

- Gaseous wastes
- Liquid wastes
- Spent ion resins
- Sludges
- Spent filters

Maintenance, giving rise to

- Fuelling machine parts
- Control rod mechanisms
- Gas circulators, including contaminated oils and fluids
- Gas circuit parts

Refuelling operations, giving rise to

- Spent fuel
- Fuel element debris

3.1 Gaseous waste

All operating power stations in the UK have authorisation for gaseous discharge with limits on key radionuclides (e.g. S-35, I-131, Ar-41, C-14 and beta activity).

Gaseous waste will arise from the ventilation of contaminated areas of the station. For gas cooled reactors, purging of the primary coolant circuit as part of reactor return to service

activities and other reactor coolant operations will also give rise to gaseous discharges, CO_2 in the case of operating UK gas reactors.

The gaseous wastes are released to atmosphere after the due process of filtration through HEPA filters and adsorption plant. Significant blowdown is treated to remove any I-131, sampled and analysed before discharge. The primary radionuclides in gaseous form will be tritium, C-14, S-35 and Ar-41. Metallic activation products are present in particulate form. Minor quantities of fission products such as isotopes of krypton and xenon and volatile iodine are also present.

It is difficult to envisage any different strategy for high temperature gas reactors, so that the principles are likely to be similar to those for current UK gas reactors, albeit with variations due to the helium coolant.

3.2 Liquid Wastes

Limits are placed on radioactive liquid effluent similar to the gaseous waste limits described above.

Liquid waste arises from:

- Effluent arising from reactor, fuel route, cooling pond and maintenance operations
- Liquid from reactor coolant gas drying
- Radioactive oils (e.g. circulator lubrication).

Generally, it has been found that fission products are not present in gas reactor liquid effluent.

Active effluent is filtered and then stored in delay tanks after the oil has been separated off. Samples are taken before discharge. Water from the CO_2 driers goes to the tritiated water storage tanks before being discharged after sampling via the same route as that used by the effluent.

Oils and organic fluids are expected to be LLW. They are retained in a storage tank before being eventually burned. For HTR designs with circulators using magnetic bearings it is anticipated that there will be less oily wastes.

3.3 Solid Wastes

The treatment of the following operational solid active waste streams are detailed in the main part of the report:

- Spent Ion exchange resins
- Sand
- Sludges
- HEPA filters
- Adsorption materials
- Fuel stringer (or element) debris
- Miscellaneous contaminated items

- Miscellaneous activated items
- Filter dust
- Desiccant
- Miscellaneous and trash LLW
- Decontamination arisings
- Spent fuel

With the exception of Spent fuel the above solid waste streams result in LLW and ILW waste. The LLW waste will be encapsulated in cement grout in approved containers and sent to Drigg for shallow land burial. The ILW waste will be stored in dry vaults designed as part of the reactor bioshield. During decommissioning (reactor dismantling) the wastes in the vaults will be treated like other ILW waste arising from decommissioning.

In the UK, gas reactor spent fuel is discharged from the reactor by the fuelling machine. The fuel is then held in ponds before being put in transport flasks and sent to Sellafield for reprocessing. Approximately, 3% of the spent fuel volume, when reprocessed, is high level waste (HLW). The treatment is currently to vitrify at Sellafield and place in a purpose built above ground store for 50 years, to allow for cooling. The treated waste will then be deposited in a UK repository, when this becomes available.

In UK AGRs (advanced Gas-cooled Reactors) the fuel stringer debris consists of miscellaneous activated components from refuelling operations. A graphite outer sleeve and graphite reflectors are included in the stringer design. Unlike proposed HTR designs, none of the graphite is integral with the fuel and hence it is easily separable. In the UK, the fuel stringer debris, including graphite components, will be stored in station vaults before being treated as other solid ILW waste during decommissioning.

For HTRs it will be necessary to develop a strategy for the disposal of the spent fuel that is embedded in the large amount of graphite serving as moderator and structure of the fuel elements. Direct disposal of the complete HTR fuel elements leads to rather high masses (typically 6000 tonne per HTR) of HLW. This can only be reduced if the coated particles of spent fuel are separated from the graphite matrix. Follow on work developing HTR technology might usefully research the methods and strategies for fuel / matrix separation.

