

GRAFEC: A New Spanish Program to Investigate Waste Management Options for Radioactive Graphite - 12399

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ABSTRACT

Spain has to manage about 3700 tons of irradiated graphite from the reactor Vandellós I as radioactive waste. 2700 tons are the stack of the reactor and are still in the reactor core waiting for retrieval. The rest of the quantities, 1000 tons, are the graphite sleeves which have been already retrieved from the reactor. During operation the graphite sleeves were stored in a silo and during the dismantling stage a retrieval process was carried out separating the wires from the graphite, which were crushed and introduced into 220 cubic containers of 6 m³ each and placed in interim storage. The graphite is an intermediate level radioactive waste but it contains long lived radionuclides like ¹⁴C which disqualifies disposal at the low level waste repository of El Cabril. Therefore, a new project has been started in order to investigate two new options for the management of this waste type. The first one is based on a selective decontamination of ¹⁴C by thermal methods. This method is based on results obtained at the Research Centre Jülich (FZJ) in the Frame of the EC programs “Raphael” and “Carbowaste. The process developed at FZJ is based on a preferential oxidation of ¹⁴C in comparison to the bulk ¹²C [1, 2, 3, 4,5]. Explanations for this effect are the inhomogeneous distribution and a weaker bounding of ¹⁴C which is not incorporated in the graphite lattice. However these investigations have only been performed with graphite from the high temperature reactor Arbeitsgemeinschaft Versuchsreaktor Jülich AVR which has been operated in a non-oxidising condition or research reactor graphite operated at room temperature. The reactor Vandellos I has been operated with CO₂ as coolant and significant amounts of graphite have been already oxidised. The aim of the project is to validate whether a ¹⁴C decontamination can also been achieved with graphite from Vandellós I. A second possibility under investigation is the encapsulation of the graphite in a long term stable glass matrix. The principal applicability has been already proved by FNAG [6, 7]. Crushed graphite mixed with a suitable glass powder has been pressed at elevated temperature under vacuum. The vacuum is required to avoid gas enclosures in the obtained product. The obtained products, named IGM for “Impermeable Graphite Matrix”, have densities above 99% of theoretical density. The amount of glass has been chosen with respect to the pore volume of the former graphite parts. The method allows the production of encapsulated graphite without increasing the disposal volume. This paper will give a short overview of characterisation results of different irradiated graphite materials obtained at CIEMAT and in the Carbowaste project as well as the proposed methods and the actual status of the program including first results about leaching of non-radioactive IGM

samples and hopefully first tendencies concerning the C-14 separation from graphite of Vandellós I by thermal treatment.

INTRODUCTION

Currently there are two reactors in Spain containing some kind of nuclear Graphite materials:

- Nuclear Power Plant of Vandellós I, located in Hospitalet de l'Infant, Tarragona.
- Material Testing Reactor JEN-1, located in Madrid.

NPP of Vandellós I is a Uranium Natural Graphite Gas reactor (UNGG). The principal design is shown in Figure 1. It was graphite moderated, cooled by carbon dioxide, and fuelled with natural uranium metal. The reactor had a power of 460 MWe and produced 56000 GWh during its operations time from 05/06/1972 to 10/19/1989. ENRESA became the owner of Vandellós I in 1998 and is responsible for the decommissioning. Decommissioning Level 2 was achieved in 2003 followed by a safe enclosure phase of 25 years.

During operation 181000 graphite sleeves were used with a mass of 1000 tons. The sleeves have been crushed to separate activated NIMONIC wires from the sleeves and introduced into 220 cubic containers of 6 m³ each and placed in interim storage. The graphite is an intermediate level radioactive waste but it contains long lived radionuclides like ¹⁴C which disqualifies disposal at the low level waste repository of El Cabril. Furthermore, the moderator graphite pile of Vandellós I contain 2680 tons of irradiated graphite which is still stored in the reactor.

The new project GRAFEC has been started in order to investigate two new options for the management of the Spanish graphite.

The first option is a thermal treatment based on results obtained at the Research Centre Jülich in the frame of the EC projects “Raphael” and “Carbowaste”.

The second option is a new development of FNAG which enables long term safe disposal based on a transition of the graphite into an impermeable graphite matrix.

The objective of this project is the evaluation whether one of these new methods or a combination of these methods will be capable of managing irradiated graphite (i-graphite) of Spain with respect to the existing regulations.

