

OVERVIEW OF GRAPHITE TREATMENT PROCESSES IN HIGH TEMPERATURE REACTORS

Fabienne DELAGE¹, Christian LATGE², Pascal THOUVENOT²

1 CEA Cadarache Fuel Study Department - 13108 Saint Paul lez Durance - France

2 CEA Cadarache Nuclear Technology Department - 13108 Saint Paul lez Durance - France

ABSTRACT: The Very High Temperature Reactors will contribute to the future of Nuclear Energy due to their advantages and efficiency. Nevertheless, large amounts of graphite (reflectors) wastes are anticipated. Thus, in order to minimize the graphite inventory, it is necessary to define a strategy : treatment-reduction of volume and/or conditioning-storage. The Department of Nuclear Technology has examined options concerning the treatment and the conditioning of contaminated and irradiated graphite from reflectors and structures, after unloading. After a brief description of the graphite characteristics, this paper presents a literature review concerning the following :

- processing and conditioning methods studied for :
 - sleeves and stacks from UNGG, MAGNOX or AGR type reactors ;
 - reflectors and structures of High Temperature industrial prototypes and experimental Reactors ;
- reduction of ¹⁴C emission from facilities, because ¹⁴C is one of the main radio-element of the HTR radiochemical spectrum ;
- evaluation of potentialities of decontamination of contaminated graphite ;

in order to identify possible processing – conditioning scenarios for future HTR reactors.

Among the management solutions identified, the following has been selected to be deeply investigated in the near future :

- transposition of the UNGG graphite management mode : packaging of objects in containers to be stored in a site dedicated to UNGG-type activity packages, and in a geological site for B category waste packages.
- decontamination of contaminated graphite (reflectors) in order to reuse it in the reactor and to reduce graphite waste inventory.
- evaluation of a treatment – conditioning scheme, with the aim of reducing volume, involving different steps :
 - gasification of graphite (possibly preceded by crushing) by means of a process to be selected (incineration, steam reforming,...) taking recent technological advances into consideration ;
 - separation of ¹⁴C and ¹²C isotopes in the combustion gas through cryogenic distillation or through implementation of emerging technologies based on plasma physics or chemical separation, with a view to limiting atmospheric emissions of ¹⁴C ;
 - cementing of incineration ashes and stabilisation products (BaCO₃ or CaCO₃) of the ¹⁴C enriched gas flux, or even, in addition, interchangeable sections of highly efficient filtration systems traditionally fitted to chimneys.

0. INTRODUCTION

The future nuclear energy systems will be supported by High Temperature Reactor technology, based on a composite particle fuel, an helium cooling circuit, graphite moderators and structures. Among

R&D actions conducted to support this reactor development, options concerning the treatment and the conditioning of graphite from fuel blocks, reflectors and structures, after unloading are examined. This paper presents, after a brief description of waste characteristics, a literature review concerning the following :

- processing and conditioning methods studied for :
 - sleeves and stacks from UNGG, MAGNOX or AGR type reactors ;
 - reflectors and structures of High Temperature industrial prototypes and experimental Reactors ;
 - studies concerning the reduction of ^{14}C emission from nuclear facilities, because ^{14}C is one of the main radioelement of the HTR radiochemical spectrum ;
 - as well as evaluation of potentialities of decontamination of contaminated graphite ;
- in order to identify possible processing – conditioning scenarios.

1. WASTE SPECIFICITY

In the High Temperature Gas-cooled Reactor type design examined, the annular shaped core is made of stacks of graphite prismatic blocks that feature vertical channels :

- some of which hold columns of fuel pellets (compacts made of fuel particles embedded in a graphite matrix), burnable poisons or control rods,
- others acting as cooling ducts (helium circulation).

Reflector blocks made of graphite are mounted on either side of the core, these may be permanent or replaceable during reactor operation, as may be the graphite on the bottom and the top of the core. This graphite is waited to be chemically pure (table I) in order to constitute good moderators.

