

# CARBOWASTE

## *Treatment and Disposal of Irradiated Graphite and Other Carbonaceous Waste*



### Work Package 6:

## DISPOSAL BEHAVIOUR OF IRRADIATED GRAPHITE & CARBONACEOUS WASTES - FINAL REPORT

Author(s): **B. Grambow (SUBATECH), S. Norris (NDA), L. Petit (EDF), L. Petit (ANDRA), V. Blin, J. Comte (CEA), E. de Visser – Týnová (NRG)**

Reporting period: e.g. 01/04/2008 – 22/02/2013

Date of issue of this report : 19/04/2013

**Project co-funded by the European Commission under the Seventh Framework Programme (2007 to 2011) of the European Atomic Energy Community (EURATOM) for nuclear research and training activities**  
Dissemination Level

|           |                                                                            |          |
|-----------|----------------------------------------------------------------------------|----------|
| <b>PU</b> | Public                                                                     | <b>X</b> |
| <b>RE</b> | Restricted to the partners of the CARBOWASTE project                       |          |
| <b>CO</b> | Confidential, only for specific distribution list defined on this document |          |

Start date of project : **01/04/2008**

Duration : **48 Months**

---

**Distribution list**

| <b>Person and organisation name<br/>and/or group</b> | <b>Comments</b> |
|------------------------------------------------------|-----------------|
| Carbowaste partners                                  |                 |
|                                                      |                 |
|                                                      |                 |
|                                                      |                 |
|                                                      |                 |
|                                                      |                 |
|                                                      |                 |
|                                                      |                 |
|                                                      |                 |
|                                                      |                 |
|                                                      |                 |
|                                                      |                 |

| <b>CARBOWASTE</b>                                      |                                                                                                            |                                                                                                       |
|--------------------------------------------------------|------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------|
| <b>Work package:</b> 6<br><br><b>Task :</b> all tasks  | <b>CARBOWASTE document no:</b><br><br>CARBOWASTE-1303-D-WP6.<br><br>(e.g. May 2008 as date of issue: 0805) | <b>Document type:</b><br><br>D=Deliverable / M=Minutes /<br>P=Progress report /<br>T=Technical Report |
| <b>Issued by:</b> SUBATECH<br><br><b>Internal no.:</b> |                                                                                                            | <b>Document status:</b><br><br>final                                                                  |

| <b>Document title</b>                |            |                   |                       |                                                                     |                                           |                                                                                       |
|--------------------------------------|------------|-------------------|-----------------------|---------------------------------------------------------------------|-------------------------------------------|---------------------------------------------------------------------------------------|
| Final report of WP6.                 |            |                   |                       |                                                                     |                                           |                                                                                       |
| <b>Executive summary</b>             |            |                   |                       |                                                                     |                                           |                                                                                       |
| See detailed executive Summary below |            |                   |                       |                                                                     |                                           |                                                                                       |
| <b>Revisions</b>                     |            |                   |                       |                                                                     |                                           |                                                                                       |
| Rev.                                 | Date       | Short description | Author                | Internal Review                                                     | Task Leader                               | WP Leader                                                                             |
| 00                                   | dd/mm/yyyy | Issue             | Name,<br>Organisation | Name,<br>Organisation<br><i>Signature</i>                           | Name,<br>Organisation<br><i>Signature</i> | Name,<br>Organisation<br><i>Signature</i>                                             |
| 01                                   | 25/03/2013 | First issue       | B. Grambow            | Simon Noris, V.<br>Blin, E. de<br>Visser, L. Petit,<br>N. Moncoffre |                                           |                                                                                       |
| 02                                   | 19/04/2013 | Final draft       | Bernd<br>Grambow      | tous                                                                |                                           |                                                                                       |
| 03                                   | 26/04/2013 | Final version     | B. Grambow            |                                                                     |                                           |  |



## CONTENTS

---

|                                                                                                     |    |
|-----------------------------------------------------------------------------------------------------|----|
| Contents                                                                                            | 6  |
| Executive summary                                                                                   | 8  |
| Task 6.1: Disposal behaviour of graphite waste                                                      | 13 |
| Purposes of task                                                                                    | 13 |
| Impact of reactor operation on chlorine behaviour in graphite                                       | 14 |
| Methodology                                                                                         | 15 |
| Characterization and thermal behaviour of constitutive chlorine                                     | 16 |
| Main results on implanted chlorine release                                                          | 17 |
| About the graphite structure evolution                                                              | 17 |
| Hydrodynamics and water uptake                                                                      | 18 |
| Methodology                                                                                         | 18 |
| Water uptake in non-irradiated graphite                                                             | 19 |
| Water uptake in irradiated graphite                                                                 | 19 |
| I-graphite leaching behaviour                                                                       | 20 |
| Chlorine 36                                                                                         | 21 |
| Carbon 14                                                                                           | 22 |
| Conclusion                                                                                          | 22 |
| Main findings                                                                                       | 22 |
| Remaining uncertainties                                                                             | 23 |
| Task 6.2: Disposal behavior of alternative waste forms                                              | 23 |
| Introduction                                                                                        | 23 |
| Disposal behavior of Carbonaceous waste                                                             | 24 |
| IGM: A porous free graphite matrix for a long term safe storage of irradiated graphite (i-graphite) | 27 |
| Conclusions and outlook                                                                             | 27 |
| Task 6.3: Waste packages                                                                            | 28 |



|                                                                                           |    |
|-------------------------------------------------------------------------------------------|----|
| Task 6.4 Performance assessment of disposal of graphite and carbonaceous wastes           | 32 |
| STATE OF THE ART: SAFETY CASE                                                             | 32 |
| SURFACE DISPOSAL FACILITY FOR GRAPHITE WASTE                                              | 35 |
| Spain: Summary of work by ENRESA – Spanish disposal concept and surface disposal analysis | 35 |
| Romania: Summary of work by INR - Romanian disposal concept and surface disposal analysis | 39 |
| GEOLOGICAL DISPOSAL FACILITY FOR GRAPHITE WASTE                                           | 46 |
| Lithuania: Summary of work by LEI - Study on geological disposal of graphite              | 46 |
| United Kingdom: Summary of work by NDA RWMD - UK study on geological disposal of graphite | 51 |
| French Irradiated Graphite Management Scenarios                                           | 54 |
| CONCLUSIONS                                                                               | 62 |
| Main findings                                                                             | 62 |
| Residual uncertainties                                                                    | 62 |
| References                                                                                | 64 |

## EXECUTIVE SUMMARY

---

The utilization of nuclear graphite in reactors as moderator, reflector or operational material leads to an accumulation of radioactivity by neutron activation both of constituent elements of the graphite and of impurities. Radionuclide inventories at reactor end-of-life depend on impurity contents, on irradiation history, on reactor temperature, cooling gas composition etc. The principal long lived radionuclide species present are  $^{14}\text{C}$  and  $^{36}\text{Cl}$ , with shorter-lived species including  $^3\text{H}$ ,  $^{60}\text{Co}$  and small quantities of fission products and actinides. A fraction of these radionuclides is released during reactor operation due to temperature and radiolytic graphite corrosion. After removal from the reactor, irradiated nuclear graphite still remains radiotoxic for hundreds of thousands of years. Today about 250 000 tonnes of irradiated graphite have been accumulated worldwide. If no reuse is undertaken, this becomes a waste material. One may treat the waste to concentrate the radionuclides in small volumes of new carbonaceous waste matrices, and different treatment and recycling options have been studied in the CARBOWASTE program. However, inevitably some or all of the irradiated graphite is likely to remain as waste, and requires management and disposal to provide isolation and containment, thus ensuring long term protection of humans and the environment.

Irradiated graphite waste and other waste products are being and will be stored for many years in interim storage sites, with the associated burden for active radioprotection and site surveillance. Disposal of radioactive waste forms a key part of international policy for long-term radioactive waste management. Disposal can be implemented by isolating the waste from the biosphere in a surface disposal facility (SDF), or in deep geological disposal facility (GDF). The irradiated graphite waste itself, whether treated or not, will likely be encapsulated in waste packages as part of the disposal process, which further provides for long term stability. Disposal facilities are designed such that they do not require active radioprotection measures and are passively safe, based on the performance of manmade and natural barriers to provide containment and isolation of the waste, and ensure any radionuclide transfer back to the environment is radiologically insignificant.

In order to assess whether irradiated graphite can be disposed of as waste without or with further treatment, either in an SDF or a GDF<sup>1</sup>, one needs to assess its behaviour under disposal conditions. Disposal conditions are influenced by the natural hydrogeological environment and by the waste package and other engineered barriers. It must be assured that any radiological risk arising from a potential release of irradiated graphite derived radionuclides to the biosphere meets regulatory criteria. Scenarios have to be developed to consider how / if groundwater could come in contact with the disposed waste product. Processes by which waste-derived radionuclides might be entrained in any groundwater pathway have to be considered, as well as processes affecting any subsequent

---

<sup>1</sup>A geological disposal facility can also be referred to as a repository, where the disposal facility is envisaged as being at depth in a suitable geological environment.

radionuclide migration in groundwater to the biosphere, and biosphere processes that could result in a radiological dose to humans or flora and fauna. Migration from a disposal facility of irradiated graphite-derived radionuclides in a gas phase also needs consideration.

In CARBOWASTE, the study of the disposal properties and disposability of irradiated graphite and carbonaceous wastes has been subdivided in four strongly interlinked tasks:

- 6.1 Disposal behaviour of graphite wastes
- 6.2 Disposal behaviour of carbonaceous wastes
- 6.3 Improving disposal behaviour by suitable waste packages
- 6.4 Assessment of waste performance under disposal conditions in the long term

**Task 6.1** of the CARBOWASTE project is devoted to the study of the mobilization of the two long-lived radionuclides  $^{14}\text{C}$  and  $^{36}\text{Cl}$  in irradiated graphite, considering irradiated graphite origin, manufacturing process and reactor operating conditions. Operating temperature could range from  $150^{\circ}\text{C}$  in the coldest parts of the first gas-cooled reactors to  $550^{\circ}\text{C}$  for the hottest parts of AGRs. Irradiation leads to defects in the polycrystalline structure whereas high temperatures promote a kind of healing process of the structure.

Radionuclide inventories and their behaviour under repository conditions both depend on the location and chemical form of radionuclides in irradiated graphite, which in turn is influenced by reactor operating conditions. The  $^{36}\text{Cl}$  inventory in French graphite waste is calculated to arise from only about 1/100th of the initial chlorine content in graphite before irradiation, controlled by significant release at hot parts of the graphite. Stable Chlorine in non-irradiated graphite samples was found by XPS both as organic and inorganic oxy-chloride species. SIMS measurements also proved that it is distributed in a diffuse manner together with small hot spots. Stable chlorine speciation in non-irradiated graphite was also confirmed by XAFS measurement. Thermodesorption experiments show that only hydrogen chloride is detected as chlorinated gaseous species.

Chlorine behaviour under reactor operating conditions was simulated using  $^{37}\text{Cl}$  implanted samples. Chlorine implantation breaks graphite crystallites even at doses of  $0.5 \text{ dpa}^2$  while thermal annealing has a recovering effect on graphite structure. Overall,  $^{37}\text{Cl}$  implanted samples are thus structurally close to irradiated graphite. Thermal treatment showed that the implanted chloride is highly mobile and starts to be released at  $200^{\circ}\text{C}$ .

Graphite is a highly porous medium. Radionuclides can only be released from the graphite if water has access not only to the outer surface of disposed graphite blocks but if it can as well impregnate within irradiated graphite porosity. The studies have shown that in absence of hydraulic gradients, water impregnation in the porous medium of non-irradiated graphite is relatively slow and seems to be

---

<sup>2</sup> dpa= "displacements per atom"= dose unit in materials describing the fraction of atoms of the material which are displaced by ballistic radiation effects

controlled by a diffusion process. Hydrodynamic dispersion coefficients and permeability values were determined. Irradiation increases the kinetics and the impregnation rate. This is correlated to the fact that radiolytic corrosion and the formation of more hydrophilic C-H or C-O bonds leads to the reduction of electrostatic repulsion and faster and higher impregnation. All results show that for disposal-relevant time periods, water impregnation is very fast and does not limit radionuclide release. In the presence of only weak hydraulic gradients in a repository, water transport in the irradiated graphite is controlled by advection and in absence of hydraulic gradients by diffusion.

Radionuclide leaching behaviour was studied under disposal conditions in order to quantify as precisely as possible long-term release of radionuclides after water ingress in the repository and into irradiated graphite products. The studies were carried out on irradiated graphite from CO<sub>2</sub>-cooled reactors: Magnox (UK) and UNGG (France) reactors. Operational waste (such as graphite sleeves) was not studied.

Chlorine 36 release from the graphite waste into groundwater occurs in two stages. The first stage shows very rapid <sup>36</sup>Cl release kinetics (labile fraction) with a rate governed by diffusion through graphite porosity. Diffusion coefficients are in the order of 10<sup>-11</sup> to 10<sup>-12</sup> m<sup>2</sup>/s. The second stage shows slow <sup>36</sup>Cl release kinetics (non-labile fraction). On the whole, <sup>36</sup>Cl release rates vary widely ranging from few % to 90% of the initial inventory. The higher the reactor operating temperature, the lower the <sup>36</sup>Cl release rate of the resulting graphite waste into water. This may be due to the fact that with increasing temperature a significant part of the labile fraction of <sup>36</sup>Cl has already been released in the reactor. Leached Cl occurs mainly in form of chloride ions but chlorite was observed as well. Chloride ions show low retention behaviour in the geosphere.

Carbon 14 release in solution is always found to be low with a fast initial release followed by near stabilization. The two stages of release of <sup>14</sup>C may be related to two different ways of production in reactor (<sup>14</sup>N activation of surface adsorbed air versus <sup>13</sup>C activation of graphite structure). However, no difference was observed for air-cooled piles compared to CO<sub>2</sub>-cooled reactors. In contrast to <sup>36</sup>Cl, release rates of <sup>14</sup>C are not controlled by diffusion in graphite pores. The chemical form of released <sup>14</sup>C strongly affects the migration properties in the repository and surrounding geology. It may be in gaseous or dissolved form, organic or inorganic. <sup>14</sup>C is found to be mainly released in solution. Gaseous species represent less than 0.01 % of the total <sup>14</sup>C activity and are only detected as organic species. Inorganic forms (CO<sub>2</sub>, CO<sub>3</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>) are strongly trapped in cementitious materials by sorption and incorporation in cement phases, whereas organic species are much more mobile, all the more so since they can be released as gaseous species.

**Task 6.2** follows task 5.2.3 “Carbonaceous ceramics for waste management” in addressing graphite canisters for waste storage as well as non-graphite uses such as silicon-carbide (SiC) and calcium carbonate. Also IGM (impermeable graphite matrix) has been studied. “Recycled products” considered in Work Package 5 include products specially manufactured to stabilise carbon in a radioactive waste disposal site, or to act as confinement or packing material for other wastes and thermal management, in a repository environment. The stability of silicon carbide formed from graphite and irradiated graphite has been studied under repository conditions, representative for

either in salt, granite or clay rock. The measured activity of C-14 leached from irradiated graphite is higher than the activity of C-14 leached from the SiC made from this graphite. Based on this, it seems that the transformation of irradiated graphite to silicon carbide could be a way of decreasing the C-14 release from the material. Because of a limited amount of irradiated graphite available to Task 6.2, the above mentioned tests were undertaken with very small amount of irradiated graphite (0.02g in 20ml leachant) compared to the amount of silicon carbide that was used (0.4g in 20 ml leachant). This could have had an influence on the leaching rates observed; further tests would be needed to confirm that silicon carbide formed from irradiated graphite could be a suitable product that has a lower C-14 release rate.

By “vitrification”, porosity of I-graphite could be closed and I-graphite could be transferred into long term stable impermeable alternative waste matrix (IGM) which would inhibit ingress of water and therefore allow for safe final disposal.

**Task 6.3:** The disposal properties of irradiated graphite waste can largely be improved by the emplacement in suitable waste packages. The French design considers for example emplacing graphite waste in metal carts which are then put into concrete containers. Cement or mortar would then be injected into the container, which would be completely closed with a concrete cap. Concrete and cement-based materials will thus play an important role, as a barrier against access of groundwater as well as against migration of radionuclides away from the waste. Cement is also used in Spain as engineered barrier material. It was shown that graphite powder is mechanically compatible with cement pastes. A particular problem is graphite dust and coated particles from HTR reactors. Special encapsulation is necessary to provide for stable waste matrices. In the CARBOWASTE project, 3 methods were successfully tested: encapsulation in cement, in cold ceramics and in glass.

In order to assess the long term performance of the various packaging concepts under repository conditions (performance calculations in Task 6.4), one needs to determine its capacity to retain radionuclides. Retention values indicate that a diffusive front of radionuclides through a barrier such as cement could be delayed by hydrodynamic and chemical processes. Retention properties depend on the mineralogical composition of the cementitious materials, their alteration state, the kinetics and reversibility of retention and the geochemical conditions of the water. Work was concentrated on the barrier function of differently altered well-aged CEM-V cement against  $^{36}\text{Cl}$  release. Degradation was confirmed by decrease of XRD data on portlandite.

A kinetic study showed a gradual increase of  $\text{Cl}^-$  retention with time suggesting “fast” sorption processes (likely surface sorption phenomena) followed by an additional slower retention. But in any case, retention of  $\text{Cl}^-$  by the cement paste was weak: a maximum  $R_d$  value of  $35 \text{ ml.g}^{-1}$  at a low chloride concentration ( $4.8 \cdot 10^{-5} \text{ mol.l}^{-1}$ ) was obtained for the degraded state. At that state retention of  $\text{Cl}^-$  was also found reversible. The value decreased when chloride concentration increased, indicating sorption site saturation by inactive chloride. Hence, if one wants to take credit for  $^{36}\text{Cl}$  retention on cementitious waste package materials, one needs to be able to identify and quantify all important chloride sources in a repository.

**Task 6.4:** The implementation of irradiated graphite disposal in an SDF or a GDF requires us to demonstrate our confidence that such a facility would be safe, during both the operational period and after it has been sealed and closed. A safety case<sup>3</sup> is the vehicle we use to demonstrate our understanding of environmental safety. Regulators have issued guidance on what they require to permit the development of an SDF or a GDF, which a safety case needs to address. Quantitative studies of post-closure safety in a safety case focus on how safety is provided for radionuclides that might dissolve in and be transported by groundwater after an SDF or a GDF is closed. After closure, this is the most likely way for radionuclides to reach those parts of the environment in contact with or readily available for use by humans (the accessible environment). However, other processes that could lead to release of radionuclides to the accessible environment in the post-closure period, including gas-phase transport and human intrusion, could also be considered.

Assessment studies have been undertaken as part of CARBOWASTE for both surface disposal facilities (ENRESA and INR), and deep geological disposal facilities (NDA RWMD and LEI) in the context of respective national waste policy, national regulations and national graphite waste inventory. The approach taken in France to irradiated graphite is also considered. Conclusions have been drawn, based on CARBOWASTE studies, of the disposability of irradiated graphite in surface disposal facilities and geological disposal facilities that are backed by participating national waste management programmes.

The analyses undertaken as part of CARBOWASTE have demonstrated that it should be possible to safely dispose of irradiated graphite wastes in isolation (i.e. in vaults containing only packages of graphite wastes) in a wide range of disposal systems (i.e. combination of disposal concept / EBS and geosphere), including in an SDF and in a GDF, and a wide range of host rocks. Assessment calculations show that regulatory guidelines can be satisfied even given conservative assessment assumptions. A broader range of systems might be suitable given less conservative calculation assumptions. One particular issue that potentially requires careful management is the potential impacts associated with disruption of, or large scale intrusion into, an SDF.

It may also be possible to safely dispose of irradiated graphite wastes in the same vaults as other intermediate level wastes (ILW) in a wide range of disposal systems. However, a broader range of processes become important, behaviour becomes more site / design specific and the important scenarios and behaviours may change as the system evolves. This makes it difficult to generically explore the suitability of graphite for geological disposal with other ILW. Specific waste types of concern are those that give rise to bulk gas generation (i.e. metals, organics, strongly irradiating wastes) and that might lead to incorporation of C-14 in methane gas (i.e. organics), and therefore increase the potential for generation and transport of C-14 labelled gases. If transport of C-14 in gas is of concern for segregated graphite waste packages, e.g. potentially in a fractured host rock, it is likely

---

<sup>3</sup> Many national programmes use the term "safety case", whereas in the UK programme the term "Environmental Safety Case" is used. Note that safety case is not synonymous with "performance assessment", which is a component of a safety case and not a safety case in itself.

that further performance benefits would be obtained from disposing graphite in concrete containers rather than steel containers, thereby reducing bulk gas generation to a very low level. Therefore, although it may not be necessary in all cases, there are advantages to disposing graphite wastes in isolation compared with co-disposal in the same vaults as other ILW.