4 Decommissioning

The principle wastes arising during decommissioning are steel, concrete and graphite. Both steel and graphite wastes can also occur during operations but concrete wastes are likely to arise exclusively from decommissioning. Within the UK, the electricity utilities have a policy of long term safestore for graphite reactors. The reactor internals will not be dismantled for 85 years. The advantage of such a delay is that radioactive decay will greatly simplify the dismantling and some components categorised as ILW at the time of shutdown will be re-categorised as LLW. Graphite wastes are an additional wastestream compared to existing mainstream LWR designs so carbonaceous wastes are condsidered separately below (section 4.2).

4.1 Methods of Treatment for Non-Carbonaceous Decommissioning Wastes (Task 4.2)

Steel and concrete wastes will arise from decommissioning of all reactor types. Steel and concrete wastes can be free release, LLW or ILW. The LLW and ILW wastes can be either activated or contaminated. The treatments for LLW and ILW will usually be similar, except that LLW wastes will be sent to Drigg for near surface burial, whilst ILW will be optimally packed in NIREX approved containers and encapsulated in cement. The containers will be stored locally awaiting the availability of the UK ILW repository. Free release steel is sold off for scrap in the open market.

The treatments, or in most cases given the relatively few nuclear power stations that have been decommissioned, the proposed treatments for steel and concrete have been extensively researched. The methods assessed in the main report for the treating of contaminated steel are: high pressure water jet, basic mechanical decontamination, heat treatment for the release of tritium, chemical decontamination, shot blasting, smelting and strippable coatings.

For contaminated concrete the methods are all based on the removal of the outer layer of contamination that extends for upto 70 mm into the concrete. The methods of treatment considered for decontamination are: high pressure waste jetting, dry mechanical scabbling, microwave scabbling, laser scabbling, electrical heating of reinforcing bars, concrete shaving, dry ice jetting, insoluble wet abrasive jetting and chemical leaching.

The advantages and disadvantages identified in the main report for each of the steel and concrete decontamination methods will generally be applicable for all types of reactor, although for direct cycle machines, e.g. BWR and designs proposed for HTRs, there will be additional active wastes arising from the decommissioning of turbines and power circuits.

4.2 Methods of Treatment for Carbonaceous Wastes (Task 4.3)

The treatment of graphite wastes for decommissioning is likely to be similar to the approach taken for the treatment of such wastes that arise during operations (assuming that HTR fuel assembly graphite will be separated from the coated fuel particles). Such waste is likely to be both LLW and ILW waste and can either be activated or contaminated. The treatment and eventual disposal of graphite benefits from a period of safestore so not many graphite moderated reactors have been fuly decommissioned. The Fort St Vrain and the WAGR are the only large graphite moderated reactors that have been dismantled to date. The AVR is about to be dismantled.

Due to the large number of graphite moderated reactors in various countries around the world, there are various schemes for the treatment and disposal of the active graphite waste. The methods being proposed by each country are presented in the main report. The advantages and disadvantages of each proposed treatment were considered as part of this work package but no sensible method has emerged that combines both decontamination and volume reduction. The following ideas have been assessed:

- Raw Storage – temporary or as safestore,
- Encapsulation –in cement grout, polymer, bitumen, resin sand and vitrification.

- Densification – an emerging technology that might be achieved by electrolytic or chemical means.
- Incineration – would require the capture of ^{14}C (could use a CaOH solution and use the carbonate formed as backfill material in a repository).
- Pyrolysis – would require the capture of ^{14}C as for incineration,
- Transmutation – currently based on theory, no practice yet for graphite,
- Recycling

All countries belonging to the European community have accepted a moratorium on sea dumping, effectively since 1984, so this was not considered further as part of this study.