TABLE I : Average chemical composition of impurities in UNGG graphite blocks [1].

impurities	B	Cs	Ca	Cl	Co	He	Fe	Li	Ni	N	Nb	U
content (ppm)	1	0	30	5	0,07	0	10	0,1	5	10	0	0,1

A HTGR 600MW_{th} reactor holds 727 metric tons (t or Mg) of graphite (table II) [1] :

- 27 Mg are in the fuel compacts matrix
- and 700 Mg constitute blocks (89 Mg), internal and external permanent reflectors (258 Mg) and internal and external replaceable reflectors (353 Mg).

Assuming periodic renewal: 301 days for assemblies (by third parties) and 6 years for replaceable reflectors, the quantity of graphite (compacts excluded) removed during the reactor life (60 years) (including dismantling of the core) would be to the order (table 2) of 3,430 m³ (or 5,965 metric tons), that is 57 m³/year/HTR or 210 m³/GWe/year [1].

For the purposes of comparison, the French UNGG nuclear reactor series currently being dismantled will have produced 14,000 m³ of graphite waste, that is, the equivalent to 4 HTR reactors.

TABLE II : Graphite waste (fuel excluded).

Type	Quantity (Mg)	Volume (m ³)	Renewal periodicity	annual volume removed (m ³)	total volume removed (m ³)
Fuel blocks	89	51	301 days (1/3)	21	1240
Replaceable reflectors	353	203	6 years	34	2040
Permanent reflectors	258	148	60 years	(2.5)	148

The radiological inventory of the waste is a function of : the fuel type, the composition of impurities contained in the graphite (and in helium), the position of the graphite blocks in the reactor as well as

the reactor's operating conditions. The first activity evolution calculations performed at various points of a model reactor concerning reference graphite (table I), subject to neutron bombardment for periods of time up to 60 years [1], revealed that the two main components of the radiochemical spectra are ^{14}C and ^3H . These two radioelements are both β emitters, ^3H has a short half-life and ^{14}C has a long half-life ; they are generated by the activation of graphite impurities : $^{13}\text{C} + ^{14}\text{N}$ and ^6Li . Other radionuclides (^{36}Cl , ^{10}Be , ^{63}Ni , ^{60}Co) found in the inventory feature lesser activities.

Furthermore, activity calculations concerning graphite blocks from reactors revealed that permanent reflectors (subject to neutron bombardment throughout the entire operating time of the reactor) feature ^{14}C (and ^3H) activities far superior to the acceptable activity limits for french category A waste [1]. Thus, permanent irradiated reflectors need to be categorised as French category B waste.

For objects that are renewed (at frequencies of 301 days or 6 years), specific activities calculated [1] have the same order of magnitude as the maximum activity values of radionuclides contained in UNGG graphite (approximately : 10^5 Bq/g for ^{14}C , 4.10^5 Bq/g for ^3H , 6.10^5 Bq/g for ^{60}Co , 10^3 Bq/g for ^{36}Cl and 2.10^5 Bq/g for ^{63}Ni). Thus, as for most UNGG graphite, the majority of renewal waste doesn't belong to waste category A due to the radiological capacity limit of the Aube Storage Centre [2] that is not far from the total ^{14}C and ^{36}Cl activity of waste generated over the entire lifetime of a single HTR reactor (table III).

Table III : Comparison between the activity of the radionuclides in graphite objects and the radiological capacity limit of the french A waste Storage Centre.

	^{14}C (TBq)	^{36}Cl (TBq)	^{60}Co (TBq)	^{63}Ni (TBq)
CSA radiological capacity limit	815	14	400000	40000
Replaceable graphite objects	570	6	3400	1100

Thus, of the $3,430 \text{ m}^3$ graphite waste (made up of fuel blocks and internal or external reflectors) produced by the High Temperature Reactor, 148 m^3 (corresponding to the permanent reflector volume) will be category B waste. The remaining graphite will have radiological characteristics similar to those of graphite irradiated in the UNGG reactor series, subject to the reservation that impurity activation products contained in helium make a negligible contribution to the radiochemical inventory.