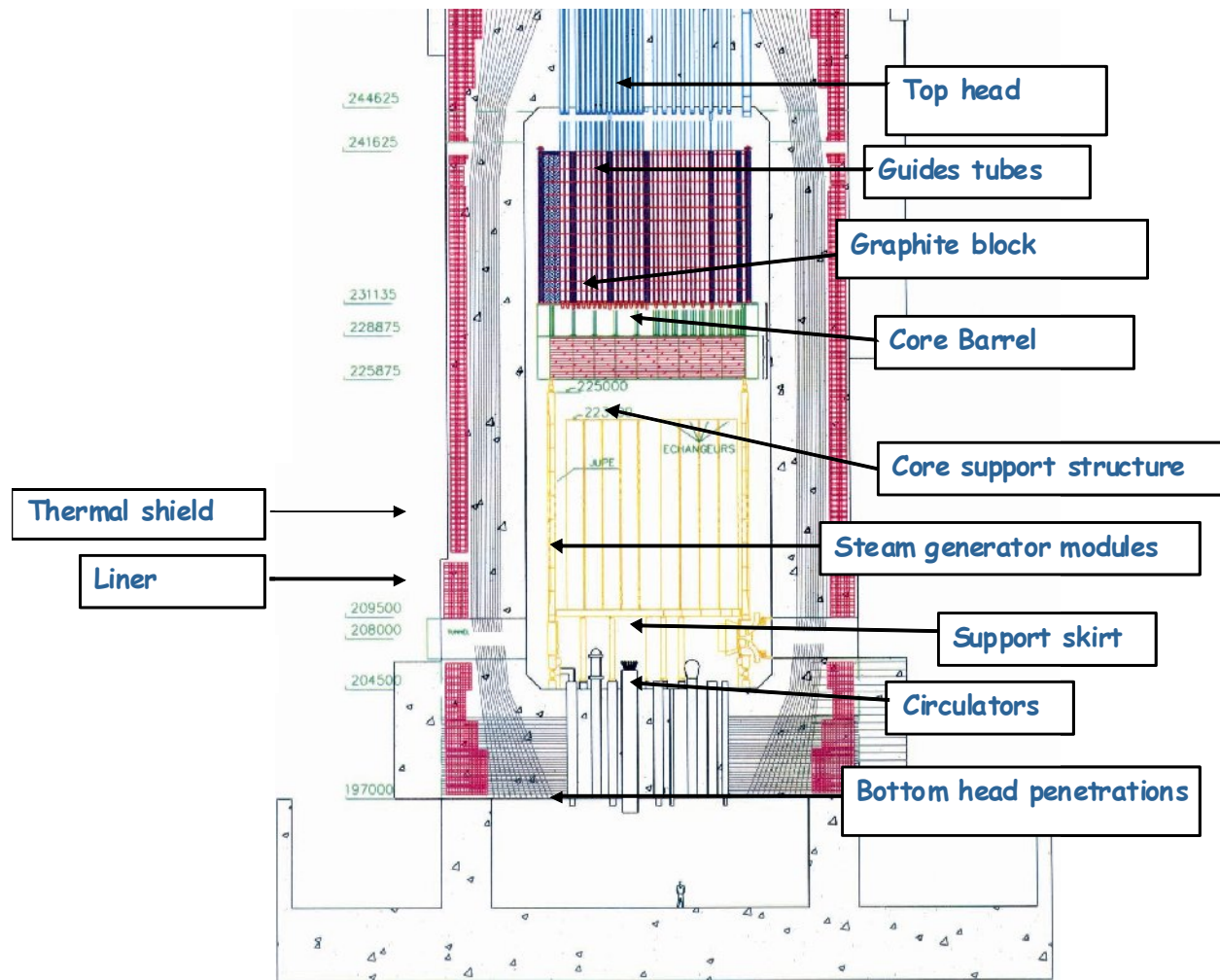


Figure 1: Schematic drawing of the reactor Vandellós I

PROJECT DESCRIPTION

The project has the following objectives:

1. Investigation of the principal applicability of a thermal decontamination for i-graphite from Vandellós I as an alternative waste management option
2. Investigation of improved waste forms for direct disposal of i-graphite from Vandellós I
3. Industrial feasibility and evaluation of the economic and safety benefits

The project started mid 2011 and the total duration will be four years. The project schedule is shown in Figure 2.

Two new methods and innovations routes will be investigated to create a new option for the waste management of the Spanish i-graphite:

- The first method is a special thermal treatment of i-graphite which allows the separation of ^{14}C from mainly unchanged remaining graphite [1, 2, 3, 4, 5]. ^{14}C is one of the key nuclides for the decontamination of i-graphite because a similar chemical behaviour can be expected for ^{14}C and the bulk ^{12}C from the graphite matrix. Therefore, the base of the thermal decontamination method is a study performed at FZ Jülich, Germany: I-graphite from the high temperature reactor AVR has been decontaminated from more than 80 % of its ^{14}C inventory by oxidizing less than 20 % of the total carbon [2]. An experimental study in lab scale will be performed to show the applicability of this thermal treatment process for the Spanish i-graphite obtained from Vandellós I.
- The second method is based on the conversion of the graphite into an impermeable graphite material (IGM) using a long term stable inorganic binder which additionally encloses the pore system [6, 7]. Beside the usage of a long term stable inorganic binder material the resulting material is homogenously filled and therefore mechanical damage would not reopen an unsealed pore system. Radiation induced graphite corrosion as well as leaching radionuclides from graphite is directly related to the open pore structure of graphite. All these effects could be neglected, if the pore system can be sealed for disposal relevant time scales. Such a new pore free graphite material has been developed by FNAG. Investigations will be performed related to the utilization of this development for the production of an improved waste form out of irradiated graphite for final disposal. This will include special investigations of the inorganic and graphite corrosion behavior in aquatic phases under γ -irradiation. A first work phase in task 2 foresees investigation of the behavior of IGM under Spanish disposal conditions. These experiments will be performed with unirradiated graphite. Especially the corrosion behavior of glass will be a key parameter for the applicability of IGM as waste matrix. Furthermore the radiolytic re-crystallization of amorphous glass compounds may disturb the matrix IGM integrity which will be simulated by γ -irradiation. Therefore additional investigations must be performed to adjust and optimize the utilized glass with respect to relevant aqueous phases of Spanish disposal sites. A second phase using i-graphite from Vandellós I will be performed when the obtained results of the first phase show the principal applicability of IGM.