With incineration and sea-dumping being perceived by the public as unacceptable, only two methods remain that are at a mature stage in their development – raw storage and encapsulation in cement type grout. The latter option is favoured by the UK. These neither reduce the contamination nor reduce the volume of the waste. Consequently, experimental work has been undertaken as part of this task using a thermal technique that has the potential to remove radioisotopes from the graphite matrix including a significant proportion of the ^{14}C. The gasification of carbon in the form of CO and then the precipitate in carbon form over a metal catalyst has also been investigated providing the possibility of carbon recycling. The findings of the experimental work at Juelich for the purification of graphite (Ref. 2) is detailed below in section 5.

5 Tests on the Purification/ Conditioning of HTR Reflector Material (Task 4.3)

At the end of the HTR life, structure graphite contains significant quantities of radionuclides and requires management for eventual disposal or reuse. As a solution it is proposed to decontaminate graphite by gasification with steam in an inert atmosphere. Gasified graphite will be separated later from volatile radionuclides by a chemical off-gas treatment. In order to enrich ^{14}C in a separated off-gas stream based on the mass difference, possible methods are under discussion. However, such enrichment has not been investigated experimentally as part of this study. Non-volatile radionuclides should stay in solid residue. Carbon monoxide can be precipitated in carbon form over metal catalysts (Fe, Ni, Co).

For investigation of the graphite oxidation in water, steam experiments with graphite powder from the AVR reflector were performed at different temperatures and saturated water vapour pressures. 0.5g of graphite powder were reacted almost completely (96 % mass loss) in 3.5 hours at a temperature of 1180°C and a saturated water vapour pressure of 1 atm (Figure 4.2). Ratio of reaction products in the gas mixture is CO/CO_2 ~4. At temperatures less then 850°C graphite oxidation hasn't been observed.

The equipment for graphite oxidation was built into a glove box (Figure 4.1). It consists of two ovens, a vessel with argon, a water steam-generator and washing bottles (one with 0.1 HNO_3 for trapping ^{3}H and two with 4M NaOH for trapping ^{14}C). The second oven contained the catalyst CuO for complete oxidation of CO to CO_2.