2. EXPERIENCE FEEDBACK FROM UNGG GAS TYPE REACTOR SERIES

The UNGG, MAGNOX and AGR nuclear reactor series, based on a combination of a fuel containing naturally occurring uranium or slightly enriched uranium, metallic or ceramic, placed in a sealed clad, with a graphite moderator and cooled by CO_2 , has been in operation since the 60s to manufacture military plutonium and subsequently to generate electricity.

The development of these reactors (~50 units) led to the usage of significant quantities of graphite (> 100,000 metric tons) to produce stacks (moderators and neutron reflectors), as well as sleeves ; thus the question of managing graphite waste generated during operation, and subsequent future dismantling, has been regularly broached [3,4].

In France, graphite wastes produced by the regular removal of fuel assemblies during reactor operating time comprise :

- sleeves (3,600 Mg of hollow cylinders) that maintained the integrity of the fuel assembly during the unloading phase prior to reprocessing ; they are mainly stored on sites ;
- sleeves breakages mixed with shards of magnesium clads and fragments of uranium, produced during fuel de-cladding operations performed prior to fuel reprocessing.

Moreover, during dismantling phases, 18500 Mg of graphite waste (in the form of hexagonal bricks) will be produced.

Management modes proposed for these various types of waste are as follows :

- storage in a dedicated surface or sub-surface site (25,000 m³) currently being designed, to hold most sleeves and blocks ;
- compacting or cementing small sleeves breakage, clads,...

Observation : The management of graphite waste generated by MAGNOX (and AGR) reactors is quite similar in principle to the French solution adopted for the UNGG reactor type : compacting of small waste followed by packing in containers, immobilisation of sleeves blocks in containers that will be stored in geological layers (at a depth of 600 m) following a interim storage period to the order of 50 years on site (corresponding to a phase to allow for the decay of ⁶⁰Co which is particularly irradiating) [5].

The radiological characteristics of irradiated graphite vary as a function of the type and content of impurities introduced upon manufacture, the position of the objects within the reactors, irradiation duration, reactor control conditions, etc. Based on several inventories performed by combining experimental analyses and calculations, a radiochemical spectrum with the following main components and content limits : ¹⁴C with 10⁵ Bq/g, ³H with 4.10⁵ Bq/g, ⁶⁰Co with 6.10⁵ Bq/g, ³⁶Cl with 10³ Bq/g and ⁶³Ni with 2.10⁵ Bq/g.

The UNGG graphite block management mode that has been adopted at this time, involves the storage of objects packed in containers on a dedicated site, this solution constitutes the best compromise between safety requirements and short-term industrial reality and economic concerns. Alternatives, the development of which was rejected, were studied in the 80s and 90s ; these mainly involved :

- graphite impregnation, with impermeable organic compounds (bitumen, thermal setting resins, mixtures of pitch and epoxide resin), to limit the dissemination of the radioelements contained in the event that water penetrates into the site [6] ;
- destruction of graphite by means of a heat treatment [7,8] followed by cementing of ashes and secondary waste generated (filters, etc.), to reduce the final waste volume.

As regards the drawbacks associated with the solutions involving impregnation by organic compounds and the incineration of graphite that led to their rejection as UNGG (MAGNOX and AGR) graphite management options, the following may be noted :

- the risk of radiolysis of organic products (with production of hydrogen) in the long-term in the storage site ;
- technical difficulties (need for prior crushing to implement most incineration processes and control of combustion, occasionally difficult to achieve), atmospheric emission of ¹⁴C (and ³H), and ⁶⁰Co concentration in ashes (particularly irradiating).