	1 st year				2 nd year				3 rd year				4 th year			
	1 Qt	2 Qt	3 Qt	4 Qt	1 Qt	2 Qt	3 Qt	4 Qt	1 Qt	2 Qt	3 Qt	4 Qt	1 Qt	2 Qt	3 Qt	4 Qt
Thermal Treatment																
Set up of equipment																
Experimental Work																
Analysis of results																
Investigation of IGM																
Phase 1 with inactive graphite																
Set up of equipment																
Experimental Work																
Interim Analysis of results																
Analysis of results																
Phase 2 with i-graphite																
Set up of equipment																
Experimental Work																
Analysis of results																
Basic design study for industrial implementation																
Final report																
Evaluation of results																
Edition of a final report																

Figure 2: Project schedule

CHARACTERISATION OF VANDELLOS I GRAPHITE

The graphite of Vandellós I was manufactured by Pechiney SA in France. The manufacturing method was not well defined; Pechiney graphite was prepared by baking a paste made of oil coke and pitch, graphitized by electrical heating.

Virgin graphite characteristics are the following:

- Porosity: about 20%
- Density: 1,8 g/cm³.
- Volatile content: 0.18% mass, mainly H₂O, to a lesser extent CO₂, CO, hydrocarbons (methane, ethane, ethylene, propane, propylene, etc.).
- Water adsorption: 2.2% mass for graphite powder.
- H₂ adsorption: it has not been observed at ambient temperatures. A light weight loss of graphite observed at high temperatures (300°) due to H₂O formation.
- Chemical impurities: N, Li, Mg, Al, Ca, Fe, Ti, Sn, Sr, Cd, Sb, Ag, Cl, Mn. Co, Ni, Be, Mo, Eu.

Isotopic composition and mean activity of sleeves and Graphite pile (01/01/2000) are [8]:

³ H	38,44%	8,93E+04 Bq/g	³ H	74,97%	2,75E+05 Bq/g
¹⁴ C	5,81%	1,35E+04 Bq/g	¹⁴ C	15,32%	5,62E+04 Bq/g
⁵⁵ Fe	11,62%	2,70E+04 Bq/g	⁵⁵ Fe	2,50%	9,15E+03 Bq/g
⁶⁰ Co	17,22%	4,00E+04 Bq/g	⁶⁰ Co	3,65%	1,34E+04 Bq/g
⁵⁹ Ni	0,27%	6,25E+02 Bq/g	⁶³ Ni	2,39%	8,77E+03 Bq/g
⁶³ Ni	25,31%	5,88E+04 Bq/g	²⁴¹ Pu	0,19%	6,89E+02 Bq/g
¹³⁷ Cs	0,16%	3,79E+02 Bq/g	TOTAL	99,02%	
¹⁵⁴ Eu	0,19%	4,35E+02 Bq/g			
²⁴¹ Pu	0,29%	6,82E+02 Bq/g			
TOTAL	99,31%				

Sleeves

Graphite Pile

Notice that sleeves were placed inside the reactor pool while removing the fuel; it means that non graphite activation products like ¹³⁷Cs, TRU, etc., have been absorbed from the pool.

Gasification of virgin graphite, in order to simulate operating conditions, produces a weight loss about 14%-47% in powdered graphite, and about 10% in graphite pieces.

Currently the graphite pile is located inside the reactor building in a safe enclosure (25 years). The sleeves were extracted as described below and temporally stored at Vandellós I in cubic containers.

There are 220 cubic containers of 6 m³ of the crushed graphite obtained in the separation process carried out in Vandellós I. The total mass of waste is 1.1E+3tons.

There are 98 cylindrical containers with the wires from the sleeves obtained in the separation process carried out in Vandellós I. The total mass of waste is 22 tons [9, 10, 11].

THERMAL TREATMENT OF I-GRAPHITE

RESULTS FROM RAPHAEL AND CARBOWASTE

Thermal treatment in presence of Cl_2 could be one promising option for the removal of most metallic radionuclides. This is a well known industrial procedure for graphite purification. Therefore, the key nuclide for decontamination will be ^{14}C because it has the same chemical properties as the bulk graphite matrix consisting of ^{12}C . Whereas the complete burning of i-graphite will cause a complete release of ^{14}C to the atmosphere, partial oxidation could be an interesting, alternative.

P. C. Schmidt [12] showed already in 1979 that ^{14}C is distributed in homogeneously in the graphite matrix of an HTR fuel pebble. Therefore he oxidised the HTR fuel pebbles at high temperatures and different oxygen concentrations. High temperatures enable the oxidation of the geometric surface of a graphite sample. The results are shown in Figure 3