The safety and environmental assessments related to irradiated graphite disposal as undertaken in the CARBOWASTE project confirm we have sufficient understanding to justify site-specific studies on the disposal of graphite wastes in an SDF or a GDF, and that we have sufficient underpinning understanding at a generic (non site-specific) level to be confident that graphite waste can be disposed in a manner such that relevant radiological protection regulations can be attained. Our confidence that we can develop an SDF or a GDF is built on our understanding of how multiple barriers – engineered barriers and natural barriers - can work together to ensure safety. We therefore have confidence that, for specific site and disposal concept, we can develop an optimised design that meets all environmental safety requirements.

Residual uncertainties for irradiated graphite disposal, which could be progressed via future research, have been identified as part of the assessment studies undertaken in CARBOWASTE WP6.4. Such future research could assist in optimisation studies for an SDF or a GDF. However, it is to be emphasised that, even in the absence of such future work, **we have a sufficient understanding of irradiated graphite now to conclude with confidence, on the basis of work undertaken in the EC CARBOWASTE project, that irradiated graphite waste can be safely disposed in a wide range of disposal systems.**

## TASK 6.1: DISPOSAL BEHAVIOUR OF GRAPHITE WASTE

### PURPOSES OF TASK

Disposal behaviour is one of the main issues when considering graphite waste management scenarios. In this regard, carbon 14 and chlorine 36 are of particular interest owing to their long half-lives and their potential dose impact:

- carbon 14 (5730 yr) is one of the main radionuclide in i-graphite on the activity level viewpoint (up to  $10^4$  to  $10^6$  Bq / g). Its mobility under disposal conditions highly depends on its chemical form
- chlorine 36 ( $3.02 \times 10^5$  yr) content in i-graphite is very low (some tens of Bq / g) but features a high mobility in cementitious materials commonly used in disposal and the geological environment

They are both weak  $\beta$ -emitters that do not present an external radiation hazard, but because of their ease of incorporation into living organism, it is very important to assess and understand their release rate and mechanism in disposal conditions.

Task 6.1 of the Carbowaste project is devoted to the study of the mobilisation of these two long-lived radionuclides in i-graphite. In order to be able to reach reliable conclusions, specific studies must take into account the diversity of i-graphite as their origin, manufacturing process and operational history are of significant importance.

Indeed, the different petroleum cokes that were used for graphite manufacture led to a modulation of graphite properties (degree of anisotropy). Although purification steps were performed during manufacture, some impurities remain at trace level in the nuclear graphite. These impurities were activated under neutron flux. During operation, they were partly released due to temperature and graphite radiolytic corrosion. The resulting radiological inventories thus strongly depend on reactor operating conditions.

Reactor operating conditions also have a strong impact on i-graphite properties and radionuclide behaviour. Operating temperature could range from 150°C in the coldest parts of the first gas-cooled reactors to 550°C for the hottest parts of AGRs. Neutron flux also greatly varied from one reactor to another depending on their design, the nuclear fuel and the in-service operation, but also within each reactor depending on graphite location. For instance, the moderating process amounts in i-graphite from few dpa in natural uranium fuelled reactors up to 25 dpa in uranium enriched fuelled reactors during reactor lifetime. Irradiation has led to defects in the polycrystalline structure whereas high temperatures have promoted a kind of healing process of the structure. These aspects were studied in Work Package 3.

Task 6.1 studies presented in this section can be divided into three main topics, which are connected to one another:

- The first part of task 6.1 is dedicated to chlorine 36 behaviour in graphite under reactor operating conditions. It can indeed be assumed that radionuclides behaviour under repository conditions depends on their location and chemical form in i-graphite.
- The second part of task 6.1 is devoted to water impregnation within i-graphite porosity as such a process can limit radionuclide release.
- Finally, the last study focuses on radionuclide leaching behaviour under disposal conditions in order to quantify as precisely as possible radionuclides long-term release after water ingress in the repository.

It should be noted that due to Carbowaste members strategy on graphite waste management, studies carried out within the framework of the Carbowaste project on disposal behaviour are exclusively focused on i-graphite from CO<sub>2</sub>-cooled reactors that is to say from Magnox (UK) and UNGG (France) reactors. Operational waste (such as graphite sleeves) was not included for time reason in these studies.

### IMPACT OF REACTOR OPERATION ON CHLORINE BEHAVIOUR IN GRAPHITE

Whereas chlorine 36 content in i-graphite is in most cases very low (less than a hundred Bq / g) its long lifetime (301,000 years) together with its high mobility in cementitious materials and geological environment can lead to significant dose impact under disposal conditions. .

In 1997 NIREX carried out a study on chlorine 36 content in i-graphite from PGA Magnox and a Gilsocarbon AGR graphite samples. It was shown that chlorine impurities are removed from graphite

by radiation and thermal processes during reactor operation, leading to the transfer of chlorine 36 to other waste streams. This observation was confirmed by measurements in reactors that evidenced chlorine 36 deposits in desiccants of the cooling circuit and onto the cold reactor components. It was also confirmed through experimental work on graphite samples irradiated with an electron beam as radiation source. It was observed that about half of the constitutive chlorine was early lost in Magnox reactors and about 30% in AGR.

Radionuclide inventory calculations were carried out on UNGG graphite with an identification calculation-measurement method developed by EDF. This method is detailed in a Carbowaste technical report "Modelling of isotope release mechanism based on fission product transport codes" issued within the framework of WP3. Results evidenced that the chlorine 36 inventory measured in various samples actually arises from about 1/100<sup>th</sup> of the initial chlorine content in graphite before irradiation. The chlorine impurity content which is consistent with the chlorine 36 inventory is in the order of a few hundred mg/t whereas the initial chlorine content in non-irradiated graphite is in the order of a few tens of mg/kg. As for British graphite, chlorine 36 deposits were also observed on the cold reactor components of UNGG reactors. Finally, inventory calculations performed on French graphite also evidenced a clear relation between the graphite coke nature and the chlorine 36 inventory.

It has to be admitted that the way the chlorine is released during reactor operation is poorly known. The effect of parameters such as temperature, neutron flux or graphite natures need better understanding. This is important not only for the robustness of the radiological inventory of graphite waste but also because it could help to understand and forecast the chlorine 36 mobility and behaviour under repository conditions.

---

## METHODOLOGY

---

The behaviour, distribution and speciation of chlorine in nuclear graphite were experienced through the study of the thermal behaviour of the constitutive chlorine<sup>4</sup> and of chlorine implanted in the graphite (chlorine 37). The use of implanted chlorine graphite samples is preferred to chlorine 36 in i-graphite samples for at least three main reasons:

- The first and most important reason is that chlorine 36 content in i-graphite from gas-cooled reactors is very low (less than a hundred Bq/g, i.e. some ppb). Its content is far below experimental detection limits for techniques allowing access to chemical speciation and location in the matrix;
- A second reason is due to the intrinsic heterogeneity of i-graphite and of the radionuclides location in available i-graphite samples trepanned from gas-cooled reactors. It is not possible to access to a parametric study with i-graphite samples whereas chlorine implanted samples prepared in a laboratory with chosen and known parameters does.
- At last, the use of i-graphite samples involves operational difficulties due to radioactivity.

The representativeness of such implanted chlorine samples is a key issue. However, when chlorine 36 is generated by chlorine 35 activation in reactor, its recoil energy is high enough to allow a

---

<sup>4</sup> Chlorine 35 is the main precursor of chlorine 36 in graphite.

displacement from its chlorine 35 original structural site. Such a process is reproduced by the implantation process. Moreover it has been shown that, implanted graphite samples feature structural modifications similar to i-graphite.

All results, experimental protocols and special treatments of the samples used to avoid any interference with pollutants are detailed in the Carrowaste technical report on “Mobility and leaching of chlorine in chlorine implanted graphite” issued April 2011 by the Institute of Nuclear physics of Lyon (IPNL).

This study was carried out on virgin graphite samples from G2 and SLA2 UNGG reactors. HOPG samples (Highly-Oriented Pyrolytic Graphite) were also used as a reference in order to study the effect of the structure and porosity of the material. The chlorine concentration profiles were determined using SIMS (Secondary Ion Mass Spectrometry) and the graphite structure was characterized by Raman microspectroscopy. Thermal desorption (TDP) was used to study the chemical forms of released chlorine at different temperatures. These experiments were performed from ambient temperature to 800 °C. XPS (X-ray Photoelectron Spectroscopy) and XANES (X-ray Adsorption Near Edge Structure) analyses were performed on virgin samples in order to characterize constitutive chlorine speciation in nuclear graphite.

For chlorine 37 implanted samples, after a pre-annealing step, it was chosen to implant chlorine 37 in the graphite at a fluence of  $5 \times 10^{13}$  per  $\text{cm}^{-2}$  and 200 or 250 keV energy, in order to simulate the chlorine 36 which is activated and then displaced from its structural site under reactor operation. After that, the samples underwent thermal annealing between 200 and 1100 °C during 2 or 4 hours to study the thermal behaviour of chlorine.

## CHARACTERIZATION AND THERMAL BEHAVIOUR OF CONSTITUTIVE CHLORINE

The distribution of constitutive (naturally-occurring) chlorine and oxygen in the nuclear graphite was studied by SIMS. **A heterogeneous distribution of constitutive chlorine and oxygen is evidenced.** This result was also observed by CEA on i-graphite samples as presented in the Carrowaste technical report “Spatial distribution analyses of chlorine 36 in UNGG graphite” issued in 2012 by CEA.

For chlorine the heterogeneous distribution is characterized by hot spots of very small size. Nevertheless, it was impossible to determine **the size of these clusters of chlorine** as they **are smaller than the spatial resolution of the used apparatus (<5  $\mu\text{m}$ )**. Chlorine spots do not correlate with that of oxygen atoms. In contrast oxygen atoms distribution seems to be related to the matrix porosity. The thermodesorption apparatus was coupled with mass spectrometry in order to characterize released chemical species. Overall, seven gaseous species were identified. Carbon dioxide, carbon monoxide and water were mostly desorbed, whereas hydrogen chloride was the less desorbed. Actually, the amount of desorbed chlorinated species was found to be about 150 times smaller than desorbed carbon dioxide and monoxide. **Only hydrogen chloride was detected as chlorinated gaseous species. No desorption of chlorine ( $\text{Cl}_2$ ) was observed. Hydrogen chloride desorbs in two stages, which may be related to two locations (different accessibility), or two chemical species.**

In order to check these hypotheses, XPS and XANES analyses were performed. **The XPS analyses highlighted the presence of two chemical forms of constitutive chlorine:  $70 \pm 9$  % of organic species (chlorine bound to a carbon atom of the graphite matrix) and  $30 \pm 9$  % of inorganic species (oxychlorine compounds).** After thermal treatment, chlorine was only detected as organic species. In

order to confirm and complete these results, the speciation and the degree of oxidation of the constitutive chlorine in the nuclear graphite was characterized by X-ray Absorption Near-Edge Structure spectroscopy (XANES). The XANES analyses of virgin nuclear graphite samples confirmed the organic speciation and degree of oxidation ( $-1$ ) of the constitutive chlorine. Nevertheless, these experiments did not allow knowing whether chlorine is covalently bound to carbon atom within linear chains or within aromatic compounds. The thermal treatment led to a decrease in the amount of chlorine species but changed neither its speciation nor its oxidation degree. Such results are consistent with those obtained by TDP.

---

### MAIN RESULTS ON IMPLANTED CHLORINE RELEASE

---

Thermal annealing experiments were performed on non irradiated graphite samples that were implanted with chlorine 37 implanted samples. No measurable diffusion or transport phenomenon was observed. Between 200 and 1100 °C, for all the nuclear graphite studied, the **main migration mechanism of chlorine is release**. The release activation energy was estimated from the Arrhenius Law to be below 0.50 eV. Since this value is very low, **the release of chlorine can be considered as a quasi-athermal process which explains that a part of the chlorine is extremely mobile in nuclear graphite during thermal annealing experiments**. It was also observed that the percentage loss of chlorine 37 increases as a function of the annealing temperature up to 800 °C, but seems to stabilize above 8 hours of treatment.

The effects of porosity and structural orientation of graphite on the release of chlorine were studied on two preferential orientations of graphite grains for SLA2 moderator nuclear graphite samples and for non-porous and very orientated monocrystalline HOPG samples. **The importance of the effects of texture and structural orientation of a matrix on the migration mechanism of an impurity**, such as chlorine, **is evidenced**. It is shown that graphite pores constitute preferential pathways for thermal release of chlorine. In the case of nuclear graphite chlorine is therefore principally released due to the porosity of the material.

---

### ABOUT THE GRAPHITE STRUCTURE EVOLUTION

---

Raman spectroscopy experiments show that graphite samples **polishing induces a decrease in the size of the crystallites and an increase in the distribution of the interplanar space dimension**. The samples are therefore altered by the polishing step, even if this is done manually. Pre-annealing enables the removal of some of the polishing defects.

Implantation induces a clear modification in graphite Raman spectra. **Chlorine implantation breaks graphite crystallites and induces a decrease in their size**. During implantation bonds between  $sp^2$ -hybridized carbon atoms located in aromatic rings are broken while bonds are formed between carbon atoms of different graphene layers. Chlorine 37 implantation generates defects even at a relatively low fluence ( $5 \times 10^{13}$  at  $cm^{-2}$ , i.e. total number of defects created in the implanted zone equals 0.5 dpa). Such defects appear in the form of vacancies and interstitials into and between graphene layers. **At the end of the implantation step the samples are thus destructured**.

By contrast, thermal **annealing enables the samples to be restructured**. Such a structural recovering effect increases with temperature but **the graphite initial structure is never recovered**.

It is important to point out that **defects created in the graphite structure by chlorine implantation and annealing**, looks from Raman spectrometry point of view, **very similar to defects observed on i-graphite samples**. This conclusion is more detailed in the Carbowaste technical report "Multiscale structural characterization of nuclear graphite" from J.N Rouzaud and R. Ammar from Ecole Normale Supérieure de Paris that was produced in the framework of WP3 (Characterization) of the Carbowaste project. It tends to prove that chlorine 37 implanted samples are not that far from real irradiated samples.

## HYDRODYNAMICS AND WATER UPTAKE

Whatever the chosen repository site for graphite waste, ground water ingress will happen in the relatively long term, resulting in radionuclide leaching from the graphite matrix. This is a key issue when considering i-graphite long term behaviour in disposal. The release of radionuclides in water depends on several physicochemical processes:

- Ingress of reagents (water) into radionuclide sites,
- Solubilisation of radionuclides,
- Transport of radionuclides in solution through graphite pores into the solution.

Analysis of the impregnation (impregnation kinetics, impregnation rate) of water into the graphite porosity represents one of the main parameters that will greatly influence the physicochemical processes controlling the release of radionuclides in solution. Unfortunately there is little information in available literature on the study of water uptake in nuclear graphite. Preliminary data collected on nuclear fuel sleeve and stack graphite, as well as on non-irradiated and irradiated samples, show that:

- **Water impregnation in the porous medium of non-irradiated graphite is relatively slow** and remains incomplete for durations up to 90 days. The saturation rate follows a proportional  $V/S$  law and seems to be related to a diffusion process (linearity according to a square-root-of-time scale),
- Tests performed at high pressure show that non irradiated graphite absorbs about 15 wt% of water, which can be considered as the maximum mass gain,
- Tests performed by SUBATECH in hydrodynamic gradients showed easy water percolation through graphite even in case of non-irradiated graphite
- **Irradiation increases the kinetics and the impregnation rate.**

There is nevertheless very little information available especially regarding the relationship between graphite samples history, their physico-chemical characteristics and water uptake.

For all these reasons, the impregnation of graphite samples from the G2 and SLA2 UNGG reactors was studied in CEA. Results are presented in Carbowaste technical report "Water impregnation kinetics in nuclear graphite samples from UNGG reactors" issued November 2010 by CEA (J. Comte and C. Guy). The measurement protocols and results of samples characterization are detailed in other another Carbowaste technical reports made in the framework of WP3 (characterization):

- "Characterisation of G2 pile graphite before and after irradiation", Carbowaste report 1007-D-WP3 task 2, 2010

-“Characterization before and after irradiation of EDF Saint-Laurent A2 reactor stack graphite”, Carbowaste report 1201-D-WP3 task 2, 2012.Methodology

---

## METHODOLOGY

---

The CEA study involved monitoring the increase in the apparent mass of samples immersed in water over time. Two techniques were used: continuous measurements for immersed samples suspended on a precision electronic scale, and occasional measurements of the mass variations in immersed samples placed in experimental vessels.

Experiments were carried out on both non-irradiated and irradiated samples from G2 and SLA2 UNGG reactors. It must be reminded that these two kinds of graphite are of different origin: G2 graphite was manufactured from Special Grade A coke whereas SLA2 graphite was manufactured from Lima coke. Moreover, these two graphite piles were subjected to very different operating conditions: low neutron flux and low temperature range in G2 vs. higher neutron flux and higher temperature range in SLA2 reactor.

Irradiated and non-irradiated samples were characterized by means of geometric density measurements (total porosity), helium pycnometry (open porosity), mercury porosimetry (pore size distribution), X-ray diffraction and Raman spectroscopy (graphite structure).

---

## WATER UPTAKE IN NON-IRRADIATED GRAPHITE

---

**Water impregnation of non-irradiated graphite samples depends on the graphite origin.** Water impregnation in non-irradiated graphite samples from the G2 reactor is slow and low whereas it is faster and higher in non-irradiated SLA2 samples. On G2 graphite samples a saturation rate of about 9% in a week is achieved whereas at least 39% is achieved for the same term in SLA2 samples. After 200 days, saturation rate is limited to about 42% on G2 samples while it reaches about 60% in SLA2 samples.

Such differences in water uptake kinetics may not be only related to the origin of the coke used but also to the graphite manufacturing process (impregnation, graphitization, purification, etc.). It was indeed observed that the non-irradiated G2 graphite structure is closer to HOPG “model” graphite structure (Highly Ordered Pyrolytic Graphite) than that of the SLA2 graphite, considering X-ray diffraction (XRD) and Raman spectrometry results. **Such results suggest that the lower water uptake rate and kinetics for G2 non irradiated samples is related to a better quality of graphitisation.**

In percolation tests with non irradiated G2 samples, small hydrodynamic gradients lead to relatively fast flow of water through the pore space of the graphite, characterised by an intrinsic permeability of  $k=(8\pm 2)\times 10^{-17} \text{ m}^2$ .

---

## WATER UPTAKE IN IRRADIATED GRAPHITE

---

**Irradiation increases the impregnation kinetics and the saturation rate of graphite.** Graphite samples, whose water uptake behaviours were very different before irradiation, become very similar after irradiation. . As show by characterization measurements, this change can be linked to the probable combined effect of the temperature, irradiation and radiolytic corrosion:

- Radiolytic corrosion increases the open porosity. However, the open porosity is only slightly increased (a few percents) while the amount of water within graphite samples is doubled in irradiated samples. Radiolytic corrosion also modifies graphite macroporosity, particularly through a widening of the pore mean diameter thus making water impregnation easier
- Irradiation and radiolytic corrosion result in breaking C-C bonds within graphite crystallites and/or grain boundaries to form more hydrophilic C-H or C-O bonds. This leads to faster and higher impregnation
- Irradiation combined with temperature change graphite crystal structure and especially lattice parameters. Electrostatic repulsions within graphite are thus modified making it more hydrophilic. However, additional studies carried out in WP3 show that the lower the irradiation temperature, the more the crystal structure undergoes modification. Defect rearrangement could be seen in both G2 and SLA2 graphite samples that were subjected to higher temperatures. There is thus no clear correlation between temperature and water impregnation.

Overall, no clear correlation can be made between each parameter and water uptake although impregnation is clearly faster and almost complete in irradiated graphite.

## I-GRAPHITE LEACHING BEHAVIOUR

Most of chlorine 36 leaching studies were performed on graphite samples trepanned from French UNGG reactors belonging to EDF (Bugey, Saint Laurent des Eaux A2) and CEA (G2 reactor in Marcoule). The only exception concerns the American Hanford reactor (light water cooled reactor). Overall, more than 60 leaching studies on chlorine 36 have been carried out in France for more than 20 years, mainly in CEA labs. This French specificity may be related to:

- The chlorine 36 issue which is of large concern in France for graphite waste disposal but which has been scarcely studied abroad;
- The fact that chlorine 36 inventory and leaching behaviour are hard to characterize (detection limits). Specific methodologies have thus been developed.

In spite of differences in the experimental protocol, all leaching studies on graphite piles show that chlorine 36 is released in 2 stages:

- The first stage shows very rapid chlorine 36 release kinetics (labile fraction) proportional to the square root of time which is a feature of a diffusion driven release process through graphite porosity;
- The second stage shows slow chlorine 36 release kinetics (non-labile fraction).