However, in the context of prospective thought concerning the management of graphite waste from future HTR reactors, the thermal destruction of graphite could constitute an interesting element of the solution due to the substantial volumes of irradiated graphite that could be generated. In fact :

- Difficulties associated with crushing and controlling combustion could be overcome :
 - With respect to incineration, difficulties were frequently encountered when using conventional ovens or fluidised beds [9] : the retention time in the flame of burner-type systems was not well controlled and hence poor control of reaction yields, or setting of the fluidised bed support during inopportune temperature increases in the reaction system, could definitively be resolved, notably through the implementation of other technologies : plasma torch [10], cold crucible [11] or power laser under gas [12]. Furthermore, the interest of laser technology for the incineration of graphite has been extensively demonstrated during UNGG graphite waste management definition studies [3]. Development completed up until now (COCA-COLA project [12]) has shown that this was a promising procedure : combustion dually controlled by the laser power and oxygen flow, incineration of large graphite parts without prior crushing. Nevertheless, the time necessary for work required to scale the procedure up to an industrial level was not compatible with the programme schedule.

- As regards graphite crushing, difficulties associated with the implementation of mechanical processes that notably generate unwanted dust loading, may be avoided :
 - either by removing the step, in the laser incineration procedure scenario,
 - or by implementing a non-mechanical technique, for example, the pulsed current method [13] that involves inducing brief high intensity current pulses within the material thus leading to its destruction.
- As regards gases generated by graphite combustion, mainly comprising $^{12}\text{CO}_2 + ^{14}\text{CO}_2$ and HTO (the other radionuclides being found in the incineration ashes or gas purification filters), two points need to be dealt with :
 - the generation of CO_2 , in an international context of reducing greenhouse gas emissions from anthropic origins, provided for in the Kyoto protocol ;
 - the compatibility of ^{14}C HTO emissions with health directives.

The information used and analysed to explore the acceptability (or not) of CO_2 emissions on the one hand and ^{14}C in gases on the other, are taken from a scenario study [14] concerning incineration in a fluidised bed of 30,000 Mg of UNGG graphite stacks and sleeves (20,000 Bq/g) at a rate of 120 kg/h (600 Mg per year and 50 years of process operation), leading to the annual production of 2.3 kilotons of CO_2 containing carbon 14 activity to the order of $1.2 \cdot 10^{13}$ Bq. Based on this data, it emerges that :

- the CO_2 contribution generated by this application would be negligible with respect to the accumulation of emissions in France : 340 Mg in 2000 and less than 315 Mg in 2012 according to the Kyoto agreements.
- On the contrary, as regards the carbon 14 emission (10^{13} Bq/an), although flow activity remains within acceptable levels with respect to health recommendations of the International Commission on Radiological Protection, this element's long half-life associated with its swift up-take in living systems, have led to the proposal of a gas treatment that would allow the gaseous emissions of ^{14}C to be reduced [14,15,16]. Isotopic separation technologies are currently available. Their application to the reduction of ^{14}C emissions from reprocessing facilities have been regularly examined and the most promising remain to be developed in this graphite incineration context.

As regards, furthermore, the presence of HTO in combustion gases, due to the short radioactive half-life of tritium and the fact that it is not as radiotoxic, it would seem that it could be released into the atmosphere without any necessity to reduce the flux. Nevertheless, treatment procedures have been developed [17], if a specific requirement to treat the tritium should be expressed.

- As regards the last set of constraints listed above, concerning the activity concentration in ashes, a consequence of the reduction in volume achieved through incineration (>95%), the problem posed by ^{60}Co is noted, that is the protection of workers against this highly irradiating radionuclide ($T_{1/2}$: 5.2 years ; β , γ emitter ; E_γ : $2.5 \cdot 10^3$ keV). The solution to this problem is notably based on the implementation of ad-hoc biological protection during incineration, conditioning, transportation and storage steps.