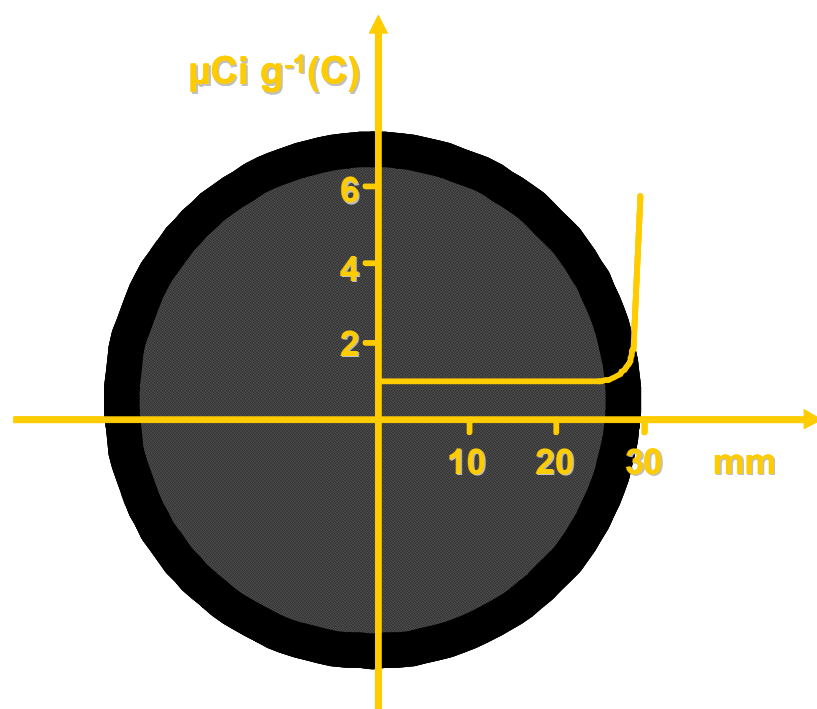


Figure 3: C-14 distribution in an HTR pebble

First investigations with i-graphite from the AVR core and the thermal column were performed by T. Podrushzina [1] at the research centre Jülich. An unexpected high ^{14}C was observed by thermal treatment in an argon atmosphere leads to a preferred release of ^{14}C with a $^{14}\text{C}/^{12}\text{C}$ ratio of about 15/1. The released ^{12}C was identified as CO_2 . This can be explained with oxidation by oxygen adsorbed at the graphite surface. This is a first hint that an enhanced ^{14}C release can be achieved with i-graphite by a surface oxidation.

△ T10 powder 1050°C ▲ T10 massive 1050°C ✕ GR-5/2 powder 1050°C ◇ T10 powder 970°C □ T10 powder 870°C

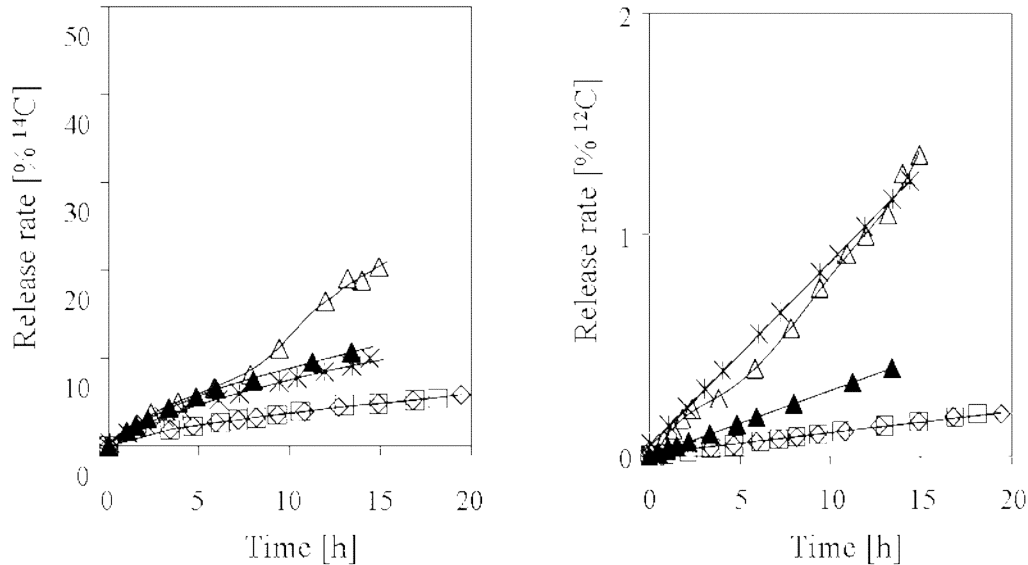


Figure 4: Thermal treatment of AVR graphite under Argon

However, the obtained total decontamination is in the range of 30 %, which is definitely not sufficient. Therefore, further experiments were performed in presence of an oxidising agent mixed with argon e.g. oxygen in the range of 1% or humidified argon [2, 3].

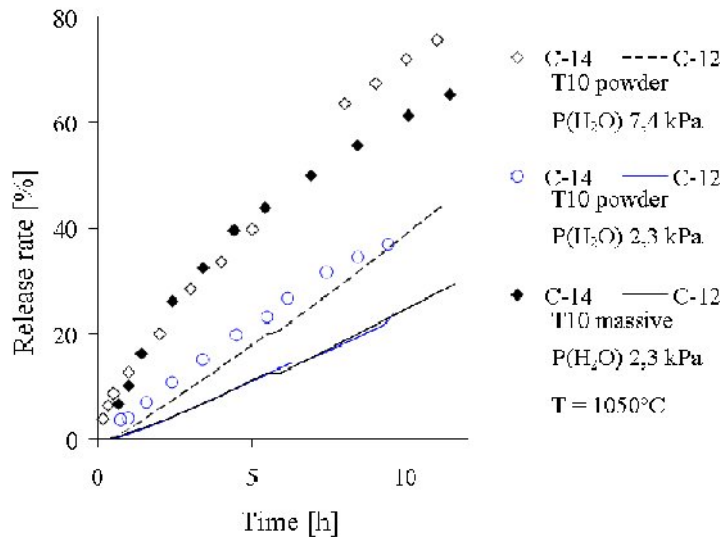


Figure 5: Treatment of AVR graphite with humidified argon.