On the whole, chlorine 36 release rates vary widely ranging from few % to 90% of the initial inventory. No correlation was found between chlorine 36 initial activity and its release in solution. However, a

clear correlation has been observed between chlorine 36 labile fraction release rate and irradiation temperatures for 3 different French graphite piles (G2, SLA2 and Bugey).

The carbon 14 issue in graphite waste is overall much more documented than that of chlorine 36 as it is the main long-lived radionuclide in terms of activity in most of graphite reactors. Several reviews have already been published on carbon 14 leaching in irradiated graphite. Overall, regardless sample history, geometry and leaching methodology, all leaching studies show similarities in carbon 14 leaching behaviour. Carbon 14 release in solution is indeed always found to be low, often below detection limits. This made results analysis difficult and it is often even impossible to identify any global trend in carbon 14 release behaviour. This implies to perform long leaching studies or to use larger samples in order to increase carbon 14 concentration in the leaching solution. When results are significant, a sharp initial release is often observed followed by a near stabilization.

Chlorine 36 and carbon 14 leaching behaviour under repository conditions was studied in the framework of the Carbowaste project WP6. Some results were also obtained in the framework of the Carbowaste project WP4 for i-graphite treatment purposes. The protocols and results are detailed in the following Carbowaste technical reports:

- "Behaviour of chlorine 36 in irradiated graphite samples from UNGG G2 reactor" issued 2010 CEA J. Comte and C. Guy;
- "Characterization and chemical treatment of irradiated UK graphite waste" issued 2011 UoM L. McDermott.

A review of leaching data available on both chlorine 36 and carbon 14 has also been recently issued ("Review of leaching data on irradiated graphite", Carbowaste report D-6-1-6, 2013)..

---

## CHLORINE 36

---

The main conclusions that can be drawn are:

- **Water impregnation** in accessible porosity occurs rather fast and **does not control the chlorine 36 release** in the leaching solution (see the previous section on "water uptake");
- As previously observed, chlorine 36 release occurs in 2 stages: a first one which exhibits very rapid chlorine 36 release kinetics (labile fraction) and a slow chlorine 36 release as second stage;
- There is a relationship between the operating sample temperature and the amount of chlorine 36 released: **the higher the operating temperature, the lower the chlorine 36 release rate**. This result is consistent with results previously observed on Bugey 1 samples but over a **smaller operating temperature range** (230 to 580°C for Bugey 1 whereas **285 to 327°C for G2**);
- The release kinetics of the labile chlorine 36 can be described by a diffusion model of dissolved chlorine through the graphite porosity;
- **Stable chlorine and chlorine 36 do not behave the same way**. This result suggests that they are not in the same chemical form in graphite or that their location is different;
- Two chemical forms of stable chlorine were identified in leaching solution: a chloride form (the most abundant) and a chlorite one.

---

## CARBON 14

---

Although carbon 14 leaching behaviour in i-graphite has been much more studied than that of chlorine 36 results are difficult to interpret as **lots of measurements are below detection limits**. Overall, as for chlorine 36, **water uptake kinetics** is rather fast in i-graphite so it **should not limit carbon 14 release**. Another interesting feature concerns the relationship between carbon 14 origin (production route) and its release behaviour. It has been several times suggested that the two stages of release of carbon 14 may be related to two different ways of production in reactor ( $^{14}\text{N}$  activation vs.  $^{13}\text{C}$  activation). As a result, it was expected that the large amount of nitrogen in the coolant for air-cooled piles should lead to a higher surface contamination in nitrogen 14, and thus to a larger carbon 14 labile fraction than in  $\text{CO}_2$ -cooled reactors. Such a comparison was performed at the University of Manchester between BEPO and Wylfa Magnox graphite samples. Actually, no clear difference in carbon 14 release was found between these 2 reactors. This result does not mean that the later assumption is wrong. Annealing periods might have reduced differences between i-graphite.

Carbon 14 speciation started to be characterized in leach studies from the end of 2000's as detection limits issues and applied experimental conditions previously prevented from monitoring carbon 14 species. It is a big issue for i-graphite disposal as carbon 14 chemical form can drastically affect the dose impact under disposal conditions. Indeed, whereas inorganic forms ( $\text{CO}_2$ ,  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ ) are strongly trapped in cementitious materials, organic species and carbon monoxide are much more mobile, all the more so since they can be released as gaseous species. Few studies are available on that topic and it was not studied within the Carbowaste framework. However a dedicated PhD work has been recently issued<sup>5</sup>. In such studies, **carbon 14 is found to be mainly released in solution. Carbon 14 gaseous species represent less than 0.01 % of the total carbon 14 activity and are only detected as organic species.**

---

## CONCLUSION

---

---

### MAIN FINDINGS

---

I-graphite water uptake is very fast and it is not the limiting step to radionuclide leaching. As soon as ground water ingress will happen in the repository site, the release of the radionuclides will happen.

Studies on virgin graphite have proved the occurrence of two  $^{35}\text{Cl}$  chemical species although  $^{35}\text{Cl}$  is mainly detected as organic species (C-Cl bonds). Chlorine is distributed in a diffuse manner together with small hot spots. It is found to be highly mobile under thermal treatment (starting at 200/300 °C) which confirms that a large part of chlorine that initially existed in virgin graphite has been released in reactor.

In contrast, the amount of chlorine 36 in i-graphite is too low to be characterized so its location and speciation is still unclear.

Chlorine 36 behaviour in repository conditions depends on i-graphite history. Release systematically follows 2 stages (labile and non-labile fractions) but the amount of the labile fraction is highly

---

<sup>5</sup> [http://tel.archives-ouvertes.fr/docs/00/77/06/71/PDF/Vende\\_L\\_10\\_2012.pdf](http://tel.archives-ouvertes.fr/docs/00/77/06/71/PDF/Vende_L_10_2012.pdf)

variable. It was confirmed that the higher the operating temperature of the graphite, the lower the release rate of chlorine 36. The effect is also evidenced on a short temperature range (around 50°C for G2 reactor). Two main phenomena could explain these results:

- A partial healing of disordered i-graphite depending on the temperature;
- Chlorine 36 speciation depending on the temperature.

For carbon 14, only leaching data are currently available. Study of carbon 14 behavior under reactor operating conditions using implanted samples, as what has been done for chlorine, is underway in France. Overall, leaching rate is found to be very low under disposal conditions (< 5% of the initial inventory). It is released in two stages but no clear correlation with the two ways of production ( $^{13}\text{C}$  vs.  $^{14}\text{N}$  activation) was found.

---

## REMAINING UNCERTAINTIES

---

Data on chlorine 36 come almost exclusively from UNGG i-graphite. Results observed on Chlorine 36 behaviour need to be extended to i-graphite from different origins (Magneox, RBMK, AVR...).

On carbon 14, it is very important to assess the amount and the rate of carbon 14 released from i-graphite in disposal conditions but also its chemical forms. It is needed to characterize volatile or non-volatile carbon 14 bearing species but not to forget dissolved organic compounds into the liquid. Carbon 14 bearing organics might represent a significant amount of carbon 14 in the leachate. These compounds are also weakly retained in the repository materials and they could transform into volatile compounds due to bacteria effect. They must be taken into account for the repository sanitary impact. The lack of data on these topics should at the end, be stressed. Studies addressing the chemical forms of released carbon 14 are very scarce. More experiments are needed, not only for repository sanitary impact assessment but also could be of interest to assess carbon 14 behaviour according to its origin.

Due to time reasons and national strategies, up to now, studies carried out on disposal behaviour of operating waste (graphite sleeves) are very poor. This issue needs also to be addressed.

## TASK 6.2: DISPOSAL BEHAVIOR OF ALTERNATIVE WASTE FORMS

---

---

### INTRODUCTION

---

In the work package 6 of the Carrowaste project disposal behaviour of graphite and carbonaceous wastes is studied. Long-lived  $^{14}\text{C}$  and  $^{36}\text{Cl}$  complicate the disposal of carbonaceous wastes and graphite. The waste is only suitable for disposal after transforming it by specific conditioning techniques in

adequate waste packages, e.g. by confining the waste in stable matrices emplaced inside containers resistant to radiation, corrosion and mechanical damage. Recycled carbon based products may contribute to the packaging and confinement function. The work package comprises four tasks dealing with the characterisation of the disposal properties of i-graphite and of other i-carbonaceous wastes, of associated waste packages and of confinement matrices to improve the disposal behaviour of these waste products. In a final task, the performances of the waste disposal is evaluated.

In task 6.2 properties of silicon carbides made from irradiated graphite are studied. Task 6.2 follows task 5.2 – sub-task 5.2.3. Carbonaceous ceramics for waste management . This sub-task addresses graphite canisters for waste storage as well as non-graphite uses of other chemical forms of carbon. The latter category includes materials such as silicon-carbide (SiC) and calcium carbonate. The definition for the purposes of this project of “recycled products” specifically includes products specially manufactured to stabilise carbon in a radioactive waste disposal site, or to act as confinement or packing material for other wastes and thermal management, in the repository site. The task will include the production of materials which are suitable for use in disposal sites as backfill, encapsulants, etc., without oxidation of the carbon and providing safety during processing. In this part, research on silicon carbide formation from graphite and irradiated graphite was done. In the following chapters details about the SiC formation and its characterization are presented.

Within task 6.2, the formed silicon carbide is studied under repository conditions by leaching experiments.

## DISPOSAL BEHAVIOR OF CARBONACEOUS WASTE

---

Literature research on SiC formation from graphite was done, several suitable methods were found and finally a technique published by A. Morançais et al. in the J. of Eur. Ceram. Soc. 23 (2003) 1949–1956 [2], was chosen as method to be tested. In the paper, the method is called “a process involving an SHS stage.”

The preparation of porous SiC ceramics from stoichiometric mixtures of silicon and graphite has been studied. Products with very high pore contents ( $\approx 80\%$ ) were obtained using a process, shown in the following figure, which consisted of heating the reactive pellets in purified argon, at  $15\text{ }^{\circ}\text{C min}^{-1}$ , up to  $1430\text{ }^{\circ}\text{C}$  and applying a weak d.c. voltage across the sample for 20 s. The resulting electrical current was necessary for the ignition of a SHS reaction simultaneously in the whole sample. The analysis of the sample microstructure evolution all along the process has enabled the identification of the different mechanisms involved in the SiC formation. Before the SHS stage, the formation of silicon carbide, during heating from about  $1325$  up to  $1430\text{ }^{\circ}\text{C}$ , is associated with a large sample expansion, which mainly determined the final pore volume fraction. The pore transfer mechanisms, which occur during the SHS stage at  $1430\text{ }^{\circ}\text{C}$ , have a specific influence on the pore development. Since the final pore size distribution is strongly related to silicon grain size distribution, the porosity of the porous SiC ceramic, obtained by this process, can be easily modulated.

This method was applied first to virgin graphite; when the method was modified and established, irradiated graphite was used. The same procedure was applied to the irradiated graphite;

unfortunately these two graphite types seem not to react in the same way. Reaction conditions were varied to optimize the procedure to get pure SiC using the irradiated graphite. However, besides the SiC a small amount (less than 5%) of free carbon was always still present after the reaction process.

The synthesis and characterization of SiC was done. This material was used for the leaching experiments within the WP6 – task 6.2.

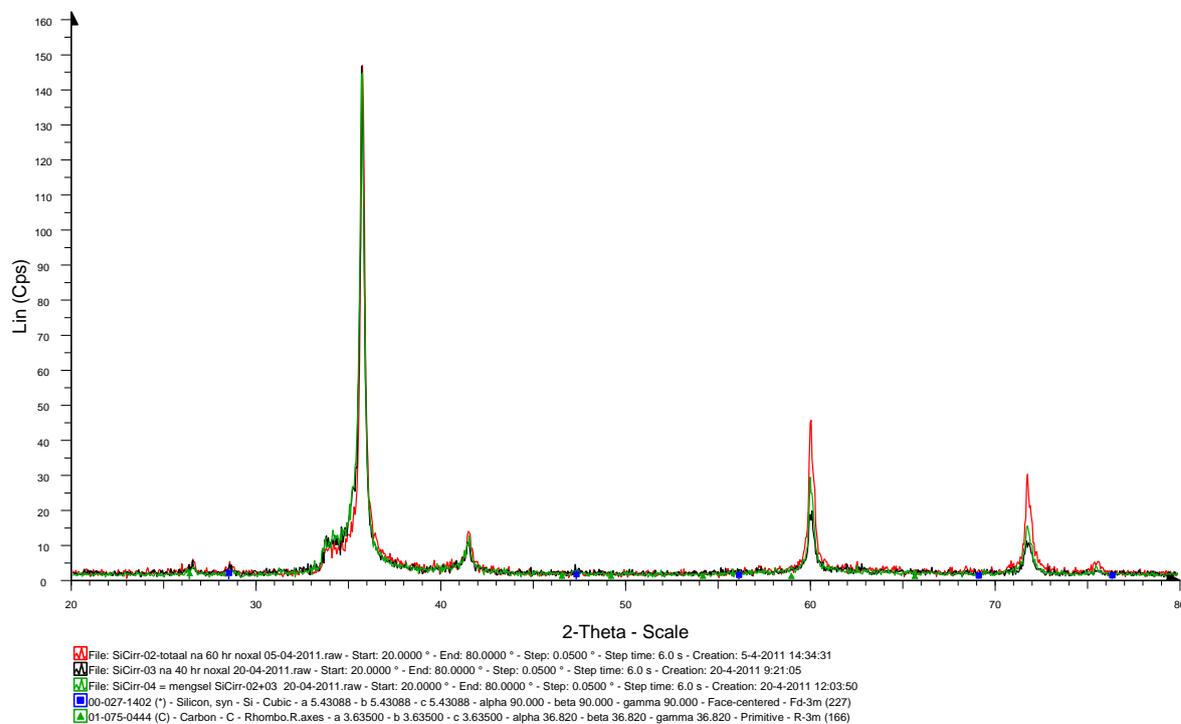


FIGURE 1 XRD OF SiC FOR THE LEACHING EXPERIMENTS

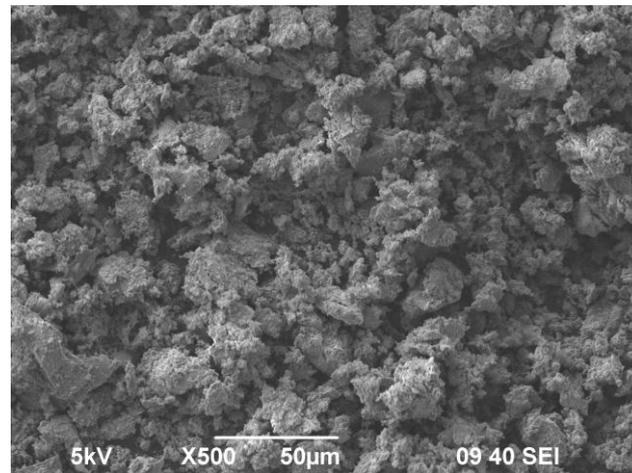


FIGURE 2 SEM PICTURE OF SiC FORMED FROM IRRADIATED GRAPHITE

The formed SiC powder will be studied under repository conditions such as salt domes, granite-based repositories and clay formations.

The formed SiC powder was studied under repository conditions such as salt domes, granite-based repositories and clay formations. The leaching experiments were performed in three types of leachants: Q-brine, clay and pore water, at the room temperature and at 90°C. The formed SiC and irradiated graphite (material used in the RRT test in WP3) were leached during a period of 160 days with sampling each 40 days. After sampling, the C-14 activity was determined by Liquid scintillation counting method.

For SiC at the room temperature after 40 days, the highest activity of C-14 was measured in Q-Brine, granite water and sample for clay water, resp. During the other sampling periods, the activity measured in Q-Brine and granite water decreased slightly and remained constant during the leaching period. In clay water, the measured activity remained about constant during the whole leaching period.

The SiC powder leached at the temperature of 90°C showed measured activity in all three leachants remaining about constant during the whole leaching period. The measured activity in Q-Brine is 10 times higher than in the other two leachants.

The measured activity of C-14 in Q-Brine is about two –three times higher at the temperature of 90°C than at the room temperature. It seems that there is no significant influence of temperature on the leaching behaviour of the SiC powder in clay water, in the granite water the higher activities are measured at the room temperature.

For the irradiated graphite, the highest activity of C-14 is found in the Q-brine water (about 2-3 times higher compared to other leachants). The measured C-14 activity in the granite water was during the

whole leaching period constant. For the clay water, the activity was more or less constant during the first 80 days, thereafter it decreased a bit.

The experiments performed at 90°C showed that the highest activity of C-14 was measured in the Q-brine leachant. In the granite water, the measured activity of C-14 was about constant, at 160 days measuring point a significant increase (two times higher) is found. The activity of C-14 in clay pore was similar to granite water values, but remained constant during the 160 days.

### **IGM: A POROUS FREE GRAPHITE MATRIX FOR A LONG TERM SAFE STORAGE OF IRRADIATED GRAPHITE (I-GRAPHITE)**

---

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 long term stable impermeable matrix (impermeable graphite matrix IGM) which would inhibit ingress of water and therefore allow a safe final disposal. IGM is a development of FNAG as an alternative waste form for the management of irradiated graphite. It can be assumed as a vitrification of i-graphite. However the glass has only be a volume ratio of 20% which is close to the former pore volume of the graphite. The manufacturing of IGM is based on a hot pressing of the glass-graphite mixture in vacuum. This leads to a material with densities better than 98% of theoretical density and has no significant open pores larger than 0.1 µm. The possibility has been demonstrated to embed other radioactive waste stream in IGM

The glass corrosion has been investigated by weight changes and potassium release of IGM samples with different glass types immersed in water and magnesium rich salt brine. The glass 8800 of Schott has been identified as the most corrosion resistant glass type.

Therefore further investigations will have to be focused on this glass type for the qualification of IGM as waste embedding matrix.

### **CONCLUSIONS AND OUTLOOK**

---

The measured activities of C-14 leached from irradiated graphite are much higher comparing to the ones leached from the SiC made from this graphite. Based on that, it seems that the transformation of irradiated graphite into silicon carbide could be a way of decreasing of the C-14 release from the material. It is expected that also the formation of IGM will strongly decrease radionuclide release. Because of limited amount of available irradiated graphite, the leaching tests with are done with very small amount of irradiated graphite (0.02 g in 20ml leachant) comparing to the silicon carbide (0.4g in 20 ml leachant), this (different S/V ratio) could have influence on the leaching rates. To confirm that silicon carbide could be a suitable product formed from irradiated graphite concerning the lower C-14 release, more tests must be performed. Long-term tests should be done, better comparable amount of materials to be leached should be studied and material in the form of pellets should be leached as well (if SiC is used as e.g. container material).

In addition, since the trace amount of free carbon in the synthesized SiC could be responsible for the observed C-14 leaching, it is also important to further optimize the synthesis procedure.

## TASK 6.3: WASTE PACKAGES

Irradiated graphite waste from the first generation gas-cooled reactors (UNGG) is classified in France as low-level and long-lived radioactive waste (LLW-LL). At the present time, the French design considers emplacing graphite waste in metal carts which are then put into concrete containers. Cement or mortar would then be injected into the container, which would be completely closed with a concrete cap. Concrete and cement-based materials will thus play an important role, as container and backfill materials, in the disposal concept under study. The disposal behaviour can be improved by a design of appropriate waste packages. So, it is important to study the various interactions involved between the radionuclides released from graphite and the concrete or cement-based materials.

In a general way, in order to evaluate the impact of a geological disposal of radioactive waste, it is necessary to determine the transfer properties of the constituent barriers of the disposal: engineered barriers as well as the geological barrier. An important concern is the mobility of radionuclides in the waste packages and their surrounding under repository conditions prior to and after water access. The approach developed here is based on the determination of radionuclide retention onto cementitious materials. Retention values indicate if a diffusive front of radionuclides through one barrier could be delayed by chemical processes. The validity of the measured parameter, the distribution ratio of a radionuclide between solid and solution, is limited to the physicochemical conditions of the experiment.

Available data on irradiated graphite waste show that the long-lived activation product  $^{36}\text{Cl}$  ( $T_{1/2} = 3.01 \cdot 10^5$  years) is produced from  $^{35}\text{Cl}$  impurities during reactor operation [1]. Although its content in irradiated graphite is very low,  $^{36}\text{Cl}$  is a highly soluble element in water and mobile in environment so that it may contribute to a significant dose peak at the outlet after water ingress into a repository site. Understanding behaviour of  $^{36}\text{Cl}$  towards cement-based materials is then of interest for long-term performance assessment.