Thus, experience acquired during research into a UNGG (or MAGNOX) graphite waste management system has revealed two possibilities for the management of graphite objects from future HTR reactors :

- selection of the solution adopted for UNGG graphite, implementation of which is simple : packaging objects in containers to be stored :
 - in a dedicated site for UNGG-type activity packages
 - and in a geological site for B waste packages, this will lead to a significant investment in the storage step due to the huge volumes of HTR graphite expected ;

- selection of a treatment – conditioning scenario with the objective of reducing the volumes of packages to be stocked, comprising :
 - as regards treatment, an incineration step (possibly preceded by graphite crushing) by means of a process to be redefined as a function of the latest technological progress and $^{14}\text{C}/^{12}\text{C}$ separation procedures that could be implemented ;
 - and an incineration ash and ^{14}C enriched gas flux conditioning procedure (or even interchangeable sections of highly efficient filtration systems traditionally fitted to chimneys), that would satisfy both the volume reduction objective and the constraints intrinsic to the types of waste ultimately generated.

Observation : Work conducted in Japan concerning the management of graphite waste that would be produced by dismantling the Tokai-I AGR type reactor, compares two management options similar to those presented for future HTR graphite :

- *burying graphite in geological storage after conditioning in containers, reducing volumes by judiciously cutting and crushing some of the objects in order to achieve maximum occupation by waste of interstitial spaces in the containers [18] ;*
- *graphite incineration followed by $^{14}\text{C}/^{12}\text{C}$ isotopic separation of combustion gases by selective adsorption on zeolites followed by $^{14}\text{CO}_2$ reduction in carbon prior to cementing [19].*

The initial economic assessment of the two options revealed that the second is more profitable than the first, although the reduction of volume in the storage site achieved can be as much as 30% by densely stacking graphite in the containers.

3. CONDITIONING GRAPHITE FROM FIRST HTR

During the 50s, developments associated with the use of nuclear energy were marked increasing numbers of concepts intended to enhance the physical characteristics or efficiency of reactors. Around 1956, when the first carbon gas reactors were being built, HTR reactor projects began to break through in the United States and in Europe. These reactors differ from those of the uranium graphite carbon dioxide gas reactor series as follows :

- they are cooled by Helium, this allows high thermo-dynamic yields to be achieved through access to high temperatures ($\sim 850^\circ\text{C}$) and pumping powers limited through operation at high pressures ;
- they use finely divided fuel made of particles containing fissile materials dispersed in a spherical (bullet) or cylindrical (compact) shaped graphite matrix ; an inherently safe design (thermal stability is higher than $1,600^\circ\text{C}$) that confers high burn-up fraction capacities on the system ;
- and it is possible to use various types of nuclear materials.

The generic questions associated with the dismantling of HTR facilities, as well as waste management (treatment – conditioning – packaging in containers – storage of graphite from reflectors and fuel) were broached when the research and prototype reactors were shut down, incorporating operational criteria : volumes of ultimate waste generated, characteristics of storage sites required, costs, management of secondary effluents, etc. The main studies conducted concern management options similar to those previously listed :

- packing of graphite blocks in containers followed by geological storage [20,21,22] ;
- crushing followed by incineration of graphite reflectors or compacts or bullets with the aim of reducing the volume or even fuel separation [8,23], taking the question of the acceptability of $^{14}\text{CO}_2$ emissions [20,24] or $^{14}\text{CO}_2$ fixation solutions into consideration [25] (precipitation of BaCO_3 or CaCO_3 followed by cementing).

Bibliographic references are scarce, those that do exist suggest two other graphite management options that complete those already listed :

- decontamination of the reflector surface [24] with the aim of removing the radiological inventory from the irradiated graphite blocks ; this could allow some waste to be decategorised ;
- recycling carbon in SiC deposit as a particle coating or by temperature moulding of a graphite nickel sulphate mixture to create containers for irradiated fuels [26].

Thus, works performed concerning management of graphite waste from the first HTR have led to a complementary solution to manage graphite waste from future reactors of the same type : this involves decontaminating the surface of objects in order to decategorise some waste. Given current knowledge, recycling would not seem to be very promising, because implementation would notably impose the nuclearisation of recycling product manufacturing equipment.