These experiments show higher ^{14}C decontamination rates but an increase of the $^{14}\text{C}/^{12}\text{C}$ ratio. Figure 5 shows an example with AVR graphite and humidified argon. ^{14}C release rates up to 80% have been achieved. Further investigations have been performed by R. Jansen [3] and M. Florjan [2] at FZJ to optimise the decontamination process. The best results with ^{14}C release rates above 90% combined with total oxidation rates below 10% were obtained by M. Florjan [2]. However these results could not be validated until now by further examinations. Anyhow these results are related to the question why ^{14}C reacts differently than the bulk ^{12}C . The explanation must be related to an inhomogeneous distribution, a different chemical bonding of ^{12}C and ^{14}C or a combination of these two effects.

For the AVR, nitrogen is the main source for ^{14}C produced by a (n, γ) reaction. The nitrogen occurs as impurity in the graphite matrix and in the cooling gas. This explains an enrichment of nitrogen on the surface of the graphite samples. Furthermore nitrogen impurities in the graphite matrix are located at grain boundaries and eventually at lattice defects. An activation of this nitrogen will generate ^{14}C not incorporated into the bulk graphite lattice. An alternative route for the generation of ^{14}C is the activation of ^{13}C . Such a reaction is always combined with a recoil effect and may disorder the graphite lattice which would lead to zones with an enhanced reactivity. A complete understanding of these effects requires further investigation. Such programs are under the way at the Research Centre Jülich, the University of Manchester and the University of Idaho. An interesting result has been recently published by M.L. Dounzik-Gougar et. al. at the ANS winter meeting 2011 in Washington [13]. They showed an agglomeration of nitrogen on the edges of graphite planes after irradiation of graphite samples.

However all the thermal treatment experiments at FZJ had been performed with i-graphite at low temperatures (Merlin graphite) or under an inert Helium atmosphere (AVR). The reactor Vandellós I utilized CO_2 as coolant which causes additional oxidation reactions during reactor operation. Therefore the results of these thermal treatment experiments may not be valid for the UNGG graphite and experimental investigations are required to evaluate the option of a thermal treatment as a waste management route in Spain.

PROCESS DESCRIPTION

Based on these results a decontamination process (Figure 6) can be proposed, which is based on the partial oxidation of the contaminated graphite. Beside the release of ^{14}C most of the Tritium and Chlorine will be released from the graphite matrix. The off gas enriched with ^{14}C can be precipitated and fixed in a tailor-made waste matrix for disposal after separation from other volatile radionuclides. Optionally, the enrichment of ^{14}C may be increased, e.g. by a pressure swing sorption process, to a level that it can be used as source for the production of ^{14}C labeled compounds. The Tritium should be oxidized and stored for about 100 years for decay. The residual graphite can be encapsulated in a tailor-made matrix, e.g. IGM, for disposal or, if the ^{14}C decontamination factor is sufficient, completely oxidized. Also the reuse of the decontaminated graphite in the nuclear industry could be an alternative.

An experimental device in lab scale as shown in Figure 7 will be installed at CIEMAT in order to study this process. The main components are a rotating furnace with a maximum operational temperature of 1500°C and a pneumatic injector system for the transfer of the graphite into the furnace. Both components have a design which allows scale up to industrial components easily.