Concrete waste packages are going to be altered during the disposal due to leaching by natural water entering in the system. Retention properties of such packages depend on the mineralogical composition of the cementitious materials, their alteration state and the geochemical conditions of the water. Wet chemistry measurements have been performed to investigate the  $\text{Cl}^-$  retention onto a CEM-V cement paste (a previous study was focused on a F44-like cement paste, Edf reference concrete [2]). The distribution ratio of  $\text{Cl}^-$  between solid phases and equilibrium solutions ( $R_d$ ) has been measured under controlled atmosphere in order to prevent carbonation of the cement pastes. Several parameters have been taken into account:

- ✓ Dependency with the alteration state of the cement paste;
- ✓ Kinetics of retention;
- ✓ Reversibility of retention;
- ✓ Sorption-site saturation effect arising from stable chloride already present in natural water.

The cement paste studied has been prepared from an Origny cement (CEM-V/A), which has been mixed with water in 1997 (water to cement ratio, w/c = 0.38). During four years, the resulting CEM-V paste has been kept in a portlandite ( $\text{Ca}(\text{OH})_2$ ) saturated solution to prevent carbonation and continue the hydration processes. In 2001, the samples have been dried, crushed and sieved under a flow of argon. Several sieved fractions have then been stored in HDPE vials into desiccators flushed with argon before closure [3]. A specific fraction of the powder is used in the present study ( $100 \mu\text{m} < \varnothing < 200 \mu\text{m}$ ).

Studying the  $^{36}\text{Cl}$  retention as a function of the alteration state of the cement pastes requires an accurate characterization of the material prior to measurements. Fresh, deteriorated and degraded cement pastes have been obtained by leaching different amounts of cement powder in closed batches under various conditions (solid to water ratio and composition of solution).

The fresh state has been characterized by a pH of 13.2 and  $[\text{Ca}]$  of  $8.4 \cdot 10^{-4} \text{ mol.l}^{-1}$ , the deteriorated state by a pH of 12.5 and  $[\text{Ca}]$  of  $9.2 \cdot 10^{-3} \text{ mol.l}^{-1}$  and the degraded state by a pH of about 12 and  $[\text{Ca}]$  of  $6.0 \cdot 10^{-3} \text{ mol.l}^{-1}$  (see Figure 1).

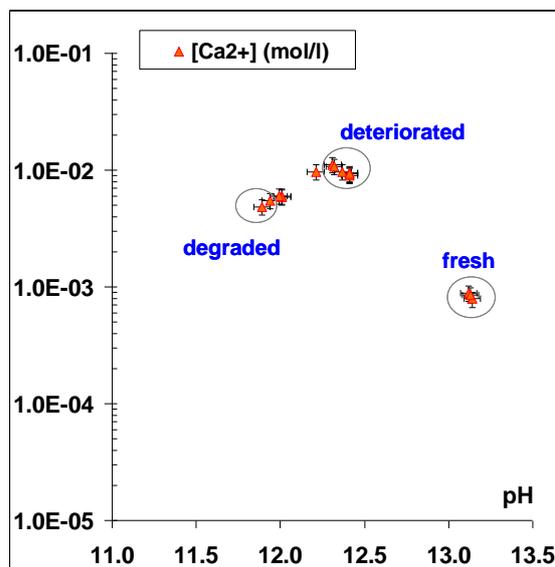


Figure 1: Concentration of calcium vs. pH values measured in solutions at equilibrium with the CEM-V cement paste (uncertainties on pH values and Ca concentration measurements are 0.05 and 15%, respectively)

Solid characterization based on qualitative X-Ray Diffraction measurement (XRD) has also been carried out and confirmed the degradation of the cement paste by the decrease of portlandite characteristic peaks with degradation.

Then, for every alteration states,  $R_d$  values have been measured as a function of time and stable chloride concentration in the equilibrium solutions (chloride from the solid paste, from a specific amount of a NaCl solution addition and, in one case, from synthesized “natural” water).

The kinetic study showed a gradual increase of  $\text{Cl}^-$  distribution ratio vs. time suggesting “fast” sorption processes (likely surface sorption phenomena) that could be slowed by a phenomenon of hydration inside the grains. Whatever the case, the  $R_d$  values slightly increased during the first month, and no evolution was observed afterwards. Beyond one month  $R_d$  reached a steady mean value.

But in any case, retention of  $\text{Cl}^-$  by the cement paste was weak: a maximum  $R_d$  value of  $35 \text{ ml.g}^{-1}$  was obtained for the degraded state.

The retention isotherms of  $\text{Cl}^-$  showed a decrease of retention when chloride concentration increases, especially at degraded and deteriorated states (see Figure 2).

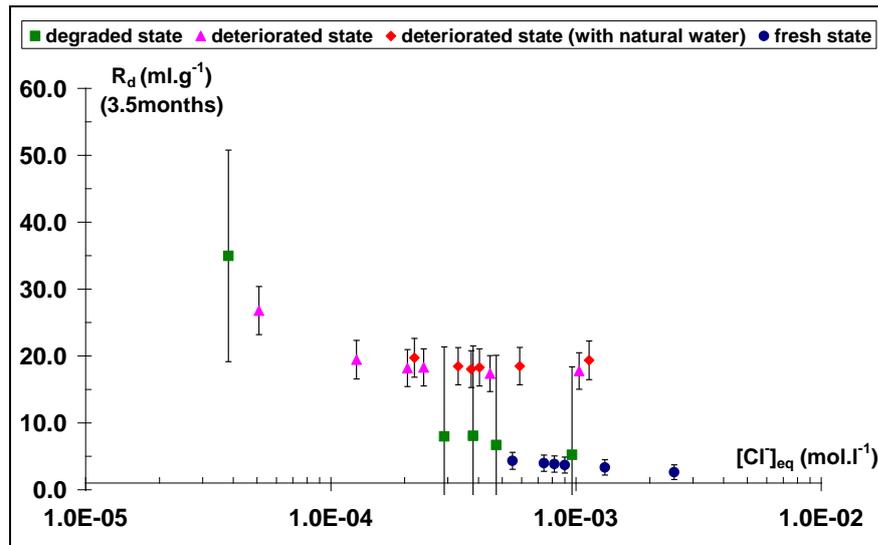


Figure 2:  $R_d$  measured after 3.5 months vs. chloride concentration at equilibrium in solution for varying alteration states

Based on these results, it appears important to be able to identify and quantify all chloride sources in a repository.

The sorption reversibility study has been limited to both deteriorated states of the cement paste (in degassed MilliQ® water or synthesized “natural” water) (see Figure 3). Taking into account measurement uncertainties, at equivalent chloride concentrations, the measured distribution ratios for sorption and desorption experiments were in the same range of values. **In these conditions,  $\text{Cl}^-$  sorption in deteriorated cement paste appears to be a reversible process.**

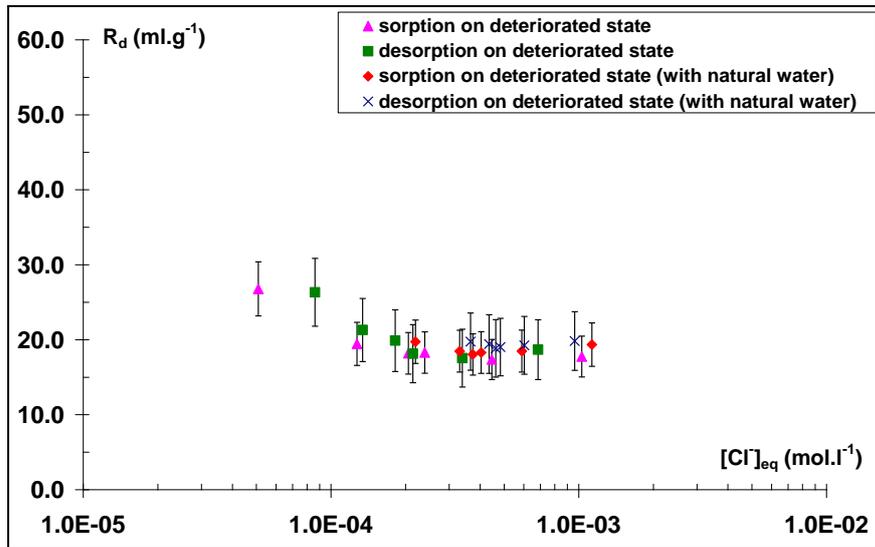


Figure 3:  $R_d$  measured after 3.5 months during sorption experiments and after 4.0 months during desorption experiments vs. chloride concentration at equilibrium in solution for the deteriorated state

Wet chemistry measurements have shown that distribution ratios ( $R_d$ ) values slowly increase during the 20 first days of contact time, and then, whatever the case,  $R_d$  reaches a steady mean value.  $R_d$  values are relatively low. The maximum  $R_d$  value ( $35 \text{ ml.g}^{-1}$ ) has been measured for the degraded state and at a low chloride concentration ( $4.8 \cdot 10^{-5} \text{ mol.l}^{-1}$ ).  $R_d$  measured values depend on the alteration state of the cement paste. Measurements at deteriorated states led to conclude that the retention process is reversible for the deteriorated state. Isotherms have shown that  $R_d$  values for  $^{36}\text{Cl}^-$  strongly depend on the stable chloride concentration in solution. At high chloride concentration, the sorption-site saturation effect is observed (non-linear sorption isotherm). Such results highlight the importance to know and quantify all main sources of stable chloride in order to be able to carry out performance assessment. However, interaction processes between the cement paste and  $\text{Cl}^-$  have not been precisely identified.

This experimental work is detailed in the corresponding deliverable "Task 6.3: Waste packages T6.3.2/D6.3.3 – Retention properties of cement for  $^{36}\text{Cl}^-$ ".

## TASK 6.4 PERFORMANCE ASSESSMENT OF DISPOSAL OF GRAPHITE AND CARBONACEOUS WASTES

### STATE OF THE ART: SAFETY CASE

The implementation of graphite disposal in e.g. a surface disposal facility (SDF) or a geological disposal facility (GDF)<sup>6</sup> requires us to demonstrate our confidence that such a facility would be safe, during both the operational period and after it has been sealed and closed. A safety case<sup>7</sup> is the vehicle we use to demonstrate our understanding of environmental safety.

Regulators have issued guidance on what they require to permit the development of an SDF or a GDF, which a safety case needs to address. Regulatory guidance provides a set of criteria, both numerical and qualitative, against which the environmental safety of an SDF or a GDF will be assessed during the operational and post-closure periods.

#### Providing confidence from international and overseas experience

Guidance on disposal has been developed over many years through such organisations as the European Commission (EC), the International Atomic Energy Agency (IAEA), and the Nuclear Energy Agency of the Organisation for Economic Co-operation and Development (NEA OECD). Regarding geological disposal, in 2008 the NEA Radioactive Waste Management Committee issued a Collective Statement that notes the following<sup>8</sup>:

*“The overwhelming scientific consensus worldwide is that geological disposal is technically feasible. This is supported by extensive experimental data accumulated for different geological formations and engineered materials from surface investigations, underground research facilities and demonstration equipment and facilities; by the current state of the art in modeling techniques; by the experience in operating underground repositories for other classes of waste; and by the advances in best practice for performing safety assessments of potential disposal systems.*

*“Disposal can be accommodated in a broad range of geological settings, as long as these settings are carefully selected and matched with appropriate facility design and configuration and engineered barriers.”*

Twenty five countries have opted for a policy of geological disposal for higher activity wastes. The US has an operational GDF for long-lived “transuranic” wastes (the Waste Isolation Pilot Plant, or WIPP), and Finland, France, and Sweden are making good progress towards establishing new GDFs. Germany

<sup>6</sup> Geological Disposal Facility” is a term used in the UK radioactive waste programme. It is synonymous with “repository” as used in other national programmes, where the disposal facility is envisaged as being at depth in a suitable geological environment.

<sup>7</sup> Many national programmes use the term “safety case”, whereas in the UK programme the term “Environmental Safety Case” is used. Note that safety case is not synonymous with “performance assessment”, which is a component of a safety case and not a safety case in itself.

<sup>8</sup> Nuclear Energy Agency, *Moving Forward with Geological Disposal of Radioactive Waste. A Collective Statement by the NEA Radioactive Waste Management Committee (RWMC)*. NEA Report No. 6433, OECD/NEA, Paris, 2008.

is now backfilling and closing a previously operational GDF (at Morsleben) and is scheduled to open a new GDF within a few years (at Konrad) for non-heat-producing wastes.

In addition, some countries (e.g. Spain and Romania) are pursuing a policy of disposal in an SDF for appropriate components of their inventory, including graphite

### Providing confidence through our safety strategy

A strategy for ensuring the environmental safety of an SDF or a GDF consists of a design and siting strategy, an assessment strategy, and a management strategy:

- **Design and siting** – The safety case can be used to assist in the siting, layout, operation and closure planning of an SDF or a GDF within the site offered and for the preferred disposal concept. Disposal facility design will consider the inventory, and will follow international good practice and regulatory requirements in providing for passive safety and using the safety functions of multiple barriers to provide that safety.
- **Assessment** – An assessment strategy has international (EC, NEA, IAEA) good practice to act as guidance, and regulatory requirements.
- **Management** – An overall management strategy needs to be designed to provide confidence that an implementer can deliver the disposal system specification, and the design and assessment strategies, in a coherent, integrated way and with appropriate quality and management accountability over the timescales for planning and delivery of an SDF or a GDF. The management strategy will need to develop in the future to meet the needs of any programme as it evolves (e.g. to control site characterisation and eventual construction, operation and closure).

Disposal concepts – for an SDF or a GDF - are all based on the principle of passive safety provided by a combination of engineered barriers designed to complement the natural barrier provided by the geological environment. The system of multiple barriers will ensure that the radioactivity in the wastes is sufficiently contained so that regulatory requirements are met. Regulations typically require exposures resulting from any releases to the surface to be as low as reasonably achievable and, in any event, less than a small fraction of the exposures everyone receives each year from naturally occurring sources of radioactivity in the environment. A post-closure safety assessment is undertaken to build confidence that the facility will be passively safe.

Evaluation of impacts on the environment and people from an SDF or a GDF during the operational phase is much the same process and is based on similar techniques to those used in assessing such impacts from other operating nuclear facilities (such as radioactive waste stores).

### Confidence in operational environmental safety

Confidence in environmental safety during the operational period arises from the safety features inherent in waste packaging specifications, and the safety procedures and management in place during the operational period. Inherent safety features of the waste packages include the solid form of the wastes; their packaging; and their disposal in robust containers that provide the necessary degree of radiation shielding and containment, and are capable of normal handling during storage,

transport and disposal operations.<sup>9</sup> Any operational discharges into the atmosphere in particulate form would be controlled by the use of high-efficiency air filters. Any discharges of radionuclides dissolved in water would be controlled by collection of contaminated water and appropriate treatment prior to discharge. Any possible discharges of radioactive gases from an SDF or a GDF during the operational period need to meet regulatory requirements.

### **Confidence in post-closure safety**

The evolution of an SDF or a GDF depends on the nature and quantity of wastes for disposal, the environment, the design of the engineered barrier system, and any external environmental change that could impact on the safety function provided by the geology and/or engineered barrier system (EBS). A safety case needs to demonstrate via both qualitative and quantitative reasoning an understanding of how an SDF or a GDF would evolve once it is closed, and to build confidence in how environmental safety could be provided by a system of multiple barriers working together.

Key lines of reasoning that provide confidence in the understanding of post-closure performance and statements on environmental safety of an SDF or a GDF will come from:

- description and analysis of the expected evolution of the system based on understanding of the environmental safety functions provided by different disposal concepts and sites and coming from work conducted by our research, design and site characterisation programmes;
- the results of experiments, in underground research laboratories where appropriate, under in situ conditions and long-term demonstration experiments;
- studies of archaeological analogues, that is, materials that people have been using for hundreds or thousands of years and that have survived in the environment over long timescales and that are similar to the materials that could form part of the engineered barrier system of a disposal facility (e.g. glass, cement and iron);
- studies of natural systems that provide analogues for processes important in containing and retarding radionuclides in the multi-barrier system and which can provide information over timescales comparable to or longer than those considered in our quantitative assessments (e.g. uranium-ore deposits);
- site-specific natural indicators of safety once we have candidate sites to consider (e.g. indicators of containment and retardation in the geological environment); and
- demonstration that the disposal system is robust to expected evolution (degradation of the wastes and EBS, impacts of climate change), the occurrence of unexpected events (e.g. seismic events or human intrusion), uncertainties (e.g. concerning site-specific understanding), and decisions (e.g. whether graphite wastes should be disposed in isolation, or if they can be safely co-disposed with other wastes).

Quantitative studies of post-closure safety in a safety case focus on how safety is provided for radionuclides that might dissolve in and be transported by groundwater after an SDF or a GDF is closed. After closure, this is the most likely way for radionuclides to reach those parts of the environment in contact with or readily available for use by humans (the accessible environment).

---

<sup>9</sup> The containers also need to be able to withstand specific accident conditions (such as impact or fire) with little or no release of radioactivity or loss of shielding.

However, other processes that could lead to release of radionuclides to the accessible environment in the post-closure period, including gas-phase transport and human intrusion, could also be considered.

For the calculations undertaken as part of a safety case, the performance of the barriers is often represented in a simplified manner although the specific approach taken in any national programme is frequently driven by the maturity of the programme and national regulations. Thus it is possible to identify and vary the key model parameters that represent the key Features, Events and Processes (FEPs), in order to understand and illustrate the potential radiological impacts of disposing of the inventory using different types of waste container in different kinds of geological environment. These calculations indicate the barrier performance requirements for different possible disposal concepts that would enable an implementer to satisfy radiological protection requirements. This gives confidence that a safe SDF or GDF could be designed.

The following sections summarise assessment studies undertaken as part of CARBOWASTE for both surface disposal facilities (ENRESA and INR), and deep geological disposal facilities (NDA RWMD and LEI) in the context of respective national waste policy, national regulations and national graphite waste inventory. The approach taken in France to irradiated graphite is also considered. Conclusions are drawn, based on CARBOWASTE studies, of the disposability of irradiated graphite in surface disposal facilities and geological disposal facilities that are backed by participating national waste management programmes.

---

## SURFACE DISPOSAL FACILITY FOR GRAPHITE WASTE

---

---

### SPAIN: SUMMARY OF WORK BY ENRESA – SPANISH DISPOSAL CONCEPT AND SURFACE DISPOSAL ANALYSIS

---

The long term safety assessment of the disposal system, for radionuclide release, is directly linked with the concept of radionuclide retention properties of the different media considered, that oppose to the migration from the waste to the biosphere, analyzing the behavior of the barriers applied (wasteform-condition material, container, cell, backfill, geosphere).

On the other hand, for the scenario analysis of human intrusion after surveillance period of 300 years, the most important issue with regard to Waste Acceptance Criteria, WAC, is the activity content of the wastes.

#### **Disposal unit description**

A “disposal unit” is the minimum object over which the Waste Acceptance Criteria are applied, and it is comprised of the following components:

- Concrete container.
- Conditioned waste packages put inside.
- Mortar that fill the gaps between packages.

The concrete container is considered as confining object due to the fulfillment of the retainable properties of annual fraction of activity release. For this purpose, transport properties analysis has been performed to quantify the effective diffusion coefficient,  $D_e$ , distribution coefficient,  $K_d$ , permeability and hydraulic conductivity.

Waste packages also have to fulfill retention properties, leaching rate for those waste incorporated in cement, and diffusion values for those waste conditioned using a mortar envelope. All these properties are required to be reported to the producers, and finally a quality control process is applied in order to verify the process complies with the WAC.

In addition, the mortar that fills the gaps between packages is also supposed to meet the WAC requirement in relation to the retainable properties.

The final described ensemble, termed Disposal Unit, is modeled in radionuclide transport processes involving water as a media. Therefore there are three barriers connected in series that oppose to the radionuclide release.