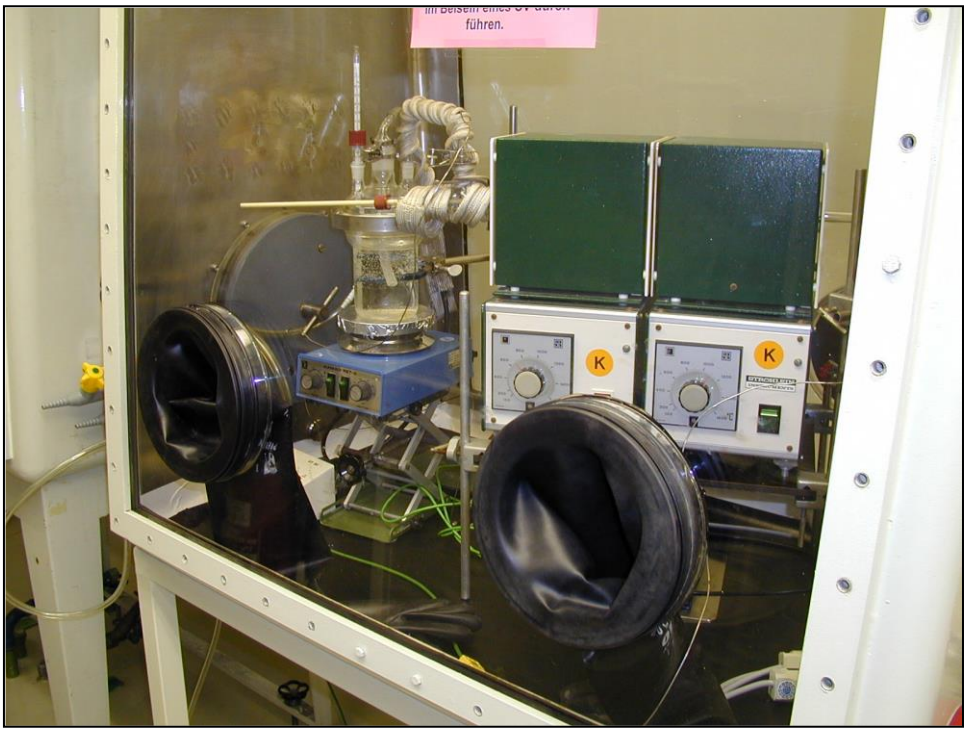

Figure 4.1: Thermal reactor for graphite treatment in a glove box

In order to investigate the complete process of graphite calcination, cleaning and precipitation, the following experiments with contaminated graphite from Merlin thermal columns have been performed. A graphite sample has been settled in horizontal reactor tube and flown with argon and water steam mixture with successive heating up to 400°C - 800°C - 965°C - 1055°C.

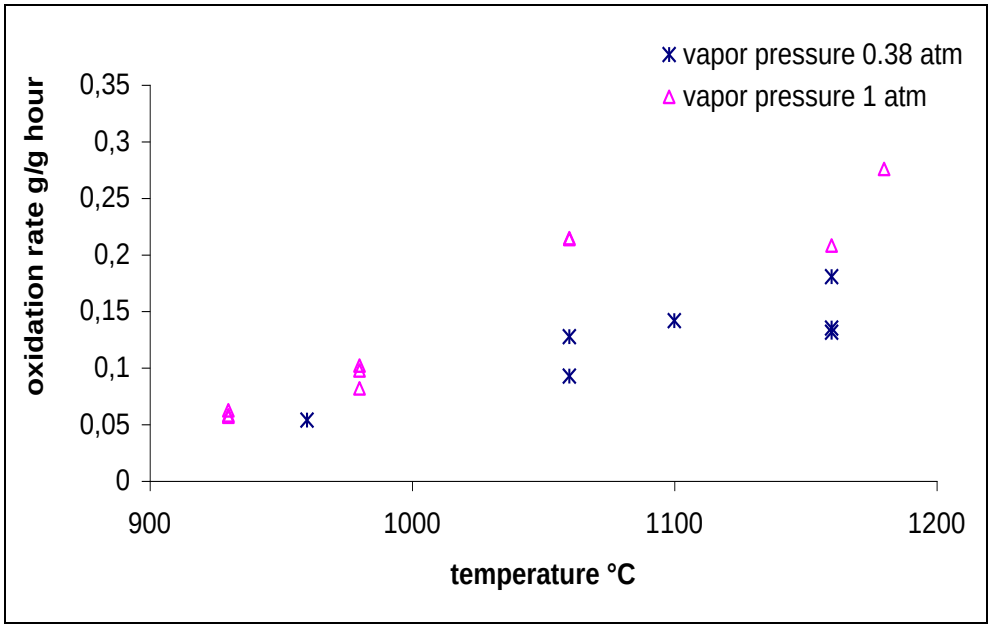

Figure 4.2: Oxidation of graphite under water vapour

During this procedure ^{3}H and ^{14}C release has been observed (preliminary content of these radionuclides in the graphite sample was determined by incineration of graphite in oxygen). The experiment at fixed temperatures lasted 5 hours from the moment when the furnace was heated up to the required temperature. Sampling from washing bottles was made every hour and then probes were analysed by Liquid Scintillation Counter. The ^{14}C and ^{3}H release are presented as Figure 4.3 and 4.4.