4. REDUCTION OF ^{14}C EMISSIONS FROM FUEL REPROCESSING FACILITIES

The reduction of gaseous emissions at the PWR reactor series fuel reprocessing facility chimney outlets is a subject that is regularly studied. Studies generally focus on trapping $^{14}\text{CO}_2$ and conditioning treatment products. $^{14}\text{C}/^{12}\text{C}$ isotopic separation prior to trapping in order to combine the decrease in ^{14}C gaseous emissions with a reduction in ultimate waste volume, rarely dealt with in publications between the 70s and 90s, is currently undergoing a revival in Japan. A synopsis of works published on the themes : isotopic separation, CO_2 trapping and conditioning of treatment products, performed with the aim of reducing $^{14}\text{CO}_2$ gas emissions is presented below.

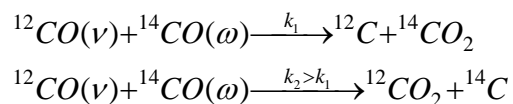
4.1. $^{14}\text{C}/^{12}\text{C}$ Separation

Isotopic effects are generally very weak and fractioning, or even total separation of isotopes is rendered possible by the implementation of discriminatory techniques notably based on variations between isotopes or isotopic compounds that feature :

- physical characteristics (that vary with weight) : density, melting point and boiling point, latent heat, diffusion rate, etc.)
- chemical reactivity caused by differences in the vibration energy of isotopic molecule bonds.

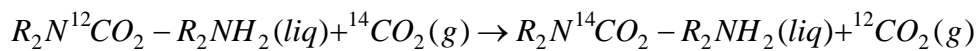
Studies performed concerning the separation of carbon 14 isotopes led to the emergence of several technologies :

- one involves cryogenic fractional distillation, in which the separation factor is based on differences in vapour pressure between the carbon monoxide isotopic compounds [27]. This process, the implementation of which requires several thousand distillation plates to obtain significant enrichment, was successfully applied in the 50s and 70s to achieve the enrichment of ^{13}C with respect to ^{12}C to the order of 60-70% [28] and 95% [29,30,31] (for an initial isotopic ratio $^{13}\text{C}/^{12}\text{C}$ of ~1%). The Harwell distillation unit generated 0.4 g/day of ^{13}C enriched to 60-70% ; that installed at Los Alamos generated 4 kg/year of ^{13}C enriched to 90%. Similar informations concerning the $^{14}\text{C}/^{12}\text{C}$ separation yield and production capacity are unfortunately absent of the litterature. Since 1950's, large improvements have been made on packings and modelling (non-equilibrium models) : thus, a new assessment of the potentialities of isotopic distillation by cryogenic distillation should be performed.
- The second technology developed up now at laboratory scale, belongs to the field of numerous applications of cold plasmas, out of thermodynamic equilibrium [32,33,34]. The basic principle involves transferring electrical energy to a gaseous flux containing all or some of the $^{14}\text{CO}+^{12}\text{CO}$ isotopic mixture through a discharge generated between two electrodes. Excitation thus generated at the carbon monoxide bonds associated with differences between the ν and ω energies of the 2 isotopic molecules is at the origin of reactions :



Thus, the gaseous environment is enriched in ^{14}C . The separation factor $((^{14}\text{C}/^{12}\text{C})_{\text{output}}/({}^{14}\text{C}/^{12}\text{C})_{\text{input}})$ that depends notably on pressure conditions in the system, voltage and intensity of the plasma discharge current and the composition of gaseous medium input may reach a value of 14.6.