### **Engineering barriers**

The following describes the whole barrier system at El Cabril disposal center, from top to bottom:

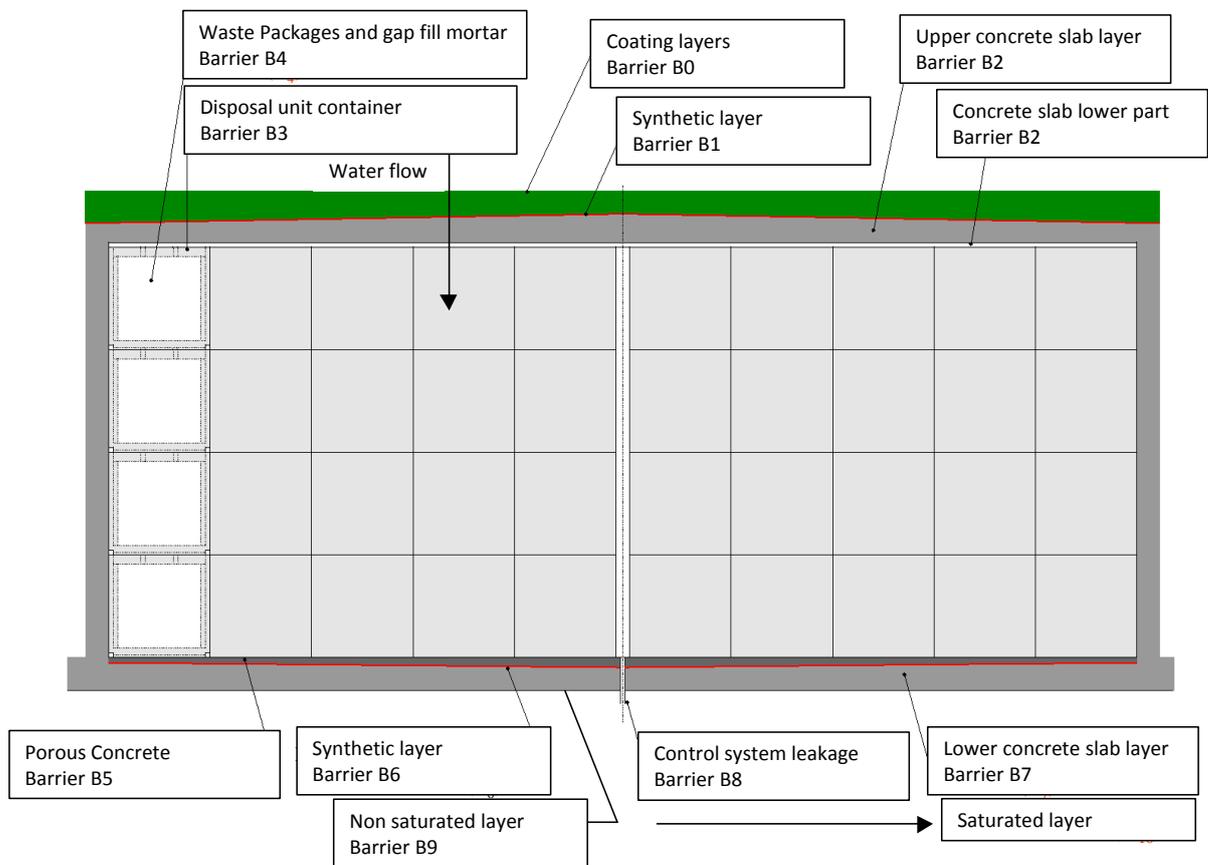
- Multiple coating layers.
- Synthetic non permeable layer.
- Concrete slab layer over the cells.
- Concrete containers (Disposal Units).
- Layer of porous concrete.
- Synthetic non permeable layer.
- Concrete slab layer under the cells.
- Control System of leakage

The barriers considered in transport processes of radionuclides are all but synthetic barriers and the control system of leakage.

**Table 1** summarizes the properties of different layers indicated, and Figure 3 depicts the El Cabril barriers.

| <b>Barrier</b>                                        | <b>Function</b>                                                                                                           | <b>Material</b>                                                                  | <b>Properties</b>                                                                                                                 | <b>Main parameters involved in long term safety assessment</b>                             |
|-------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------|
| Coating layers (Barrier B <sub>0</sub> )              | Structural stability<br>Hydraulic resistant<br>Thermal insulating<br>Erosion protection<br>Biological intruder protection | Ensemble of different material layers which drain and have very low permeability | Low permeability/<br>drainage                                                                                                     | Permeability/Hydraulic conductivity<br>Thickness                                           |
| Concrete slab over cells (Barrier B <sub>2</sub> )    | Withstand the upper coating layers<br>Structural stability<br>Hydraulic resistant                                         | Concrete                                                                         | Mechanical strength<br>Very Low permeability                                                                                      | Permeability/Hydraulic conductivity<br>Diffusion coefficient<br>Distribution coefficient   |
| Container of Disposal Units (Barrier B <sub>3</sub> ) | Structural stability<br>Hydraulic resistant<br>Retainable properties                                                      | Concrete                                                                         | Mechanical strength<br>Thermal cycles<br>Irradiation resistance<br>Low permeability.<br>Low release of activity                   | Permeability/Hydraulic conductivity<br>Annual Release Fraction<br>Distribution coefficient |
| Conditioned waste packages (Barrier B <sub>4</sub> )  | Structural stability<br>Retention of<br>Retainable properties                                                             | Cement matrices<br>Mortar envelopes                                              | Mechanical strength<br>Thermal cycles<br>Irradiation resistance<br>Leaching values<br>Diffusion values<br>Low release of activity | Leaching rate<br>Diffusion coefficient<br>Distribution coefficient                         |
| Gap fill mortar (Barrier B <sub>4</sub> )             | Structural stability<br>Retainable properties                                                                             | Filling mortar<br>Sealed mortar                                                  | Mechanical strength<br>Thermal cycles<br>Irradiation resistance<br>Leaching values<br>Diffusion values<br>Low release of activity | Leaching rate<br>Diffusion coefficient<br>Distribution coefficient                         |
| Concrete slab under cells (Barrier B <sub>7</sub> )   | Structural stability<br>Hydraulic resistant<br>contaminants                                                               | Concrete                                                                         | Mechanical strength<br>Very Low permeability                                                                                      | Permeability/Hydraulic conductivity<br>Diffusion coefficient<br>Distribution coefficient   |

**Table 1 Barrier system at El Cabril disposal centre -Summary of properties of different layers**



**Figure 3 Barrier system at El Cabril disposal centre**

Gaseous release is also considered by means of anaerobic corrosion of metallic containers of packages, water radiolysis and, in a lesser extends, biologic degradation of organic carbon. Gaseous release is much lower than water release.

### Disposal of graphite

The most important issues for the Vandellos 1 irradiated graphite to be disposed in El Cabril are the C-14 activity content, and the release of the liable fraction of C-14 and H-3 that are present along with the fixed fraction. The graphite matrix is itself a very stable material, and many leaching tests have concluded that the fixed H-3 and C-14 are quite stable in the irradiated graphite matrix in time.

Before putting the graphite inside any container, a treatment of the graphite is required for the fulfillment of WAC. The main treatment to be applied to the graphite is the following:

- Thermal decontamination under controlled non oxidizing atmosphere. This process will remove the labile fraction, which will be trapped in secondary waste. Additional C-14 and almost all H-3 is foreseen to be released.
- Impermeable Glass Matrix applied to the thermal decontaminated graphite. The final product is a very stable material, with a negligible or inexistent release rate of radionuclides.

Currently under study the kind of silicates that better fit to both the Vandellos 1 graphite and the El Cabril water. The values of release rate to be used in the transport processes involved are expected to be quite below the WAC rates, therefore decreasing the release flux of C-14 and increasing the delay date of maximum release to the biosphere.

### **Intrusion scenarios after surveillance period**

In addition to the activity release described, after the operational phase of the repository, the human intrusion scenarios are the other way by which radionuclides can be release to the biosphere.

The dose limits considered for the scenarios involved are in general 1 mSv/year and some added scenarios consider 0.1 mSv/y. The total number of scenarios considered after institutional period of 300-500 years is five.

Alpha emitters are low in the irradiated graphite, and strong gamma emitters (Co-60 mainly) are expected to be quite low after that period of surveillance. These considerations, along with the radionuclides discarded during thermal decontamination and the amount of irradiated graphite (3500 tons), make the doses produced by irradiated graphite in intruder scenarios equivalent or lower than the doses caused by other wastes.

The scenarios are related to the construction of public building or residence ones with agriculture activities. Exposure and inhalation doses are the general pathways, but also in some scenarios the ingestion via is also taken into account.

---

## **ROMANIA: SUMMARY OF WORK BY INR - ROMANIAN DISPOSAL CONCEPT AND SURFACE DISPOSAL ANALYSIS**

---

### **Conceptual design**

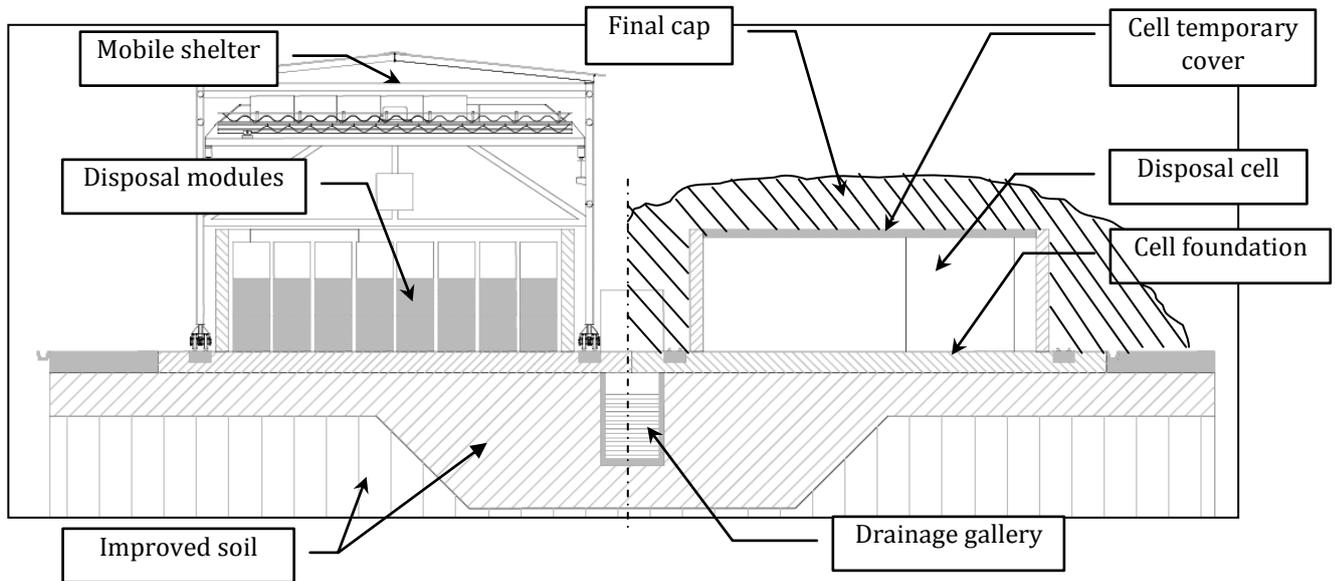
The mass of nuclear irradiated graphite in Romania does not exceed 10 tonnes, coming partly from the thermal column of TRIGA reactor at INR site, and partly from decommissioning of the VVRS reactor in Bucharest. The most important radioisotopes for long term activity of disposed irradiated graphite are C-14 and Cl-36.

The C-14 inventory estimated from combined graphite measurements and ORIGEN simulations in irradiated graphite from TRIGA reactor is 2.1010 Bq [i]. For the Cl-36 inventory only, ORIGEN simulations are available that estimate it at 8.5.109 Bq [i].

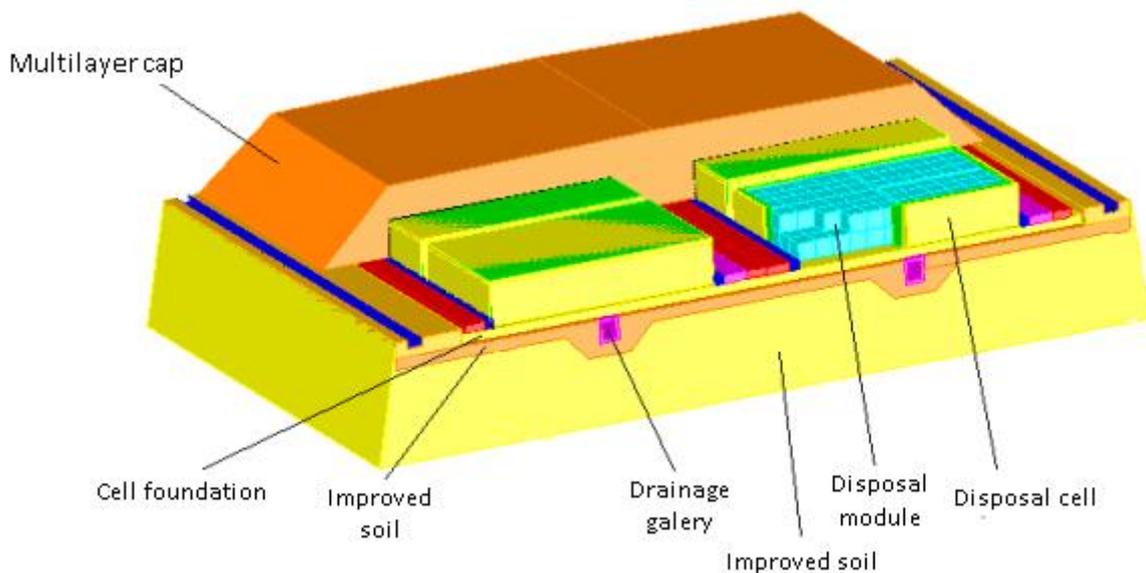
An optimal solution for the final disposal of irradiated graphite is sought and the most favoured option currently converges to the disposal in a near surface repository, considering the plan of building a low and intermediate level waste repository at Saligny site, near the Cernavoda NPP.

Performance assessment was accomplished with GoldSim software for irradiated graphite from TRIGA reactor. The dose contribution was computed only for C-14 (gas and water pathway) and Cl-36 (water pathway). Two cases were considered: no engineered barriers - in order to obtain the most conservative dose value; and concrete as graphite encapsulation and disposal matrix.

This multi-barrier disposal facility illustrated in Figure 4 and Figure 5.



**Figure 4** The cross section of the repository



**Figure 5** General view of the disposal system

This ensures the safe isolation of the waste through the combination of the natural barrier (Saligny geology) with the following engineered barriers [ii]:

- the waste form (mainly cemented waste);
- disposal module (container) – durable element, prefabricated from reinforced concrete in order to ensure the long term radionuclides retention

- the disposal cell, together with the separated drain water systems for the cell infiltrated water and of the meteoric waters;
- the improved foundation ground; and
- the multi-layers closing system (isolating and draining layers) of the cells acting as a long-term protection barrier against rainwater infiltration inside the disposal unit consists of compacted loess and bentonite combined with different synthetic layers.
- the geological environment consisting in 50m unsaturated zone of loess and clay layers laying on a limestone platform, hosting the main aquifer.

The Saligny repository is intended to host operational LIL-SL waste but also same limited amounts of LL radionuclides [iii] such as C-14, I-129, Cl-36.

### **Assessment of radiological impact of C-14 and Cl-36 from irradiated graphite surface disposal**

The dose assessment model proposed by INR is rather conceptual than realistic, aiming to serve as a template on which adjustments are still to be made as soon as new data become available. The study assumes the independent disposal of 2.5 tones of irradiated graphite accounting for the TRIGA graphite inventory in a near surface facility having Saligny site characteristics. Only dose produced by C-14 and C-36l potential releases are assessed.

C-14 has an extremely complex behavior in geological environment and may be partitioned between liquid, gaseous and solid phases, its distribution being controlled by the carbonate chemistry, microbial and gas generating processes. The current performance assessment of the near surface disposal does not take all these into account.

Cl-36 behaves much simpler, being potentially released only in liquid phase and with no significant interaction with materials expected in a geological disposal facility.

### **Source term**

The inventory of C-14 was considered 2.1010 Bq based on radionuclide measurement of samples from TRIGA reactor and complies the Waste Acceptance Criteria (WAC) established for Saligny repository (MAAL=1.105 Bq/g).

The inventory of Cl-36 amounting 8.5.109 Bq was inferred from computation using the ORIGEN code, in the absence of experimental data. This amount exceeds with two orders of magnitude the WAC (MAAL=10 Bq/g). Future experimental measurements on irradiated samples must confirm the simulated amount.

The C-14 release is not well understood yet and data from literature show that different graphite samples behave differently and different testing laboratories have not obtained the same values of leaching rates on equivalent samples when comparison have been made [iv]. In the absence of dedicated studies to determine the leaching rate of C-14 and respectively Cl-36 from irradiated graphite of the TRIGA thermal column, the model uses the fractional release rates from [v], namely  $1.7 \cdot 10^{-2}$  1/yr for C-14 and  $3.7 \cdot 10^{-1}$  1/yr for Cl-36.

Two distinct cases were analyzed:

- Case 1 assumes that both C-14 and Cl-36 are available for transport neglecting the concrete surrounding the irradiated graphite, and

- Case 2 considers 300 years of concrete barrier embedding irradiated graphite dispersed inside a disposal cell, 1m high concrete liner as cell foundation and 0.60m concrete walls around. To conform with the WAC for Cl-36, irradiated graphite disposal in a separate disposal cell is assumed. Sorption on concrete of  $K_d=5\text{cm}^3/\text{g}$  for Cl-36, and  $K_d=2.10^3\text{cm}^3/\text{g}$  for C-14 is used for assessing the effect of retardation.

### **Assumptions for C-14 and Cl-36 transport**

Gaseous C-14 is supposed to migrate in the cover system of the repository through advection and diffusion. The advective characteristics were determined in laboratory on compacted loess and clay samples with porosities and saturation specific for the cover layers [vi] as part of WP6.4. It is considered that C-14 is released initially in aqueous phase and it is further partitioned between gaseous and aqueous phase according to Henry law. Cl-36 will not be transported through the cover material.

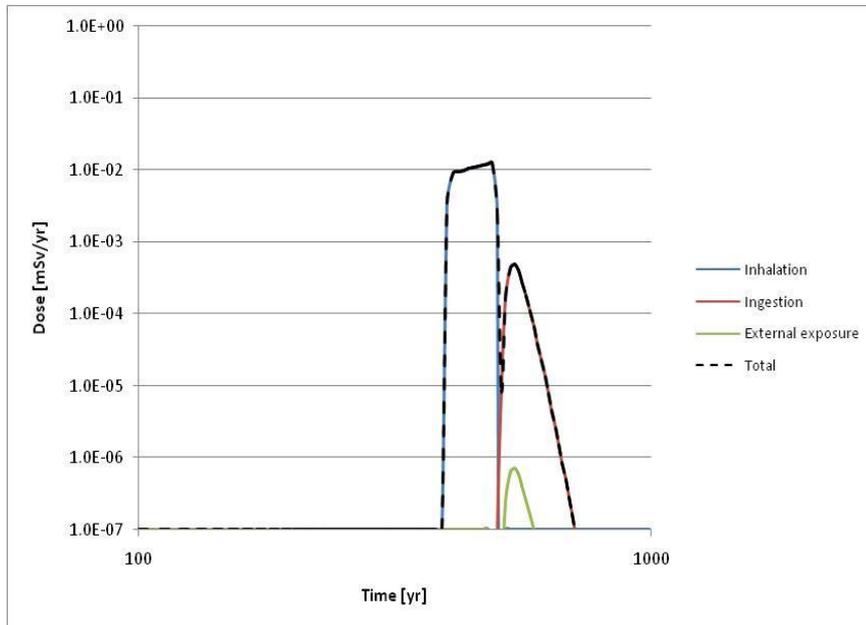
In order to assess the impact on the annual individual dose, the model takes into account all contamination pathways: ingestion, inhalation and external exposure [vii] using the reference scenario corresponding to a residence farm built on the site after 300 years when the institutional surveillance ends.

### **Dose assessment for C-14 and Cl-36 released from irradiated graphite**

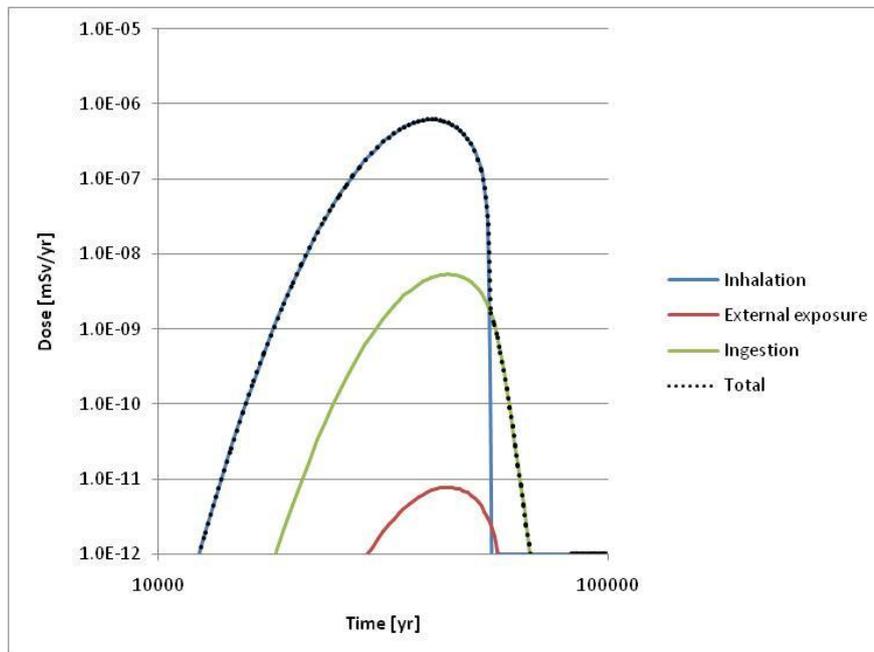
The entire computation was performed using GoldSim software based on submodels for transport and dose conversion developed as part of the INR work in WP6.4 [vi]. Concentration of C-14 in the atmosphere and concentration of C-14 and Cl-36 in a fountain located at 100 m far away from the disposal area were converted to dose inside the Biosphere Submodel. The Biosphere Submodel contains several expressions and parameters taken from the conceptual model ERMYN (Environmental Radiation Model for Yucca Mountain, Nevada) [viii, ix, x].