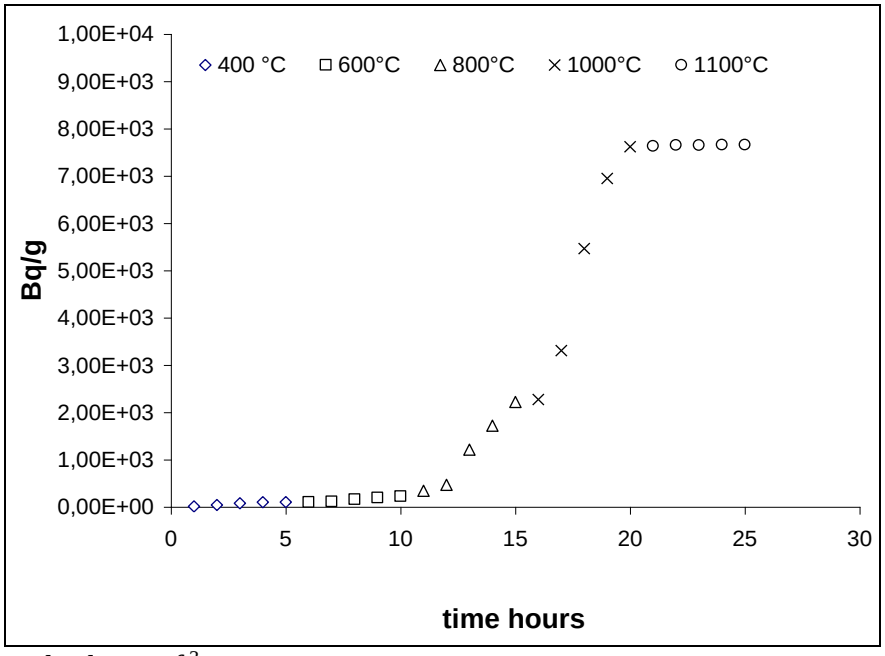

Figure 4.3: Total release of ^{3}H

^{3}H starts to release at 400°C in small amounts, the rate increasing with further increases of temperature. In order to determine the amount of tritium chemically bound to graphite it is proposed to carry out experiments in an argon atmosphere at 400°C for a longer time period (10 h).

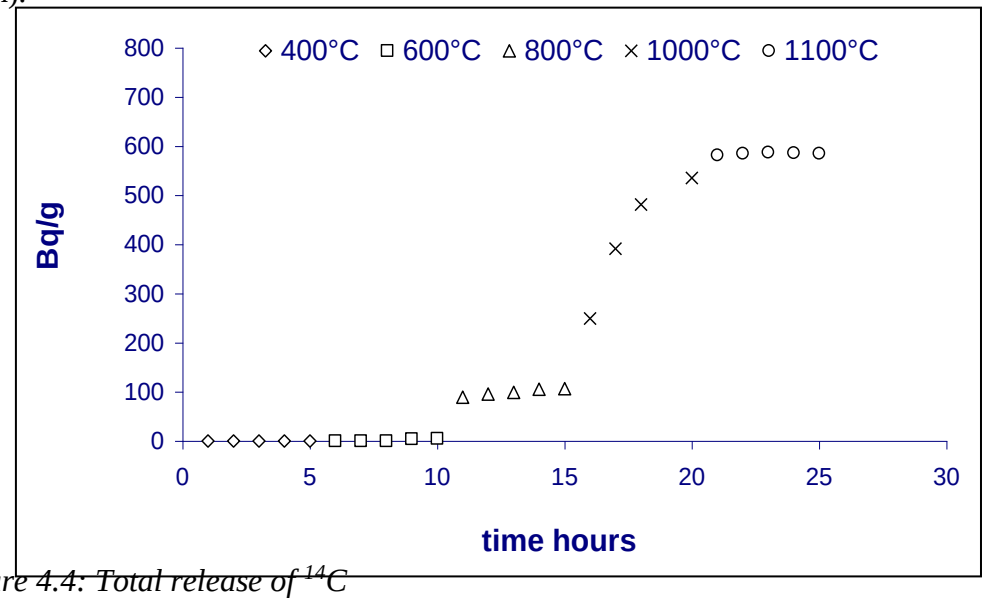

Figure 4.4: Total release of ^{14}C

^{14}C starts to release at 800°C and stops at approximately the same temperature as for tritium. The amount of tritium and ^{14}C released in the experiments described above corresponds well to the total graphite inventory. The Figure 5 shows the release of ^{14}C and the mass lost of the graphite sample, which is equal to the ^{12}C release, at a constant temperature of 1060°C. It can be seen that the release of ^{14}C decreases with time whereas the mass lost is linear.