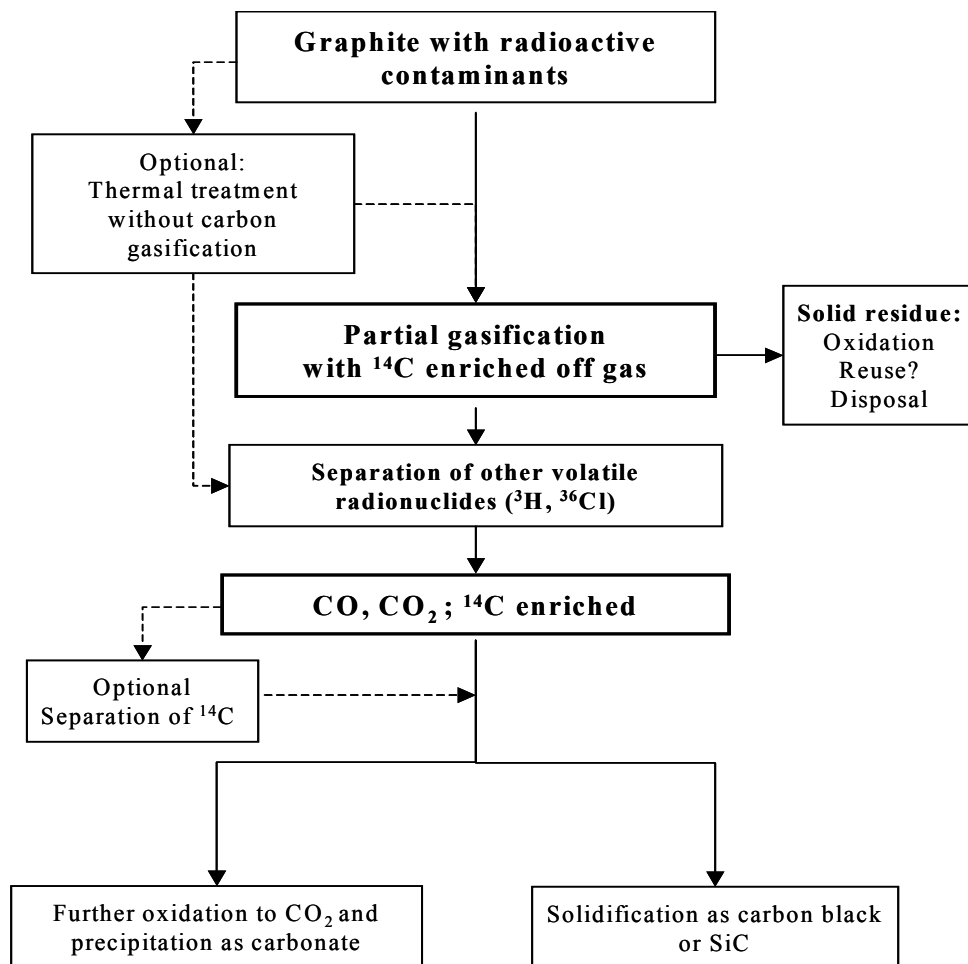


Figure 6: Proposed process scheme for thermal treatment

The mass spectrometer and the washing bottles are foreseen for analytical purposes. The set up of the system is proposed for January 2012 and first results are expected in February.

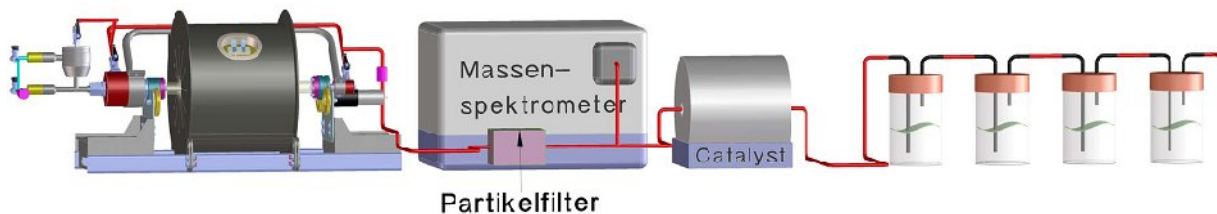


Figure 7: Schematic drawing of the proposed lab scale furnace system for treatment of i-graphite

IGM

Graphite itself is a geologically stable material proven by its natural occurrence. However its porous structure enables the penetration of aqueous phases into the graphite and therefore radionuclides can be leached. However i-graphite could be transferred into a long term stable impermeable matrix (impermeable graphite matrix IGM), which would inhibit ingress of water and therefore allow safe final disposal. Such a graphite composite material with glass as an inorganic binder has been developed by FNAG. The composite has densities better than 99 % of theoretical density and therefore a negligible porosity. Figure 8 shows such an IGM sample. The inner zone consists of virgin graphite material from UK Magnox reactors mixed with mineral and metallic scrap. The outer zone is made of natural graphite which represents an inactive coating of the radioactive material in the proposed final product. This shows also the possibility to utilize raw crushed i-graphite inclusive scrap in the proposed process and the possibility to embed other radioactive waste streams in IGM.



Figure 8: IGM sample with virgin Magnox graphite mixed with mineral and metallic scrap

PROCESS DESCRIPTION

The first step will be the granulation of the i-graphite after retrieval from the reactor vessel or an in situ granulation inside the vessel. Such processing has already been performed with the sleeve graphite. The granulated i-graphite will be mixed with an inorganic binder, e.g. borosilicate glass. The amount of the inorganic binder is in the same range as the pore volume of the former graphite parts.

In a first moulding step the outer shell will be manufactured out of natural graphite and glass. Then i-graphite mixed with the inorganic binder and optional natural graphite will be filled into this form and covered with the same mixture used for the outer shell. The final manufacturing step is hot pressing under vacuum. The pressing temperature depends on the viscosity properties of the used glass. The vacuum is required to remove gases from granulates to avoid the creation of pores. This can be done by an axial hot vacuum press or by hot isostatic pressing. The process scheme is shown in Figure 9.