### **Results**

The maximum total annual dose due to the C-14 summing all contamination pathways is estimated to an order of  $10^{-2}$  mSv/year (Figure 4) if no engineered barriers are considered and decreases to  $10^{-6}$  mSv/yr when cementitious barriers and sorption on cement are considered (Figure 5). The most important contribution to the dose is given by C-14 inhalation as  $^{14}\text{CO}_2$ , in both cases while external exposure contribution to the dose is negligible.

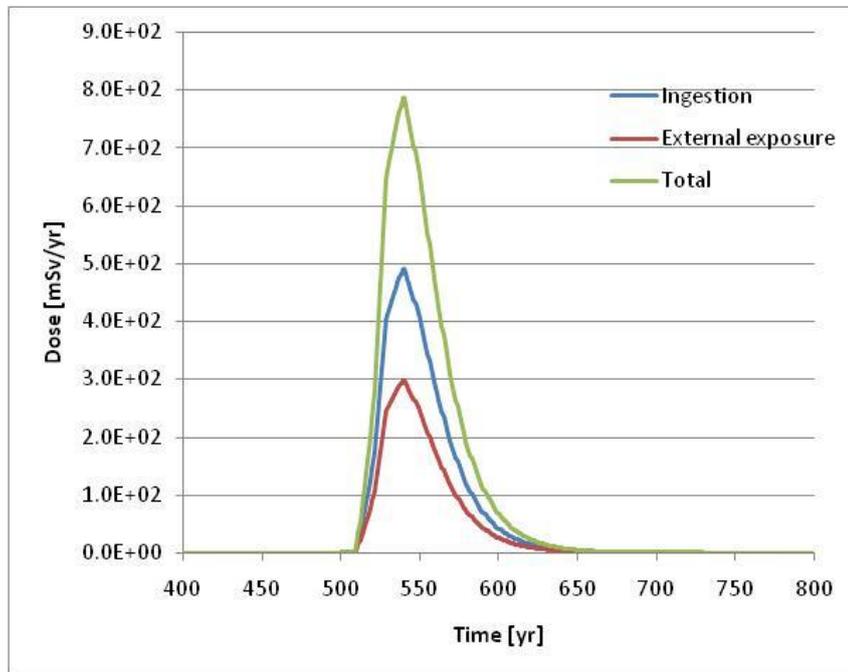


**FIGURE 6. ANNUAL INDIVIDUAL DOSE DUE TO C-14 RELEASE FROM IRRADIATED GRAPHITE IF NO ENGINEERED BARRIERS ARE CONSIDERED (CASE 1)**



**FIGURE 7. ANNUAL INDIVIDUAL DOSE DUE TO C-14 RELEASE FROM IRRADIATED GRAPHITE IF CEMENTITIOUS BARRIERS ARE CONSIDERED (CASE 2)**

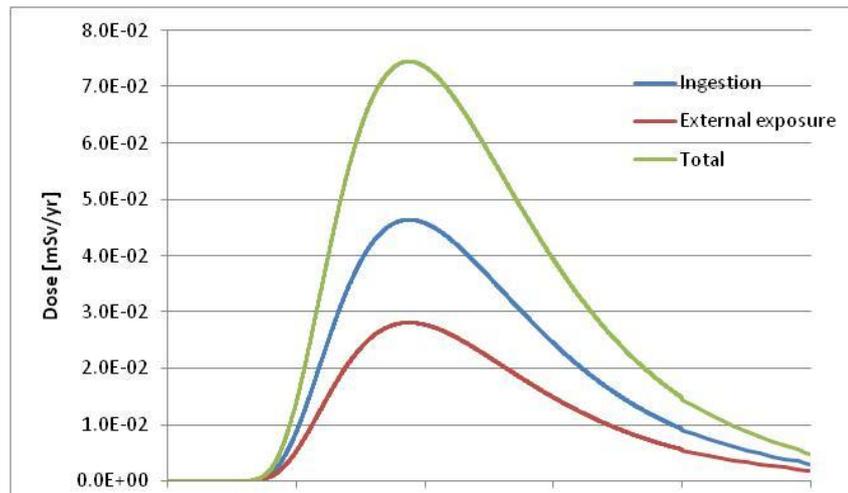
If no engineered barriers are considered (case 1), the value for Cl-36 dose largely exceeds the accepted dose limit (1 mSv/year) (Figure 6).



**FIGURE 8. INDIVIDUAL ANNUAL DOSE DUE TO CL-36 RELEASE IF NO ENGINEERING BARRIERS ARE CONSIDERED (CASE 1)**

If the graphite is dispersed in a cementitious matrix inside a disposal cell, the dose value becomes acceptable, the maximum having the order of  $10^{-2}$  mSv/yr (Figure 7). However, due to its higher radiotoxicity, the value is much higher than the one estimated for C-14 in the same conditions ( $10^{-6}$  mSv/yr). For Cl-36 the most significant contribution to the dose is given by ingestion, in both cases.

Summarizing, C-14 does not represent a concern for surface disposal of irradiated graphite from TRIGA reactor, neither as gas nor as solute. Cl-36 could be accommodated in a surface repository if



**FIGURE 9. INDIVIDUAL ANNUAL DOSE CONSIDERING CEMENTITIOUS BARRIERS (CASE2)**

appropriate disposal concept minimizing the specific activity under the WAC limit is considered. Under these conditions, the dose constrain is fulfilled.

---

## GEOLOGICAL DISPOSAL FACILITY FOR GRAPHITE WASTE

---

---

### LITHUANIA: SUMMARY OF WORK BY LEI - STUDY ON GEOLOGICAL DISPOSAL OF GRAPHITE

---

#### **Lithuanian repository concept**

The graphite reactor core elements from the Lithuanian nuclear power plant at the Ignalina site are from RBMK-1500 reactors. Two units of Ignalina NPP were equipped with RBMK type reactors consisting of graphite as a moderator and reflector. There is no final decision on the long-lived intermediate level waste (ILW) disposal option or disposal container in Lithuania. The ILW (including irradiated graphite) are planned to be stored in the steel containers at interim storage facility until the final decision will be made [xi]. According to proposed generic repository concept for RBMK-1500 spent nuclear fuel (SNF) disposal in the crystalline rocks in Lithuania, the long-lived intermediate level waste (ILW) could be disposed at the same repository at certain distance from SNF emplacement tunnels [xii]. The ILW emplacement tunnels could be approximately 16 × 16 m in cross-section. Within this study, a cementitious grout (NRVB backfill) was assumed as proposed in the Nirex concept (United Kingdom) to fill void regions within the tunnels after the emplacement of the ILW. In the case of RBMK-1500 graphite disposal in crystalline rocks in Lithuania, the far field will consist of crystalline host rocks and a cover of sedimentary rocks of different hydrogeological properties (forming aquifers and aquitards). As there are no outcrops of the crystalline basement in Lithuania it will be difficult to find crystalline rocks at the depth smaller than 200–300 m. In the south of Lithuania, crystalline rocks occur at the depths ranging from 210 m to 700 m, while in most of Lithuania the depth of the basement exceeds 700 m, reaching 2300 m in the west.

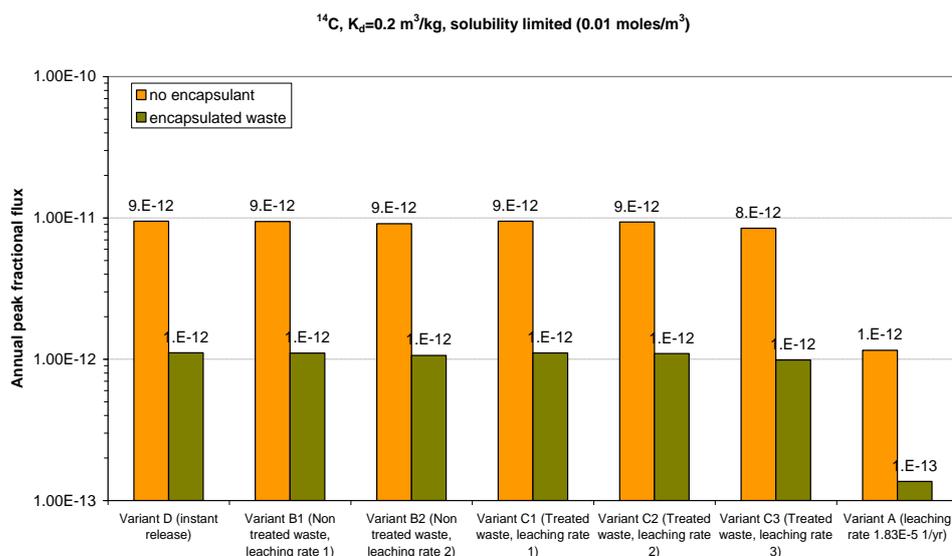
The main task for LEI was to study the differences between treatment and disposal options on the behaviour of RBMK-1500 graphite in crystalline rock. The source term was based on the analysis performed by LEI within CARBOWASTE WP3. The graphite blocks are of GR-280 type and the graphite sleeves are of GRP-2-125 type. Based on the results of WP3 [xiii] and taking into consideration the maximum concentration of initial nitrogen impurities in graphite matrix and nitrogen present in all (open and closed) graphite pores, the maximum activity of GR-280 type graphite was used. The amount of graphite waste coming from the Ignalina NPP Unit 1 and Unit 2 has been taken into account (in total ~3800 tonnes) [xi]. The release rate at which the radionuclide is being released by leaching in groundwater depends on the waste matrix itself and whether or not the waste form has been pre-treated.

Leaching experiments of graphite indicate an initially higher release rate upon the contact with repository water and a slower release rate at longer times. This corresponds to the different location and origin of C-14 within the waste and its availability to be released. Different treatment options may lead to the removal of the more labile part of inventory during the process. Due to lack of empirical data the illustrative rates (Table 2) were selected in this study to represent possible differences on non-treated/treated graphite for the analysis of C-14 migration from the graphite disposed of and to evaluate the impact of these differences on the radionuclide flux to geosphere. The importance of the waste leaching rate was analyzed within the context of different performance of engineered barriers considering 3 different cases each supplemented by a number of variants (Table 2).

| Cases                                                                                           |                                |                                                              |
|-------------------------------------------------------------------------------------------------|--------------------------------|--------------------------------------------------------------|
| <b>Case 1: <math>K_d=0</math>, no solubility limitation</b>                                     |                                |                                                              |
| <b>Case 2: <math>K_d=0</math>, solubility limit=0.01 moles/m<sup>3</sup></b>                    |                                |                                                              |
| <b>Case 3: <math>K_d=0.2</math> m<sup>3</sup>/kg, solubility limit=0.01 moles/m<sup>3</sup></b> |                                |                                                              |
| Variants based on fractional leaching rate (1/yr) of C-14 from graphite (for each case):        |                                |                                                              |
| Variant A                                                                                       | $1.83 \cdot 10^{-5}$           | Experimentally measured rate [xiv]                           |
| Variant B1                                                                                      | <10 yr - 0.1<br>>10 yr - 0.01  | Corresponds to not treated waste, higher leaching rate [xiv] |
| Variant B2                                                                                      | <10 yr - 0.1<br>>10 yr - 0.001 | Corresponds to not treated waste, lower leaching rate [xiv]  |
| Variant C1                                                                                      | 0.1                            | Corresponds to treated waste, highest leaching rate [xiv]    |
| Variant C2                                                                                      | 0.01                           | Corresponds to treated waste, lower leaching rate [xiv]      |
| Variant C3                                                                                      | 0.001                          | Corresponds to treated waste, the lowest leaching rate [xiv] |
| Variant D                                                                                       | instant release from waste     | Barrier function of solid waste matrix disregarded           |

**Table 2 Analyzed cases and variants based on leaching rate and cementitious barrier performance**

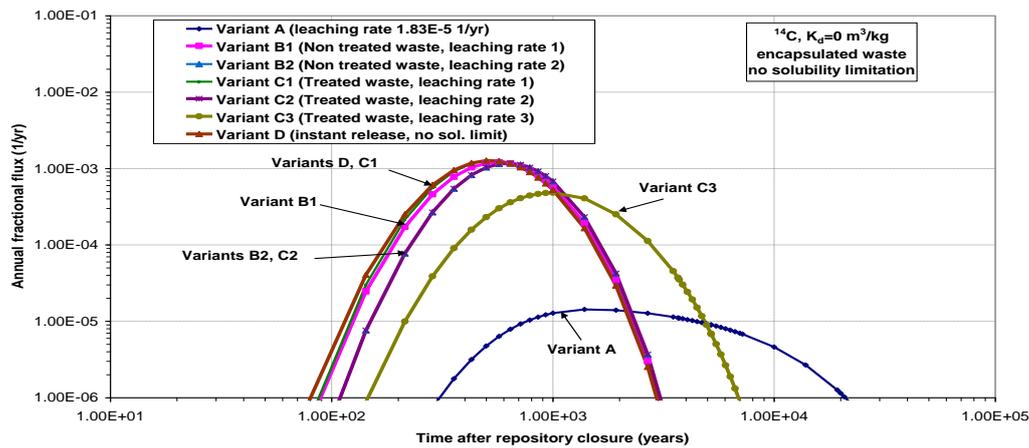
Modeling of the radionuclide migration within the near field was performed using the AMBER code (UK). The model for the radionuclide transport through the geological formations was developed with the TOUGH2 (USA) computer code. Modeling was undertaken for two options, one using the reference near field model (for non-encapsulated waste) and an alternative near field model (considering possible encapsulation). The comparison of the results for one of the analyzed cases is presented in Figure 10.



**Figure 10 Comparison of peak release for non encapsulated and encapsulated waste (results of Case 3, considering sorption and solubility limitation)**

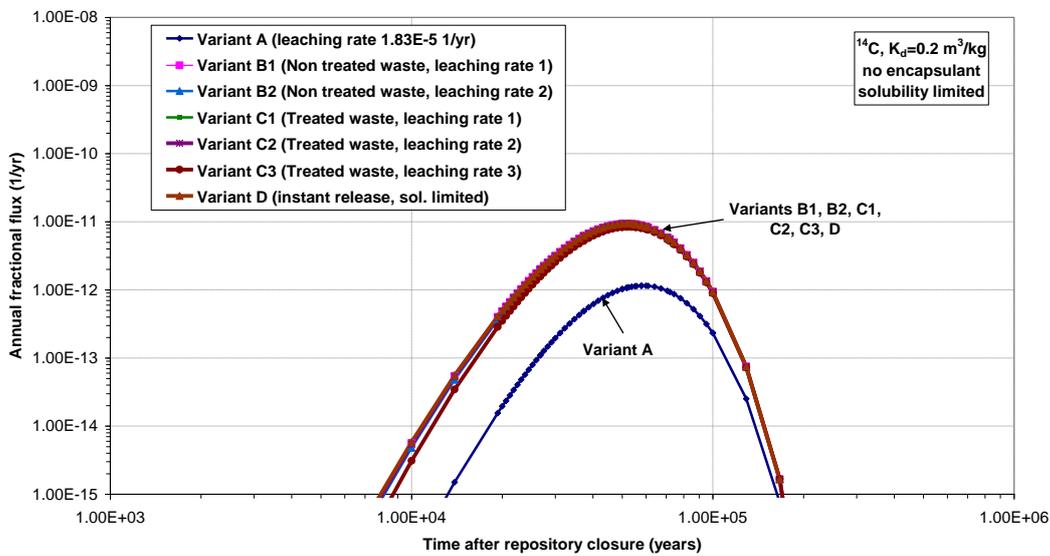
Considering sorption, the impact of waste encapsulation is significant and leads to a decreased peak C-14 flux by up to approximately one order of magnitude in comparison to the non-encapsulated waste.

Modeling results of C-14 transport with no interaction in the near field showed that the differences in leaching rates do not lead to the same differences in the peak flux to the geosphere (Figure 11).



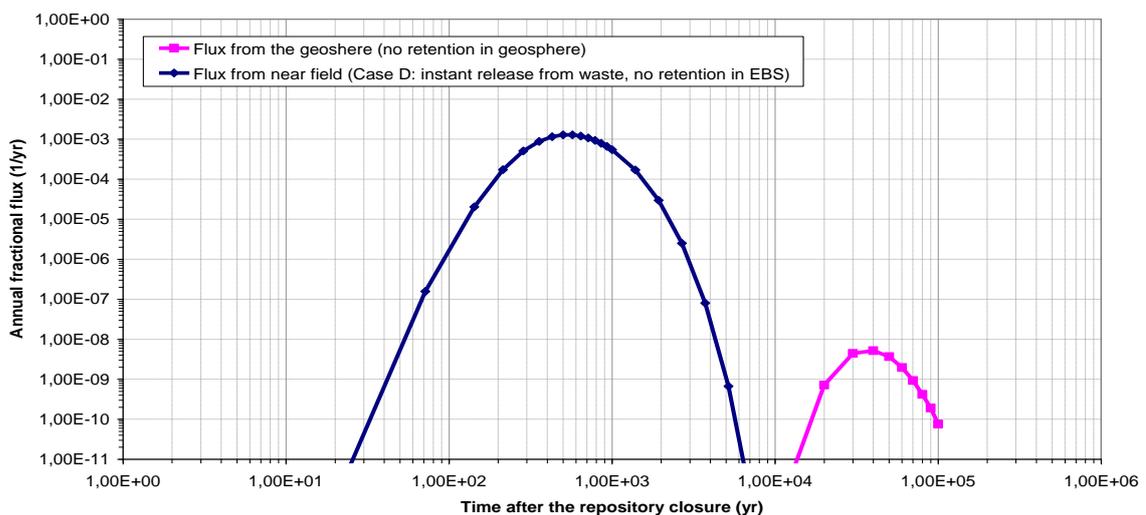
**Figure 11 Release of C-14 to the geosphere from one disposal container with non encapsulated waste (results of Case 1, sorption and solubility limit disregarded)**

Radionuclides released from graphite at rates of the order of  $10^{-2} - 10^{-1}$  1/yr (variants B1, B2, C1, C2) were released to the geosphere at similar rate as in case of instant release. If the radionuclides were released at lower rates (or the order of  $10^{-3}, 10^{-5}$  1/yr with RBMK-1500 inventory) the flux to the geosphere becomes more dependent on the leaching rate. Due to transport and chemical interaction with a tunnel backfill material (in terms of sorption and solubility), the C-14 flux to the geosphere was significantly decreased and the maximal fractional flux is in the range of  $10^{-12}-10^{-11}$  1/yr (Figure 12) in comparison to  $10^{-5}-10^{-3}$  1/yr without consideration of these two processes. No plateau in the profile was observed indicating the concentration in the pore water was not solubility limited, as a large part of leached inventory could be removed from liquid phase by undergoing sorption (Figure 12).



**Figure 12 Release of C-14 to the geosphere from one disposal container with non encapsulated waste (results of Case 3, considering sorption and solubility limitation)**

C-14 flux results from Case 1 (sorption and solubility limit disregarded) and instantly released inventory from the waste matrix were transferred to the far field model built in TOUGH2 (Figure 13). Modeling results showed that the natural barrier system contributes to the significant delay of radionuclides even with conservative assumptions on engineered and natural barriers, with a significant decrease of the maximal peak flux rate by at least five orders of magnitude.



**Figure 13 Release of C-14 from the backfill and geosphere**

The peak fractional flux of dissolved C-14 from the near field and far field was compared to the transfer rate metric based on UK graphite inventory and a generic terrestrial biosphere model [xv].

This metric corresponds to the transfer rate which could give a rise to the impacts from UK inventory around the regulatory guidance levels. Modeling results showed that for much lower amount of RBMK-1500 graphite than in UK case the peak fractional flux would be less than the transfer rate metric even with conservative assumptions on the near field and far field performance. The compliance with the metric ( $7 \cdot 10^{-6}$  1/yr) would support the geological disposability of RBMK-1500 graphite in respect of C-14 migration in water.

In summary the importance of waste leaching rate depends on several aspects: on the performance of the backfill and natural barrier system (on the scope of its impact on the attenuation of the radionuclide flux). The impact of the options (treatment vs no treatment of graphite) on the C-14 flux to geosphere is not straightforward. While assessing the options of treating/not treating the inventory, leaching rates, barrier performance and transport conditions need to be considered.