- The literature review performed concerning carbon isotopic separation modes also led to the identification of a third technology, compatible with $^{14}\text{C}/^{12}\text{C}$ separation : laser induced enrichment [35,36,37]. This process, discovered in the 70s and developed in the context of medical applications for $^{13}\text{C}/^{12}\text{C}$ separation, is based on a photochemical separation principle : under the effect of pulses, wavelength that coincide with an adsorption band of $^{13}\text{CHClF}_2$ (Freon-22), induces a reaction promoting the enrichment of the gas on ^{13}C . Nevertheless, the presence of fluor in reaction products (C_2F_4) is restricting in the selection of a conditioning process.
- The last promising technology is based on a chemical exchange between CO_2 and chemical complexe amine in nonaqueous solvent [38,39], in which the liquid phase is enriched with heavier carbon isotope. Thus, the reaction of $^{14}\text{CO}_2$ with amine (done on an exchange column) produces amine- CO_2 complexes :



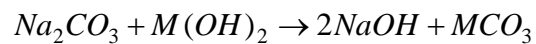
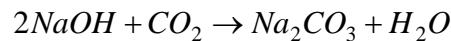
$^{14}\text{CO}_2$ is then released in gas form by heating the ^{14}C -carbamate product in a boiler.

Takeshita et al. [40] studied the interest of the method to the recovery of ^{14}C form 1600 Mg graphite moderator of Tokai-1 gas cooled reactor, after incineration. The applicability of the process seems to be demonstrated.

4.2. CO_2 Trapping

Among CO_2 trapping procedures developed in the chemical industry, potentially transposable to the nuclear industry notably through their ease of implementation, the following were selected [41] :

- dual alkaline washing with, in fine, precipitation of alkaline earth carbonates (BaCO_3 , CaCO_3 or SrCO_3) :



↓

- direct precipitation of an insoluble carbonate (BaCO_3 , CaCO_3 or SrCO_3) by reaction with a hydroxide ;
- solid-gas reaction with the placement of carbon dioxide in contact with highly reactive solid hydroxides: $\text{Ba}(\text{OH})_2$ or $\text{Ca}(\text{OH})_2$, leading to the formation of the relevant carbonates ;
- the adsorption of CO_2 in cold traps made of 4A zeolithes.

The author expressed a preference for dual washing with sodium hydroxide and the gas solid reaction to arrive at a barium or calcium carbonate-type treatment product (less toxic than strontium).

4.3. Alkaline earths carbonate conditioning.

Among the matrices and procedures that may be implemented to barium or calcium carbonate conditioning, interest focused on cements has been noted [41,42].

Matrices that need to be manufactured at high temperatures (glass and ceramics) are ejected due to the high costs of these processes, development R&D requirements as well as difficulties in implementation.

Organic matrices are not selected because of safety and cost issues and also because of questions concerning the thermodynamic stability of carbonates, which are better in the alkaline environment made by interstitial solutions of cements.

As regards the other advantages of cementing, the low cost of raw materials and the fact that the process has been extensively tested for conditioning of nuclear waste should be noted. Furthermore,

relatively little works have been undertaken up until now, to assess the proper loading of the cement matrix, an encapsulation rate of 30 to 35% by weight in a Portland type cement (CPA) would seem to be realistic [41]. Moreover, alteration resistance models found in literature propose a ^{14}C leaching rate to the order of 2% for CaCO_3 in a CPA matrix at the end of carbon 14 radioactive period (5,730 years) [43]. Lastly, because ^{14}C is a weak beta emitter, the effects of long term radiation, gas evolution from radiolysis and heat generation on the stability of the concrete matrix are expected to be minimal [42].

4.4. Conclusion

Carbon 14 is an activation product generated during the irradiation of fuels in pressurised water reactors, partially released into the atmosphere as $^{14}\text{CO}_2$ during fuel reprocessing. Studies were conducted with the aim of reducing these gas emissions, these concerned trapping $^{14}\text{CO}_2$, conditioning the product created, other studies focused on $^{14}\text{C}/^{12}\text{C}$ isotopic separation prior to trapping in order to reduce the volumes of waste.