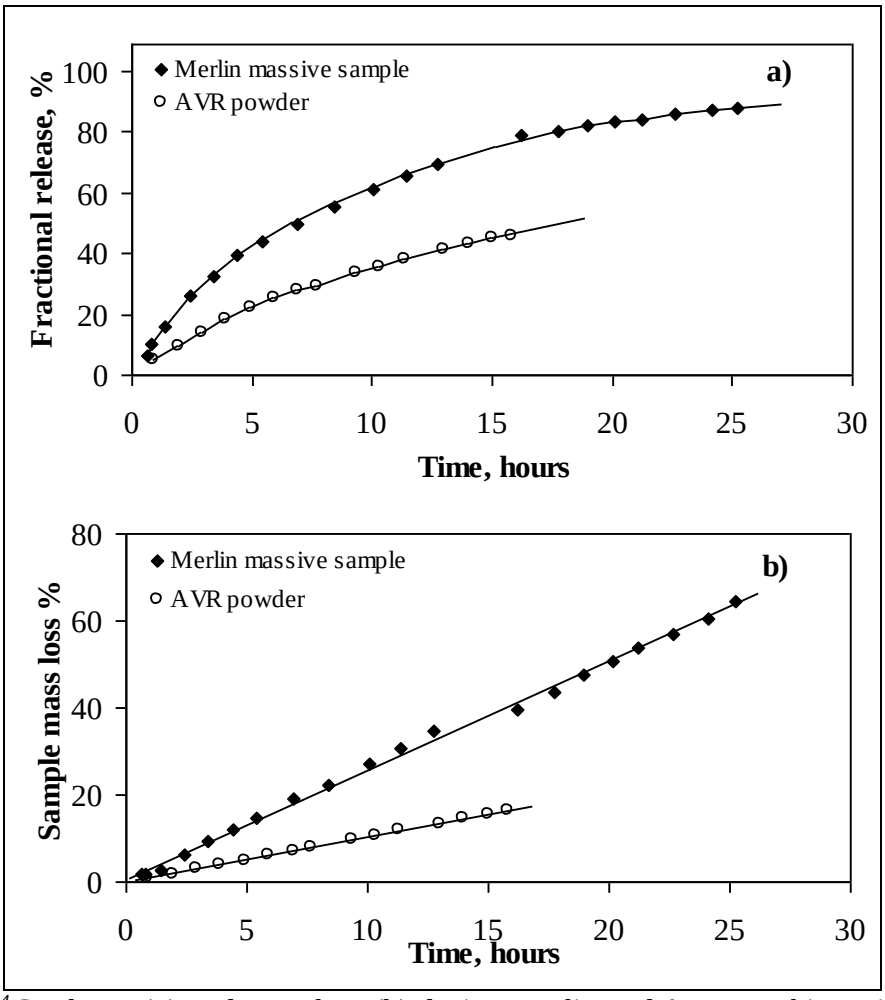

Figure 4.5: ^{14}C release (a) and mass loss (b) during Merlin and AVR graphite oxidation with water steam (water vapor pressure 2.3 kPa)

This interesting effect is related to the preferential release of ^{14}C in comparison to ^{12}C during the thermal treatment which can be seen better in the Figures 4.6 and 4.7. Obviously, we have fast desorption of ^{14}C from the surface. Later at higher temperatures, when graphite oxidation takes place, ^{14}C is released from matrix together with ^{12}C. The highest $^{14}C/^{12}C$ ratios are obtained in an inert atmosphere but with a low total yield of ^{14}C. The oxidation in the steam atmosphere increases the ^{14}C yield but with a decreased $^{14}C/^{12}C$ ratio.

Based on these results a patent was applied for the decontamination of graphite based on the thermal treatment. However the process has to be optimised with respect to the separation ratio and total yield before technical application.