### Conclusions of Lithuanian study

From the evaluation of the C-14 migration undertaken using the developed numerical models for RBMK-1500 irradiated graphite disposed of in the crystalline rocks for different options, it is concluded that:

- The peak fractional flux from the near field would vary within approximately 1-2 orders of magnitude due to different leaching rates from the graphite waste (difference in the leaching rate was within app. 5 orders of magnitude);
- The radionuclide transport analysis considering the possible graphite waste encapsulation in the cement material revealed that waste encapsulation could give a benefit for the radionuclide flux attenuation up to approximately one order of magnitude;
- For the conservative far field modeling case (instant release from waste, no sorption in the near field and far field, repository location in upward flow conditions), the natural barriers contribute to the delay and decrease of dissolved C-14 flux from the generic repository with RBMK-1500 irradiated graphite by at least by 5 orders of magnitude.

For much lower amount of RBMK-1500 graphite than in UK case the peak fractional flux would be less than the UK inventory based transfer rate metric even with our conservative assumptions on the near field and far field performance. The compliance with the metric ( $7 \cdot 10^{-6}$  1/yr) would support the geological disposability of RBMK-1500 graphite in respect of C-14 migration in water.

---

## UNITED KINGDOM: SUMMARY OF WORK BY NDA RWMD - UK STUDY ON GEOLOGICAL DISPOSAL OF GRAPHITE

---

NDA RWMD commissioned a study to support its contributions to CARBOWASTE [xv]. The objective of this study is to examine the suitability of irradiated graphite wastes for geological disposal. This is achieved by testing whether graphite can be safely disposed in a wide range of disposal systems, where a disposal system comprises the near-field and geosphere barriers.

The analysis is not tied to a specific disposal concept, geosphere environment, or facility depth. Instead the performance of the different barriers that may be included in a disposal concept and can contribute to the post-closure safety is explored. Reference [xv] is therefore relevant to all organisations considering geological disposal of graphite (RWMD, other participants within CARBOWASTE and other waste management organisations, including those considering shallow geological and near-surface disposal).

Calculations in support of the analysis have been undertaken for the UK national inventory of irradiated graphite wastes, which comprises a significant volume of waste and a significant associated radionuclide inventory. Therefore conclusions that are drawn regarding the suitability of irradiated graphite wastes for geological disposal are relevant to large waste inventories, not only small quantities of irradiated graphite.

### **Key messages**

The analysis presented in [xv] has demonstrated that it should be possible to safely dispose of irradiated graphite wastes in isolation (i.e. in vaults containing only packages of graphite wastes) in a wide range of disposal systems (i.e. combination of disposal concept / EBS and geosphere); including near-surface, shallow and deep geological disposal and a wide range of host rocks. Assessment calculations show that regulatory guidelines can be satisfied even given conservative assessment assumptions. A broader range of systems might be suitable given less conservative calculation assumptions. One particular issue that potentially requires careful management is the potential impacts associated with disruption of, or large scale intrusion into, near-surface facilities.

It may also be possible to safely dispose of irradiated graphite wastes in the same vaults as other ILW in a wide range of disposal systems. However, a broader range of processes become important, behaviour becomes more site / design specific and the important scenarios and behaviours may change as the system evolves. This makes it difficult to generically explore the suitability of graphite for geological disposal with other ILW.

Specific waste types of concern are those that give rise to bulk gas generation (i.e. metals, organics, strongly irradiating wastes) and that might lead to incorporation of C-14 in methane gas (i.e. organics), and therefore increase the potential for generation and transport of C-14 labelled gases. The potential for transport of C-14 labelled gases is particularly important for fractured host rocks and potentially for lower permeability host rocks where the concept includes an Engineered Gas Transport System (EGTS) to control the peak gas pressure.

Therefore, although it may not be necessary in all cases, there are advantages to disposing graphite wastes in isolation compared with co-disposal in the same vaults as other ILW. These include:

- simpler, more predictable behaviour;
- improved performance, e.g. transport in gas not likely to be an issue; and

- simplified safety arguments and safety case.

In the UK, the majority of the graphite waste (by volume and radionuclide inventory) is classified as Shielded ILW (SILW). SILW contains relatively little quantities of organic and reactive metals, which are largely associated with Unshielded ILW (UILW) wastes. Further segregation of graphite from other SILW should be relatively straightforward and might offer performance benefits, for example through the ability to optimise the disposal concept for graphite wastes.

If transport of C-14 in gas is of concern for segregated graphite waste packages, e.g. potentially in a fractured host rock, it is likely that further performance benefits would be obtained from disposing graphite in concrete containers rather than steel containers, thereby reducing bulk gas generation to a very low level. This would also reduce the potential for reduction of inorganic C-14 to  $^{14}\text{CH}_4(\text{g})$  by autotrophic bacteria, using  $\text{H}_2$  derived from anaerobic corrosion of steel, to a very low level. The potential significance of this process for isolated packages of graphite waste in steel containers is uncertain, although the available information and expert judgements indicate that it is unlikely to be significant.

### Summary of system performance

A comprehensive analysis of the potential impacts arising from geological disposal of graphite wastes has been undertaken and is reported in [xv]. The findings are summarised as follows.

The key radionuclides associated with irradiated graphite are C-14 and Cl-36. Transport in water (C-14 and Cl-36) and gas (C-14) are the key processes of concern in relation to the normal evolution of the geological disposal facility. Transport in gas is unlikely to be a significant issue for graphite wastes that are disposed in isolation from other wastes, and near-field and geosphere barrier properties that are consistent with performance for transport in water have been calculated.

Potential doses associated with human intrusion into a GDF containing graphite wastes are not insignificant. However doses associated with graphite wastes are likely to be lower than those associated with other waste types likely to be consigned to such a facility. This is because the dominant radionuclides for such scenarios (strong gamma emitters and alpha-emitters) are not present at significant concentrations in graphite. Therefore, external doses from examining borehole cores and associated situations are lower than for other ILW types.

Potential doses associated with human intrusion into **untreated** graphite wastes are significantly greater for an SDF where large scale excavation of solid material is possible. Similarly, large scale disruption of an SDF by natural processes and events could lead to significant doses to subsequent site occupiers, compared with regulatory guidelines. In both cases doses are due to uptake via the foodchain. Therefore for an SDF, were untreated graphite wastes to be disposed, the significant potential for large scale human intrusion and the fate of exposed material could be important considerations in determining the acceptability of the concept.

If packages of graphite wastes are disposed in the same vault as packages of other ILW, the system behaviour may be more complex and hence less readily predictable than for a vault containing only packages of graphite wastes. For example, the presence of organic wastes may lead to methanogenic conditions being established upon their degradation, thus increasing the potential for incorporation of C-14 in methane gas and thereby increasing the potential mobility of C-14 and potential C-14 fluxes to the biosphere. In such cases, the individual waste packages may be important barriers to prevent interaction between graphite and organic wastes and incorporation of C-14 in methane. (It should be possible to maintain container integrity until methane generation from organic wastes has reduced to low levels).

With increasing organic and metal (particularly reactive metal) waste inventories in the disposal vaults, the potential total bulk gas generation rate will also increase (given certain assumptions, in particular assuming sufficient water is available to support corrosion). This has the potential to significantly increase the mobility of C-14 via a number of complex processes:

- in higher strength host rock, bulk gas acts as a carrier gas for C-14 labelled trace gases, e.g. by establishing a gas pathway to the surface or near-surface environment, including a shallow aquifer;
- in lower strength sedimentary host rock, bulk gas may lead to pressurisation and potential for fluids to be driven through the EDZ and any poorly performing seals; and
- potential for ejection of C-14 in water, slurry and particulates following intrusion into a pressurised GDF (see below).

For graphite wastes, the highest potential doses from an intrusive event are associated with site occupancy following surface release of C-14 and Cl-36 from a borehole in water, entrained particulates or slurry. Ejection of such material is more likely where there is significant gas generation leading to pressurisation in the vaults.

For deep geological disposal, natural disruptive events are very unlikely to significantly enhance the potential dose from graphite wastes. An event could potentially result in a more conductive groundwater pathway to the surface. However, the key radionuclide in graphite wastes for such a pathway, Cl-36, is sufficiently long-lived and mobile that, for many host rocks, an enhanced pathway is unlikely to significantly affect the peak dose or risk, just the time at which it may arise.

---

## FRENCH IRRADIATED GRAPHITE MANAGEMENT SCENARIOS

---

In France, i-graphite accounts for c. 23,000 tons of low level waste, and mainly arises from former UNGG reactors (graphite moderated reactors, fuelled with natural uranium and cooled with CO<sub>2</sub>) that were operated in France from 1956 to 1994.

Initially, French i-graphite was planned to be disposed in a dedicated disposal located between 50 to 200 metres underground. Such a scenario was notably based on the i-graphite content in CI-36 which required a significant clay thickness in order to mitigate CI-36 flow rate.

Since 2010 recent developments in graphite waste treatment and progress in radiological characterization led Andra and waste owners to consider alternative management scenarios based on potential treatment and sorting, making it possible to open different disposal options. The following scenarios are thus being investigated from the perspectives of safety, cost and project risks:

- The first option considers a separate management (sorting) of graphite sleeves and piles based on their different radiological inventory. In particular, CI-36 inventory is currently assessed to be far lower in graphite piles than in graphite sleeves whereas piles represent the main part of French i-graphite tonnage (c. 18,000 tons). In this scenario, piles would be co-disposed with radium bearing waste in a shallow disposal facility while remaining graphite waste, including sleeves, would be disposed with IL-LL waste 500 meters underground in the French deep disposal "Cigéo"
- Another option is based on i-graphite treatment, ie. selective decontamination of graphite by means of thermal/chemical processes in order to make i-graphite inventory acceptable for shallow disposal. Partially decontaminated graphite would then be co-disposed with radium bearing waste in a shallow disposal facility while extracted radionuclides would be trapped, conditioned and disposed at "Cigéo" together with ILW-LL. If decontamination rates are high enough, partially decontaminated graphite could alternatively be gasified into carbon dioxide. Residual ashes would then be disposed at Cigéo.
- Design of a specific repository for the entire graphite waste inventory is still considered or alternatively direct disposal at "Cigéo" together with IL-LL waste.

Figure 14 represents these scenarios.

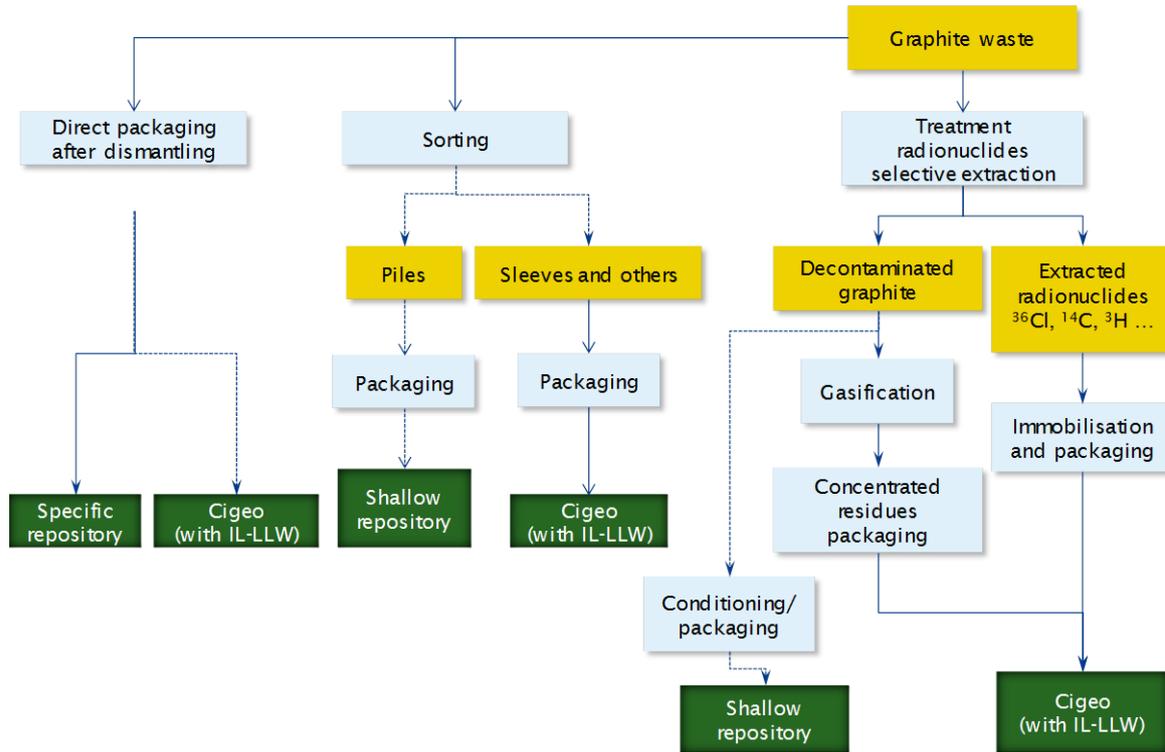


Figure 14 Potential scenario for French irradiated graphite

The following sections provide a brief overview of the shallow disposal and Cigéo facilities.

**Planned shallow disposal facility**

The shallow disposal option consists of a repository implementation within a low permeability clay formation at a depth of about 15 metres provided the host formation is outcropping (see illustration, Figure 15).

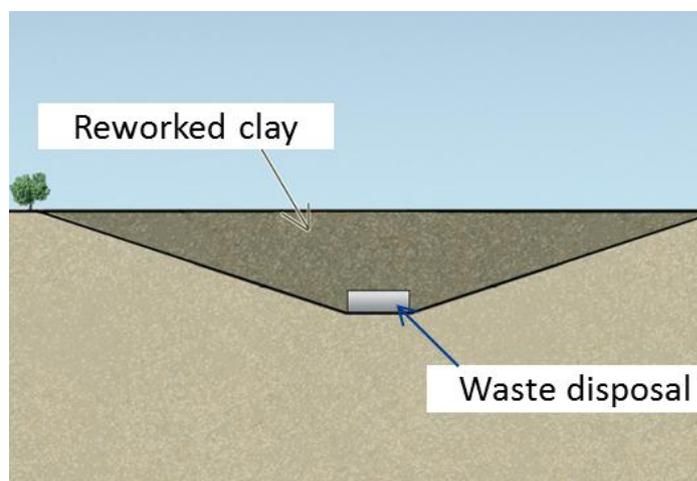


Figure 15 Schematic design of a shallow repository

The waste isolation capability is available as long as the geodynamic site evolution does not significantly modify the repository configuration (i.e. via erosion). With regard to its depth and the expected geological conditions, the stability of the repository is estimated to be about 50,000 to 100,000 years.

Consequently, the repository is designed for long-lived waste containing:

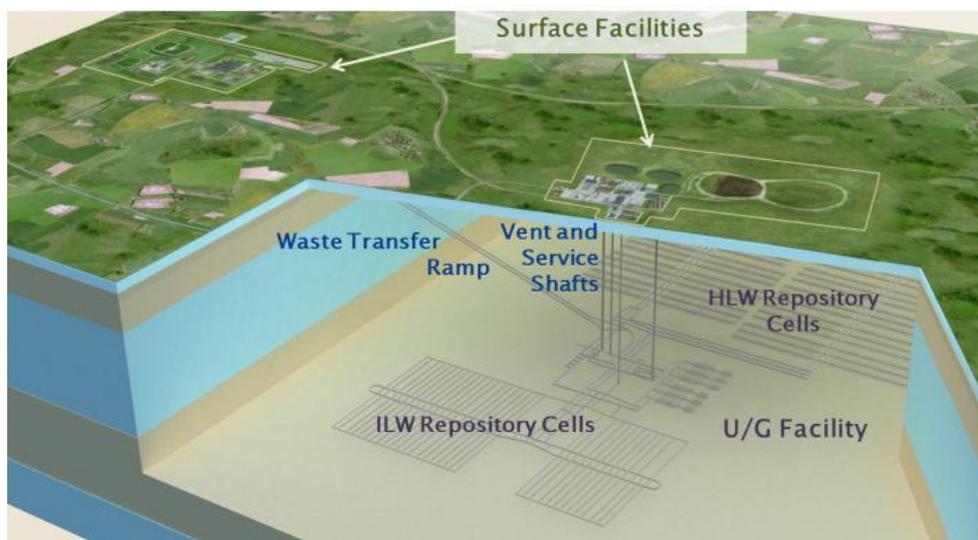
- Radionuclides with a low mobility and a radioactive period such that sufficiently low activities have been reached by decay in less than 50,000 years. The preservation of physical, chemical and hydraulic conditions limiting radionuclide mobility should be insured. The foreseen radionuclides should have a lifetime lower or equal to that of carbon-14 (half life 5,700 years), which in particular includes radium-226 (half life 1,600 years);
- A restricted activity in plutonium and americium
- A restricted activity of radionuclides that does not decay sufficiently within 50,000 to 100,000 years such as thorium-232, uranium-238 and uranium-235;
- A restricted activity of long-lived, potentially highly mobile radionuclides (e.g. chlorine-36)

Such a repository design is particularly suitable for radium bearing waste.

### Deep geological repository project

Within the framework of the Planning act of 28 June 2006, the geological repository, otherwise known as the Industrial Centre for Geological Disposal (Cigéo) is designed for high level (HLW) and intermediate level long-lived (IL-LLW) waste (see Figure 16). It will be implemented in the Meuse / Haute Marne districts in the North-East of France.

The underground repository cells are built at a depth around 500 meters below ground level within a thick clay rock layer. The disposal concept relies on the remarkable properties (retention capability, low permeability and homogeneity of the formation) of the clay rock which delays and mitigates the migration of the radionuclides contained in HLW and ILW-LL.



**Figure 16 Schematic design of the future HL/IL-LL waste repository “Cigéo”**

The Cigéo project has entered its industrial design phase in 2011. The results of 20 years of R&D have made it possible to issue detailed project technical requirements. A public debate is scheduled in 2013. The disposal facility is planned to be commissioned in 2025, subject to its authorization.

No overall performance analysis of the French case has been pursued within CARBOWASTE. Instead, a detailed modelling of waste performance has been performed.

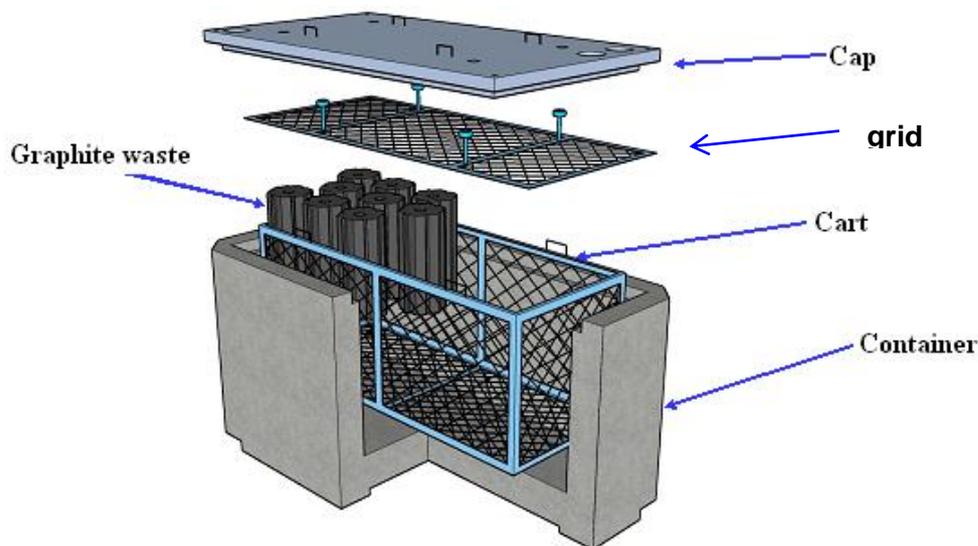
**Waste package based on CEM I and CEMV concrete**

Various alternatives of packaging concepts for graphite wastes based on CEMI and CEM V concrete were studied according to the origin of the graphite elements [xvi]. Models were developed to describe both the degradation of the cement barrier and the transport of radionuclides across this barrier.

In case of CEM I, the reinforced concrete constitutive of the container (body and cover) is a high performance concrete, containing CEM I with silica fume and black steel reinforcements. The mortar used as stamps filling contains CEM I and corresponds to that used for the packages intended for the Aube’s site.

In case of CEM V, the concrete constitutive of the packages body is made of CEM V cement coming from the factory Calcia Airvault with stainless steel fibres. The mortar is also containing CEM V cement, formulated by the “Materiaux et Durabilité des Constructions” Laboratory (LMD) of INSA Toulouse to optimize the processing, the retention of chlorine-36 and the effective diffusion coefficient.

A metal grid (structure identical to that of the cart) is positioned 10 cm under the cover intended to retain the graphite waste during the injection of the mortar limiting the presence of supernatants. This grid ensures a 10cm thickness of mortar between the top of the cart and the cover. It is represented in Figure 17 for the case of CEM I.



**Figure 17 Waste package based on CEM I concrete concept**

### Model for cement degradation and radionuclide release from the waste package

The goal of model development is to provide a chemical retention term to the source term model for C14 release. Focus is on chemical/transport interactions of Cl-36 and C14 on waste package level and no credit is taken for low release rates from the graphite (inventories instantaneously mobile). Two models were developed:

- the Diffu-Ca model from CEA, which considers cement degradation associated porosity increase and Cl-36 release [1]; and
- the model from SUBATECH avoids porosity increase due to the formation of carbonate minerals in clay water environments and describes C-14 release.