The carbon isotope separation technology field of investigation was broadened over the last years : since the end of the 90s, discharge plasma, chemical exchange,... have been ranked beside the cryogenic distillation methods developed during the 60s. These procedures are currently implemented on a laboratory scale, however due to the strong potential of these new techniques for application to the depollution of gaseous effluents in an international context of reducing greenhouse gas emissions, they could be scaled up to an industrial level in the medium term.

Of the numerous solutions available to trap CO_2 , the authors prefer carbonate synthesis procedures (CaCO_3 for example) through the double alkaline reaction (washing with sodium hydroxide followed by precipitation of the target alkaline earth carbonate) and by solid-gas reaction.

As regards conditioning of carbonates thus created, all current thought converges towards a cementing procedure because the thermodynamic stability of carbonates is favoured in a cement medium and because of technical/economic reasons (assessment performed on the basis of theoretical load rate and cement formulation).

5. DECONTAMINATION

In High Temperature Reactors, three kinds of graphite have to be examined for decontamination : fuel blocks, permanent reflectors and replaceable reflectors. Graphite from fuel blocks, activated in the bulk by neutrons, can't be decontaminated. Graphite from replaceable reflectors could be decontaminated after to be retired from the reactor. This decontaminated graphite could be reuse in the reactor, but the main goal of the decontamination operation is the reduction of the graphite waste inventory. Graphite from permanent reflectors could be decontaminated several times. The first ones (frequency is to define) would be maintenance operations. These operations must absolutely preserve the functionality of the material. The last one would have the same main objective than the replaceable reflectors graphite decontamination operation: reduction of the graphite waste inventory.

The choice of the decontamination process depends on the contamination characteristics: either the contamination is on the surface of the graphite, or the contamination has migrated into the graphite because of his high porosity. In the first case, processes leading to the graphite surface erosion could be chosen. The erosion phenomenon can be chemical or physical. In the case of migration of contamination into the material, decontamination with an electrokinetic process could be envisaged. This kind of process is already used for the dechlorination of civil engineering structures like bridges. It permits to extract mobile radionuclides from porous media, with an electric field. The technical feasibility has been demonstrated with cement materials contaminated by cesium [44]. The technical feasibility for contaminated graphite from High Temperature Reactor should now be demonstrated.

6. CONCLUSION: WASTE MANAGEMENT WAYS FOR FUTURE HTR GRAPHITE

Among the management solutions studied in the past (or even recently) for waste graphite from graphite – gas reactors, to deal with future HTR graphite, the following may initially be adopted :

- transposition of the UNGG graphite management mode : packaging objects in containers to be stored in a site dedicated to UNGG-type activity packages, and in a geological site for B category waste packages. Implementation of this solution is simple, but it would require to exceptional acquisition of storage site. On the contrary, storage costs could be reduced by decategorising some waste through surface decontamination of species notably introduced by the activation of helium impurities ;
- decontamination of contaminated graphite (reflectors) in order to reuse it in the reactor and to reduce graphite waste inventory : the decontamination process must be chosen in function of the characteristics of the contamination, surfacic or in depth.
- the selection of a treatment – conditioning scheme, with the aim of reducing volume, this will involve :
 - gasification of graphite (possibly preceded by crushing) by means of a process to be defined (incineration, steam reforming, etc.) taking recent technological advances into consideration ;
 - separation of ^{14}C and ^{12}C isotopes in the combustion gas with a view to limiting atmospheric emissions of ^{14}C ;
 - cementing of incineration ashes and stabilisation products (BaCO_3 or CaCO_3) of the ^{14}C enriched gas flux.

The scientific and technical/economic viability of this solution is a function of the following parameters : combustion and isotopic separation yields, compatibility and stabilisation product and ash load factors in the cement, but also factors as : reliability, robustness and short-term industrial maturity of components of unit operations, ease of control and nuclearisation of the process, and cost.

This initial analysis needs be followed by a phase during which the scenarios may be examined in more detail in order to support them, and thus obtain further information absolutely necessary to assess said.

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