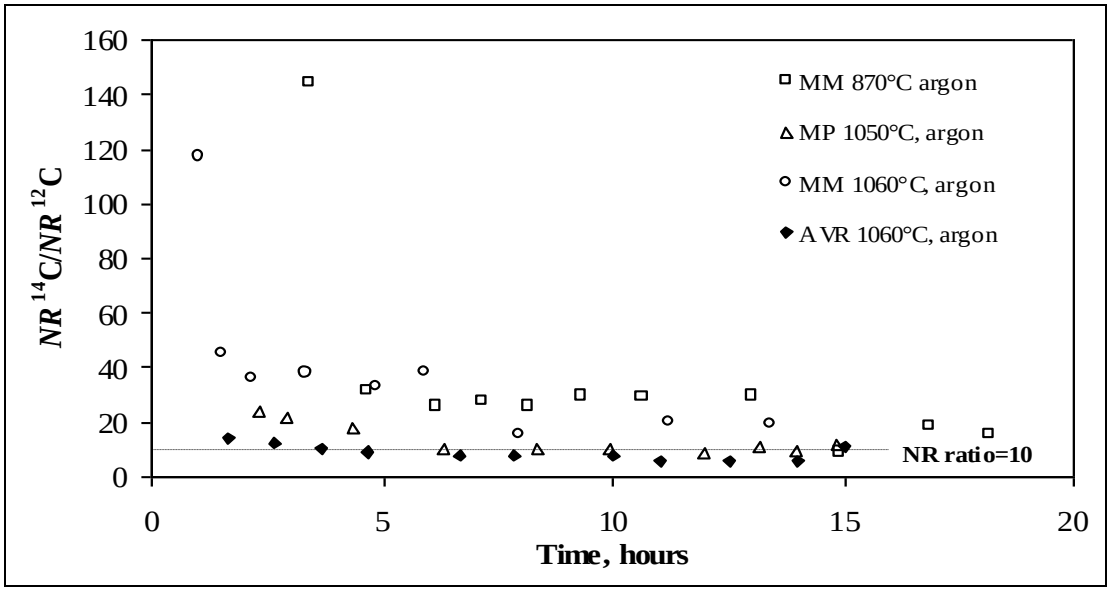

Figure 4.6: Ratio of normalised release rates during the thermal treatment in an inert atmosphere

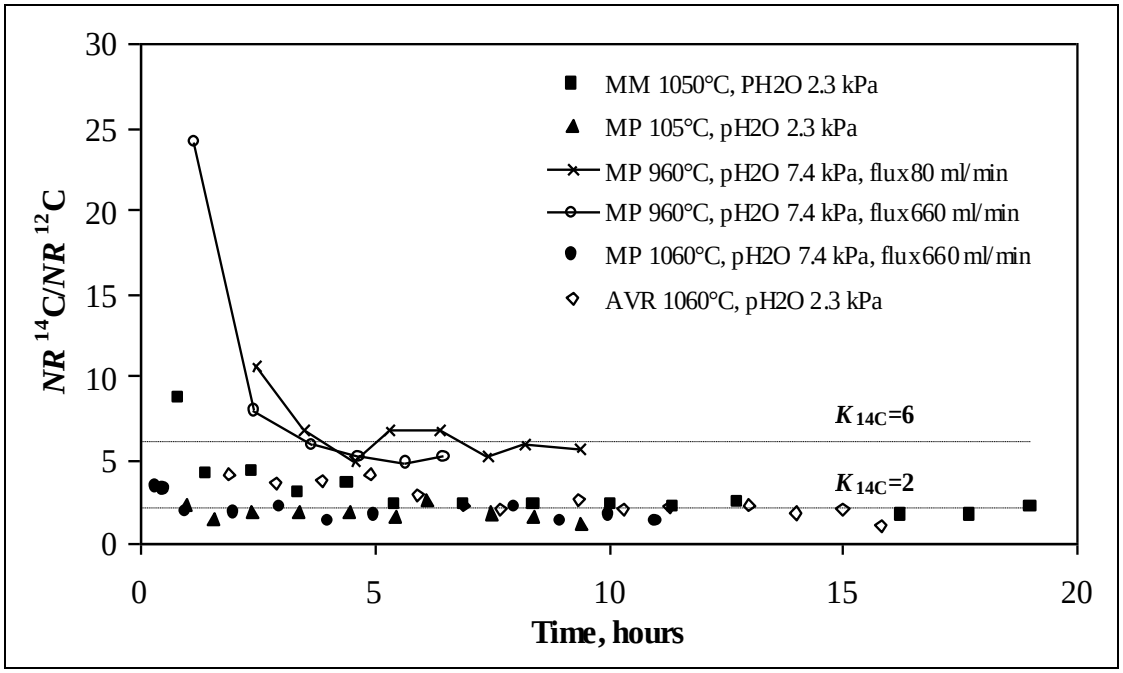

Figure4.7: Ratio of normalised release rates during the thermal treatment in a steam atmosphere