Boundary conditions were that on the outside of the waste package, Cl36 and C14 concentrations were zero. In Diffu-Ca model, decalcification is the main process of degradation of cementitious materials and is governed by evolution of calcium concentration in the materials porewater. Main parameters (porosity, solid calcium concentration, diffusion coefficient) are expressed in function of calcium concentration in solution. The concrete is composed by the following minerals: portlandite (CH), calcium silicate hydrate (CSH) and ettringite (Ett). Porosity ( $\Phi$ ) evolution is also described.

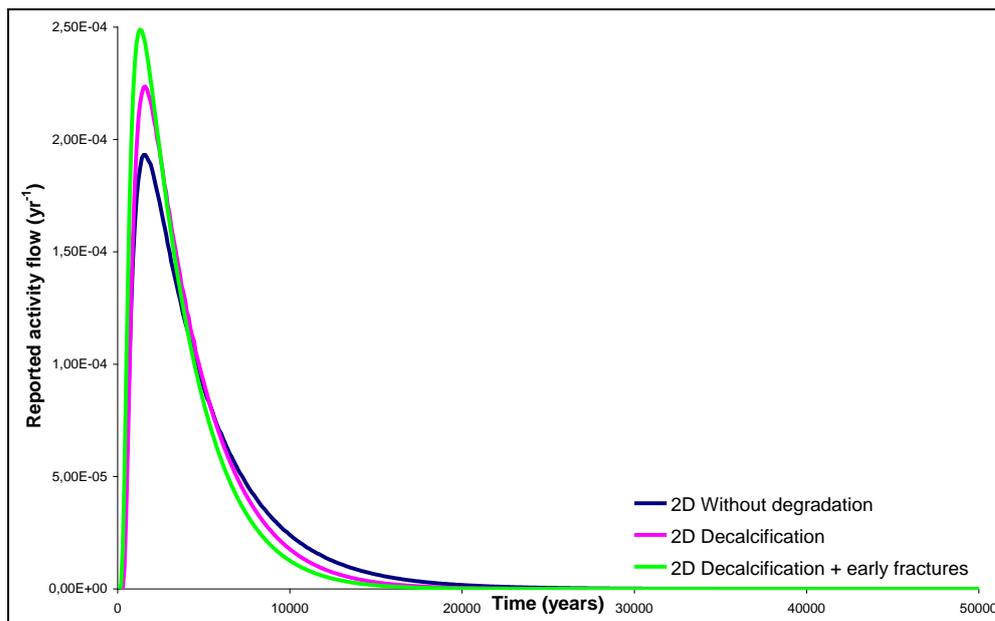
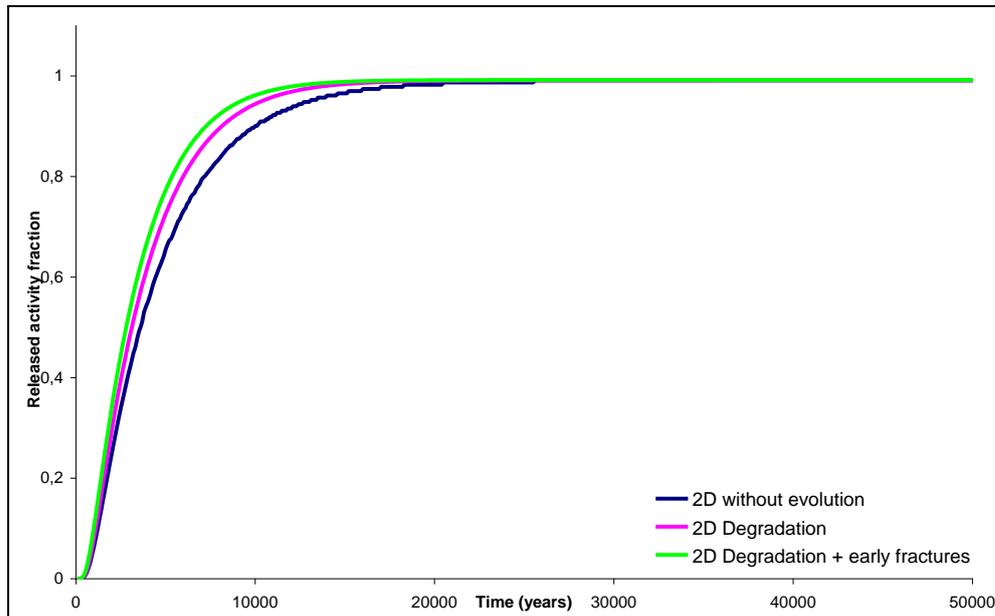
In the Diffu-Ca model, decalcification is based on the hypothesis that at first, portlandite dissolved linearly. Its dissolution is total when calcium concentration reaches  $21 \text{ mol/m}^3$ . When portlandite is totally dissolved, CSH and ettringite dissolve at the same time. The dissolution is complete when calcium concentration reaches  $2 \text{ mol/m}^3$ . Porosity evolution is expressed in function of minerals volume fraction:

$$\Phi = 1 - V_{CH} - V_{Ett} - V_{CSH}$$

Diffu-Ca model describes diffusion of radionuclides, this migration being influenced by the evolution of materials. We suppose that the radionuclides (here Cl-36) are only transported by diffusion. For the CEM I concrete formulation, laboratory measurements of tritium diffusion coefficients led to a very low value of  $5.8 \cdot 10^{-14} \text{ m}^2/\text{s}$ . In order to take into account the various phenomena occurring during the manufacturing of an industrial object (for example, early fracturing), a 10 times high conservative value of  $5 \cdot 10^{-13} \text{ m}^2/\text{s}$  was chosen. For the mortar, a tritium diffusion coefficient value of  $5 \cdot 10^{-12} \text{ m}^2/\text{s}$  is estimated from the literature.

Calcium dissolution of solid phases causes porosity increasing and therefore increases diffusion coefficient of calcium and radionuclide within the cementitious materials. Diffusion coefficient is expressed in function of porosity. The transport in graphite is described with an initial porosity of 0.2 and an effective diffusion coefficient of  $1 \cdot 10^{-11} \text{ m}^2/\text{s}$ . The calculations are running with PORFLOW, a generalized transport code developed by ACRI [xvii], considering 2D configurations with 5 mm per grids for 100 000 years.

Figure 18 shows the evolution of released fraction of activity (Cl-36) and the activity flux versus time for waste packages based on CEM I concrete. We can see that the Cl-36 is released earliest when we consider degradation due to decalcification with early fractures and that the maximum reported activity flow is the most important with the calculations considering degradation with early fractures.



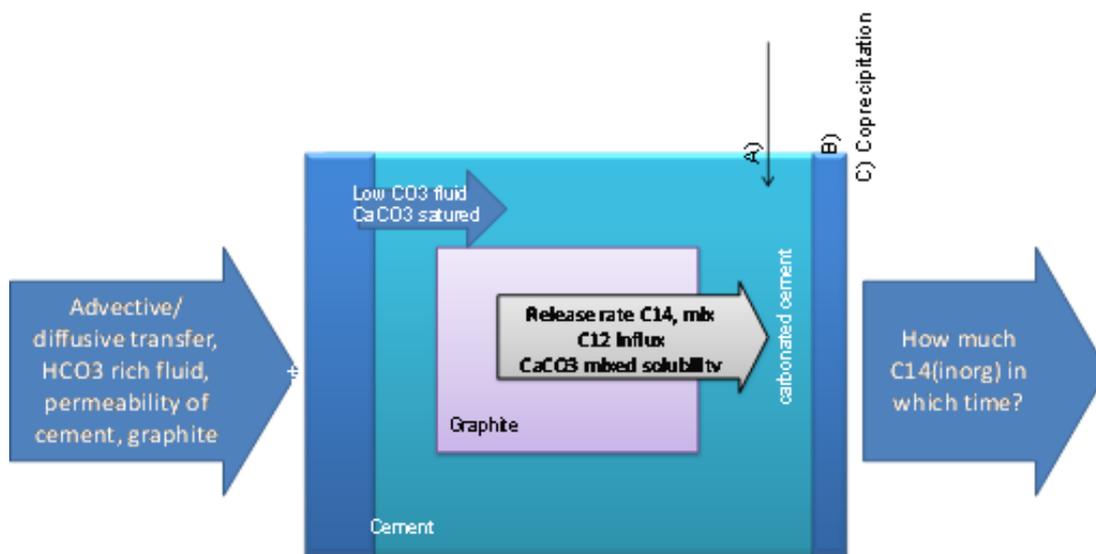
**Figure 18 Evolution of reported activity and released activity fraction versus time**

To resume containment performances of graphite waste packages (Table 3), we can see that the case considering graphite waste package with degradation of cementitious materials and early fractures has the worst performances but it's the most realistic one.

**Table 3 Containment performances of graphite waste packages based on CEM I concrete**

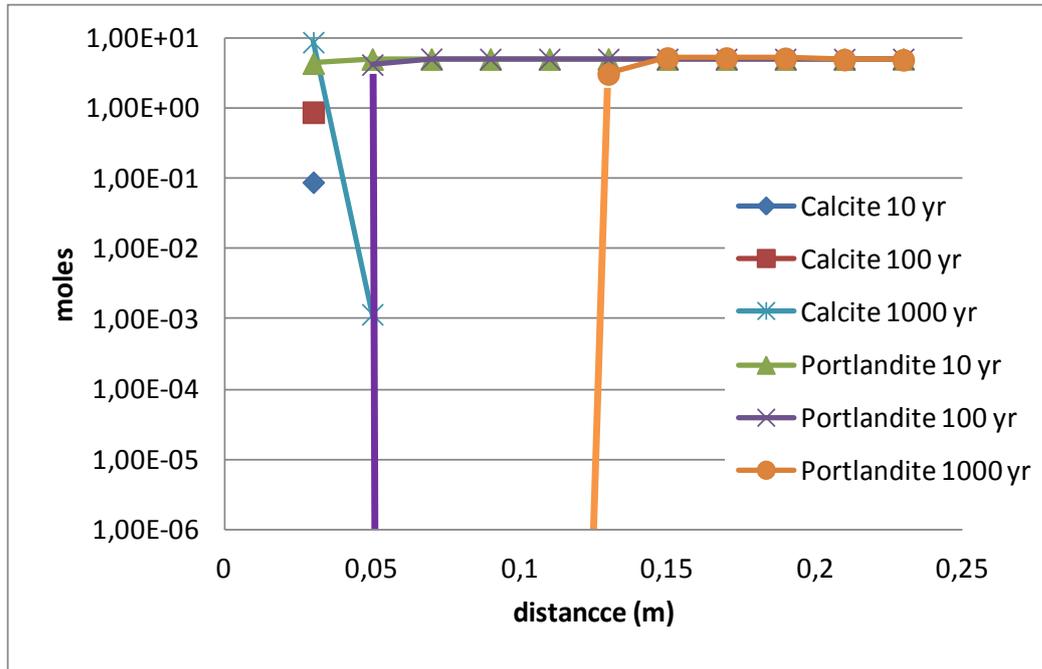
|                                                | Maximum reported activity flow (year-1) | Time of maximum reported activity flow (year) | Containment time (year) |
|------------------------------------------------|-----------------------------------------|-----------------------------------------------|-------------------------|
| Materials without degradation                  | 1,93.10-4                               | 1500                                          | 32000                   |
| Materials with degradation                     | 2,24.10-4                               | 1600                                          | 26 600                  |
| Materials with degradation and early fractures | 2,42.10-4                               | 1300                                          | 22 600                  |

A one-dimensional C14 release model has been developed by SUBATECH (Figure 19).



**Figure 19 Conceptual model for C-14 release and transport in a cemented graphite waste package**

This one-dimensional geochemical/transport model has been implanted in the geochemical code PHREEQC both for cement degradation and advective/diffusive and for pure diffusive transport of reactants and dissolved C-14. The cement composition is that of CEM I of a water/cement ratio of 0.2, considering equilibrium of cement pore water with the solid phases CSH (44 wt%), portlandite (19 wt%), ettringite (9 wt%) and hydrotalcite (4 wt%). A diffusion barrier of 20cm CEM I is considered. Effective diffusion coefficients used are similar to the CEA model. Diffusion and/or advection of carbonate rich clay pore water into the cemented waste package leads to dissolution of portlandite ( $\text{Ca}(\text{OH})_2$ ) and a reduction of Ca concentrations and pH to values between 11 and 12. Carbonation of a few outer centimetres of the cement is calculated (formation of calcite) see Figure 20.



**Figure 20 Evolution of carbonation and portlandite content during diffusion of clay water in CEM I**

Full carbonation of the cement is calculated to take well beyond 100,000 years. While no interaction of organic C-14 with the cement is considered along the transport path, co-precipitation (isotopic exchange of C-14/C-12 is calculated to occur during carbonation of the cement. This leads to accumulation of C-14 in calcite and a strong reduction of inorganic C-14 release. The retention of C-14 decreases slightly with time but even after 10,000 yr more than 99.5% of released inorganic C-14 is retained in the calcite. All retention of inorganic C-14 is calculated to occur in the few centimetres of carbonated cement at the interface to the clay rock. The results show that cement is a very effective chemical barrier against inorganic C-14 release.

---

## CONCLUSIONS

---

---

### MAIN FINDINGS

---

A safety case aims to illustrate how a surface disposal facility or a geological disposal facility for radioactive waste could be implemented safely in different environments.

Our confidence that we can develop an SDF or a GDF is built on our understanding of how multiple barriers – engineered barriers and natural barriers - can work together to ensure safety. We therefore have confidence that, for specific site and disposal concept, we can develop an optimised design that meets all environmental safety requirements.

The safety and environmental assessments related to graphite disposal as undertaken in the EC CARBOWASTE project confirm we have sufficient understanding to justify site-specific studies on the disposal of graphite wastes in an SDF or a GDF, and that we have sufficient underpinning understanding at a generic (non site-specific) level to be confident that graphite waste can be disposed in a manner such that relevant radiological protection regulations can be attained.

---

### RESIDUAL UNCERTAINTIES

---

Factors that may limit the range of disposal systems suitable for the disposal of graphite waste in an SDF or in a GDF include assumptions regarding the nature of the biosphere into which releases may occur, which tend to be more conservative for generic assessments; uncertainties regarding radionuclide release from graphite wastes; and cautious assumptions in assessment calculations.

Although significant work has been undertaken within CARBOWASTE to better understand radionuclide release from graphite, uncertainties remain regarding:

- release mechanism(s), the form(s) and release rate(s) of C-14 labelled gas(es) from dry, damp and wet graphite wastes;
- the mechanism(s) for long-term release of C-14 to water;
- the fraction of the C-14 inventory that is released; and
- the potential for release of C-14 and Cl-36 in aqueous organic compounds, and their subsequent fate and transport.

Due to these uncertainties, safety assessment calculations often include cautious assumptions that are likely to overestimate the amount of C-14 released and potentially the rate of C-14 release. It is difficult to represent the complex geochemical behaviour of C-14 in the near-field in simple safety assessment calculations. Consequently, such calculations tend to include cautious assumptions that underestimate the chemical barrier performance for concepts including a cementitious EBS.

These uncertainties do not preclude safe disposal of graphite wastes in a wide range of disposal systems, but a wider range of disposal systems might be suitable if these uncertainties were further reduced.

A second consequence of these remaining uncertainties, and how they are accounted for in assessments, is that it may be difficult to demonstrate that a disposal concept is optimised. This may mean that a cautious approach to engineering design may be required, potentially involving higher-



specification near-field barriers than might be appropriate if waste guideline performance were better understood.

Future research for graphite disposal could be undertaken on the above residual uncertainties. However, it is to be emphasised that, even in the absence of such future work, **we have a sufficient understanding of graphite now to conclude with confidence, on the basis of work undertaken in the EC CARBOWASTE project, that graphite waste can be safely disposed in a wide range of disposal systems.**

---

## REFERENCES

---

### Task 6.2

- [1] CW0711Workplan – version U
- [2] A. Morançais et al. in *J. of Eur. Ceram. Soc.* 23 (2003) 1949–1956
- [3] E. de Visser – Týnová and H.L. Cobussen – SiC formation from graphite NRG-22260/11.109977, I&D – report for Carbowaste project – task 5.2, September 2011
- [4] E. de Visser – Týnová and H.L. Cobussen - Internal communications on SiC formation
- [5] V. Smit – Groen – Internal notes on XRD on SiC and graphite samples
- [6] H.L. Cobussen – Internal note on leaching experiments 2.2260.40/12.112831 I&D/JC/PvS
- [7] T. Tomasberger – Internal notes on LSC measurements

### Task 6.3

- [1] Brown F.J., Palmer J.D., Wood P., *Nucl. Graph. Waste Manage. IAEA*, 10, 1 (1999).
- [2] Blin V., Coreau N., Herbette M., Latrille C., Pointeau I. and Petit L. (2008): <sup>36</sup>Cl sorption on a hydrated cement paste as a function of degradation state and influence of stable chloride. 2<sup>nd</sup> Workshop on mechanisms and modelling of waste/cement interactions, Le Croisic, France.
- [3] Pointeau I., Landesman C., Coreau N., Moisan C. et Reiller P., (2004) : Etude de la rétention chimique des radionucléides Cs(I), Am(III), Zr(IV), Pu(IV), Nb(V), U(VI) et Tc(IV) par les matériaux cimentaires dégradés. CEA Technical Report RT DPC/SECR 03-037a.

## Task 6.4

---

- i Iorgulis C., Diaconu D., Gugiu D., Roth C., Assessment of isotope accumulation data from MTR, Technical Report T-3.4.1 in CARBOWASTE project, released on March 2011
- ii Report on the radiological safety assessment for the near surface disposal of radioactive waste at Saligny - Phare Project RO 2006/018-147.05.01.
- iii AN&DR Annual Report 2011-  
<http://www.agentianucleara.ro/Doc/Raport%20de%20Activitate%20Anual%202011.pdf>
- iv Wickham, A.J. and Bradbury, D., Graphite Leaching: A Review of International Aqueous Leaching Data with Particular Reference to the Decommissioning of Graphite Moderated Reactors; EPRI Palo Alto CA, 2008, 1016772
- v Towler G., Wilson J., Limer L., Wickham A. J., Harvey L., Optimization for Deep Geological Disposal of Graphite Wastes, Draft for NDA RWMD review, May 2011
- vi Constantin A., Diaconu D. Report on PA for <sup>14</sup>C- (gas and liquid phase) and <sup>36</sup>Cl- (liquid phase) for the disposal, CARBOWASTE D-6.4.5, 2012
- vii Constantin A., Diaconu D., Bucur C., Raport Intern SCN 9205/2011 - Modelarea migrării C-14 în medii poroase nesaturate, 2011
- viii ANL-MGR-MD-000009 REV 03, Nominal Performance Biosphere Dose Conversion Factor Analysis, September 2004, prepared by Bechtel SAIC Company, LLC for U.S. Department of Energy
- ix J ANL-MGR-MD-000009 REV 02, Agricultural and Environmental Input Parameters for the Biosphere Model, September 2004, prepared by Bechtel SAIC Company, LLC for U.S. Department of Energy
- x ANL-MGR-MD-000005 REV 02, Characteristics of the Receptor for the Biosphere Model, prepared by Office of Civilian Radioactive Waste Management, June 2003
- xi *Poskas P. et al.* Progress of radioactive waste management in Lithuania // Progress in Nuclear Energy, vol. 54, iss. 1, p. 11-21, 2012.
- xii *Poskas P. et al.* Generic repository concept for RBMK-1500 spent nuclear fuel disposal in crystalline rocks in Lithuania // International topical meeting TOPSEAL 2006, Olkiluoto information centre, Finland, September 17-20, 2006.
- xiii Assessment of isotope-accumulation data from RBMK-1500 reactor // LEI Technical Report T-3.4.2 (CARBOWASTE project), 2012.
- xiv Limer, L., Smith, G., and Thorne, M.C. 2010. Disposal of Graphite: A Modelling Exercise to Determine Acceptable Release Rates to the Biosphere. Quintessa Report to the Nuclear Decommissioning Authority (NDA) Radioactive Waste Management Directorate (RWMD) QRS-1454A-1, Version 2.2.
- xv Geological disposal of graphite wastes, George Towler, James Penfold, Laura Limer and Elizabeth Arter, QRS-1378ZO-R2, V3.0, 2012.
- xvi Operational modelling Describing RN migration out of the waste packages, Technical Report CARBOWASTE-0412-D-WP6. Task. 4, P. Thouvenot and V. Devallois, CEA
- xvii Analytic & Computational Research, Inc., « PORFLOW user's Manual, version 6.2 Rev. 0», 2009