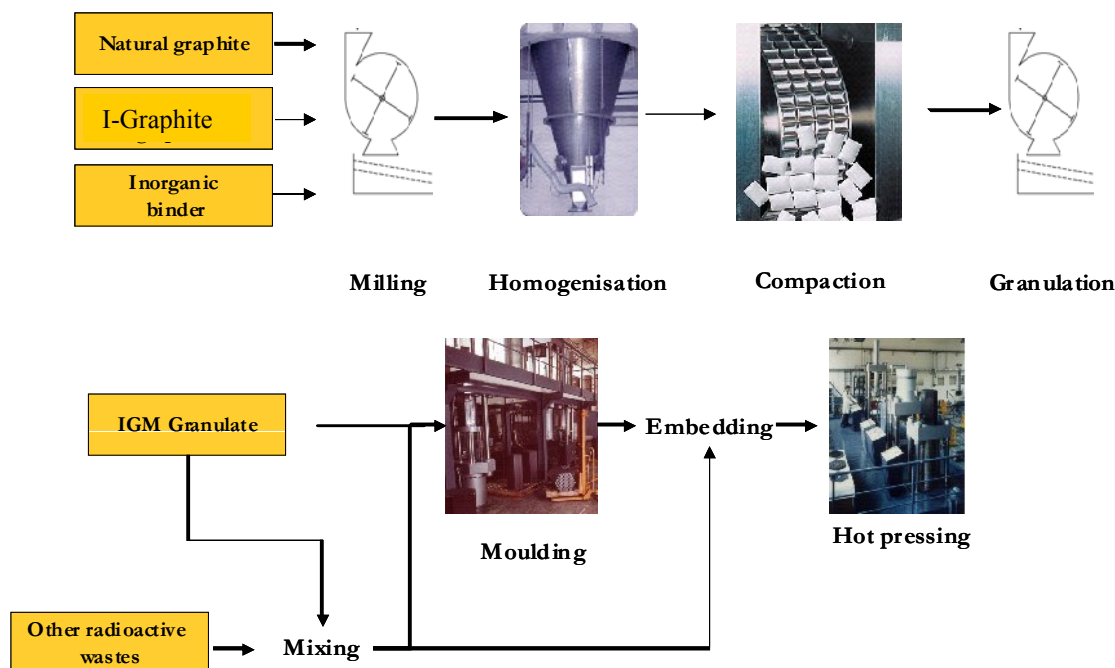


Figure 9: Scheme of the IGM manufacturing process

MATERIAL PROPERTIES

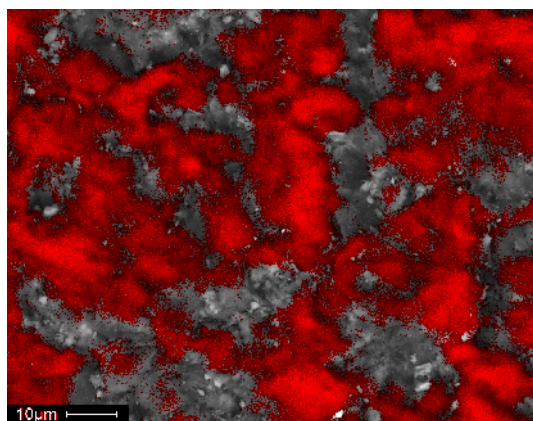
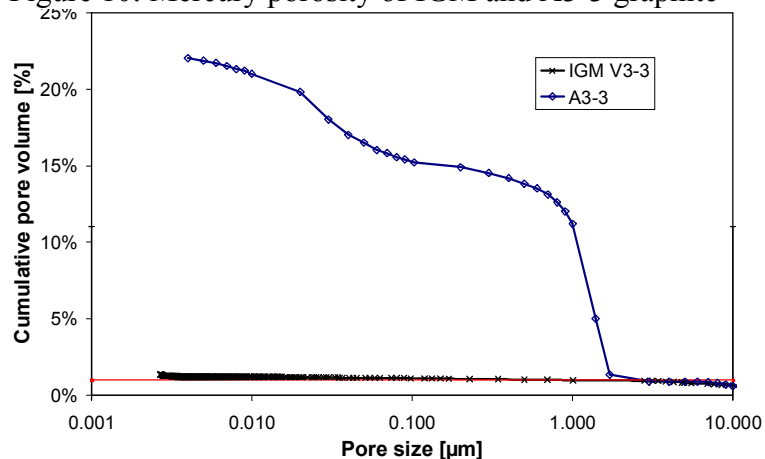
Open Porosity

The open porosity has been investigated by mercury porosity measurements. Figure 10 shows the pore volume distribution of IGM in comparison to an A3-3 graphite. The red line represents the detection limit of the measurement as a straight line parallel to the x-axis. This does not represent the increase of the detection limit for small pores and therefore it is a conservative assumption. The main open pore volume of the A3-3 material is related to a pore size of about 2 μm down to 0.8 μm . No open pores have been observed for IGM in this pore size range. Water ingress experiments showed that open pores of this size can be accessed by water whereas smaller pores will not be penetrated. Maybe this will be shifted towards smaller pore sizes under high pressure but a penetration of micro-pores seems to be not probable. In case of IGM a small pore volume of pores < 0.2 μm cannot be excluded by this measurement. This is probably related to the conservative assumption of the detection limit. But anyhow it is unlikely that pores of this small size will contribute to water penetration of the IGM.

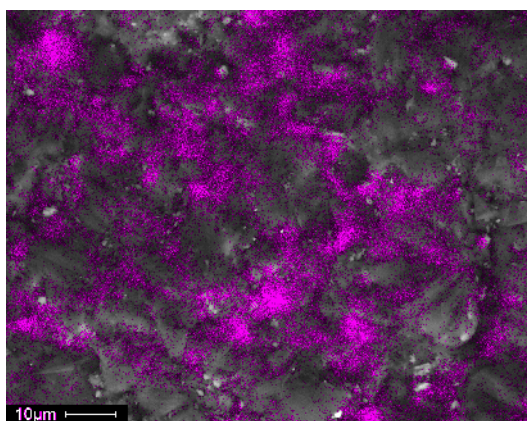
Structure of IGM

Raster electron microscopy (REM) investigations and energy dispersive x-ray examinations (EDX) has been performed at GFE, RWTH Aachen and FZ Jülich. Figure 11 A and B show the graphite in red and the glass in purple. The overlaying of these two figures (Figure 11 C) shows that the glass is percolated between graphite particles and confirmed the pore free structure already obtained by the mercury porosity measurement.