The reason for this unexpected selective extraction of ^{14}C is related to the fact that it is mainly created from activation of nitrogen which entered the pores of the graphite. The ^{14}C is then deposited at the surfaces of the pores and can obviously be removed from there by the oxidation processes. This discovery may have an important commercial value when applied to the large volumes of contaminated graphite from decommissioned graphite-moderated reactors.

6 Assessment of the Advantages of conditioning and Thermal Treatment (Task 4.4)

The work in support of this assessment is not complete. The results presented in the graphite thermal treatment report (Ref. 2) are in the process of being assimilated by the WP4 partners. In the interim, likely activity levels for thermally treated reflector graphite were determined based on the results of HTR graphite activity assessments (Ref. 1) and assuming all volatile isotopes are removed by thermal treatment (i.e. all the ^{3}H and 69.6% of the ^{14}C). The remaining ^{14}C is considered to arise from the activation of ^{13}C which is integral with the graphite matrix. The assumed proportions of ^{14}C arising from ^{13}C and nitrogen activation routes are the accepted values for AGR graphite.

From these preliminary theoretical calculations the activity of the treated reflector graphite, for a 60 year core dwell time, would remain categorised as ILW waste. For graphite integral with the fuel, replaced on a 2.5 year cycle, the treated graphite would be categorised as LLW. This assumes that technologies can be developed that successfully separate the coated fuel particles from the graphite matrix and the fuel coatings are effective in retaining all but volatile radionuclides.

7 Conclusions

The traditional treatment of wastes arising from the operation and decommissioning of nuclear power stations have been reviewed. The potential options for treating HTR wastes are essentially no different from those already considered for existing reactor designs. The graphite waste from reflector blocks and moderator structures in HTR is an additional waste stream to mainstream LWR designs. Techniques for separating the embedded coated particles of spent fuel waste from the moderator graphite still need to be developed.

Methods of treating waste graphite have been researched by those countries that have operating or shutdown graphite moderated reactors (for example: UK, France, Germany, USA, Japan, Italy, Russia etc.). The treatment and methods of eventual disposal of graphite tried, or more likely proposed since the number of dismantled graphite moderated reactors are few, have been assessed as part of this task. No sensible methods of treatments have been identified that result in both decontamination and volume reduction of the graphite. Consequently, the feasibility of a thermal treatment of graphite has been tested experimentally as part of this work package.

The thermal treatment experiment decontaminates graphite by gasification of steam in an inert atmosphere. The technique results in the release of volatile radionuclides from irradiated graphite samples from AVR and Merlin reactors and captures them in solutions. Much of the ^{14}C in irradiated graphite is from the activation of nitrogen (within the pores of the graphite) and the results show that this too is released by the thermal treatment. The process of oxidation of the graphite to carbon monoxide and the precipitation of carbon on metal catalysts has also been demonstrated. This provides the potential for purified carbon with the non-volatile radionuclides retained in a much smaller volume of solid residue.

The results from the thermal treatment have only recently been received. The formal assessment of the advantages of conditioning and thermal treatment in each country of WP4 is still outstanding.

8 References

1. Turner, J.M., Bourdeloie, C., Brücher, H., Fachinger, J., Brinkmann, G., von Lensa, W.; "HTR-Specific Wastes", Final report of HTR-N WP4, 2003, HTR-N-10/03-D-4.0.3 (Confidential).
2. Podruzhina, T, "Thermal Treatment of Radioactive Graphite as Decontamination Option", FZJ-ISR-IB-554/04.