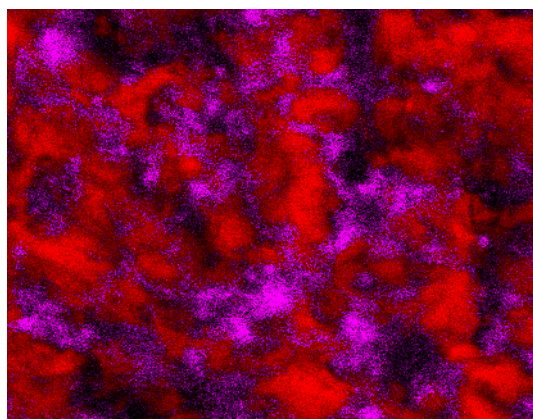
Figure 10: Mercury porosity of IGM and A3-3 graphite



A



B



C

Figure 11: and Silicon distribution in an IGM sample

A: Red Carbon
B: Purple Silicon
C: Overlay

Glass corrosion

Graphite is stable under disposal conditions and therefore no leaching of graphite is expected in aqueous phases. However, the glass may interact with aqueous phases and will be dissolved. Therefore, a leaching-resistant glass is required for the IGM in order to obtain a long-term stable

material. Therefore leaching experiments of inactive IGM samples will be performed with 15 different glass types used as inorganic binder material. Actual leaching experiments with 9 different glass types have been started already. Figure 12 shows the mass loss of the IGM samples which is only caused by the interaction of the glass with the aqueous phase. Actually the glass type C seems to be the best candidate for the IGM. However the leaching time is not long enough for a final choice of the glass material. Furthermore leaching experiments with a high corrosion sensitive glass has been started as accelerated corrosion experiment in order to study the effect on the IGM matrix.

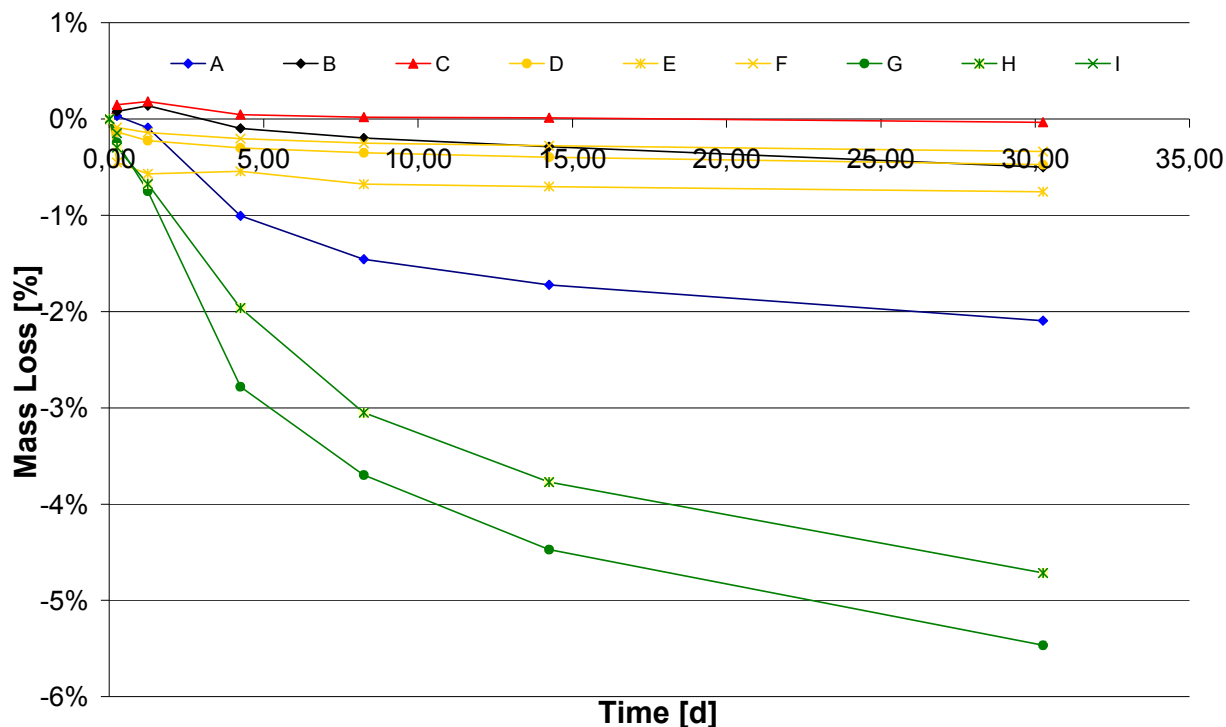


Figure 12: Mass loss of IGM by leaching in de-ionised water at 90°C

CONCLUSIONS

Both processes, the thermal treatment as well as the IGM, have the potential to solve problems related to the management of irradiated graphite in Spain. However the methods have only been tested with different types of i-graphite and virgin graphite, respectively.

Only investigations with real i-graphite from Spain will reveal whether the described methods are applicable to graphite from Vandellós I.

However all partners are convinced that one of these new methods or a combination of them will lead to a feasible option to manage i-graphite in Spain on an industrial scale.

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