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Report on PA of graphite, carbonaceous and embedded waste products

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Report on PA of graphite, carbonaceous and embedded waste products

Executive summary

A one dimensional coupled geochemical/transport model has been developed to assess the performance of concrete based waste packages for graphite. The model considers the diffusive access of clay pore water to the pore space in concrete and in graphite, kinetics of release of C-14 from the graphite grains, alteration of the concrete by clay pore water including carbonatisation of concrete and incorporation of inorganic C-14 in the carbonated concrete. The model shows that concrete is a very effective chemical barrier against inorganic C-14 release leading to inorganic C-14 activities outside of the waste package hundreds times lower than those of organic C-14. In the case of SLA2 graphite, for 500 yr, inorganic C-14 activities outside the waste package meet WHO guidance levels for drinking water. More detailed modeling is necessary to allow drawing some general conclusions: one needs to consider 3 dimensional geometry and variability of types of graphite. Also fracturing of the concrete barrier may not be entirely excluded, leading to potential advective path ways across the concrete barrier. But the data clearly indicate that in the presence of carbonate rich clay pore water, the source term for C-14 release from the waste package to the surrounding repository is essentially governed by organic C-14. Impact of carbonaceous and embedded waste products are discussed.

Revisions

Rev.	Date	Short description	Author	Internal Review	Task Leader	WP Leader
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1 Introduction

In order to assess whether radioactive nuclear reactor graphite can be disposed of as nuclear waste without or with further treatment, either in near surface or deep geological disposal, one need to assess its behavior under disposal conditions. It must be assured that the risk stemming from potential release of radionuclides to the biosphere is very small. Divers scenarios have to be developed to imagine by which chain of processes groundwater may come in contact with the disposed graphite, by which processes radionuclides might become released from the waste into this water, which processes influence the fate of the radionuclides in the water and how they might become transported in groundwater or in gas migration path ways from the waste emplacement to the human accessible environment. Transport of radionuclides may become slowed down by their adsorption (and hence, immobilization) on mineral surfaces or it may be accelerated by forming stable complexes in the flowing groundwater. The divers' processes can be integrated into overall models (geochemical-transport- models) coupling hydrogeological and chemical parameters in a consistent way. Also radiation may influence release properties.

The goal of this contribution is to provide a chemical retention term to the source term model for C14 release. Focus is on chemical/transport interactions of C14 on waste package level.

2 Disposal scenario and model description

The present work is focused on disposal of irradiated nuclear graphite in a repository in a clay rock environment. The clay rock is considered to be composed of clay minerals, tecto-silicates and carbonate minerals (calcite).

The pore water composition of the geochemical environment is considered to be in equilibrium with this mineral assemblage:

pH 7.1, in mol/L : Sr^{2+} 2e-4, K^{+} 1.03e-3, Mg^{2+} 6.7e-3 , Fe^{2+} 3E-5, Ca^{2+} 7.36e-3, Na^{+} 4.23e-2, CO_3^{-2} 3.34E-3 SO_4^{-2} 1.56E-2, Cl^{-} 4.1E-2

The waste package, which is emplaced in the clay rock environment, contains the irradiated nuclear graphite in a concrete container. The space between the container and the waste is filled by a mortar matrix. The waste package constitutes the first confinement barrier. The package considered in this study is a cuboid object of 10 m^3 made of CEM I concrete in which a cart containing graphite waste is inserted. A schematic presentation taken from CEA is given in figure 1 where:

1) cart with primary graphite waste,
2) concrete structure containing the cart,
3) mortar matrix that fills the space between the cart and the concrete structure,
4) concrete cover.

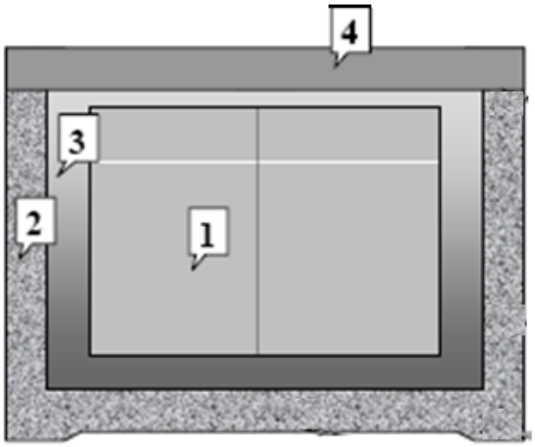

Figure 1: schematic view of the waste package (from CEA, 4th annual activity report of WP6 of carbowaste, 2012)

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. This grid ensures a 10 cm thickness of mortar between the top of the cart and the cover. It is represented in figure 2 . (from CEA, 4th annual activity report of WP6 of carbowaste, 2012).

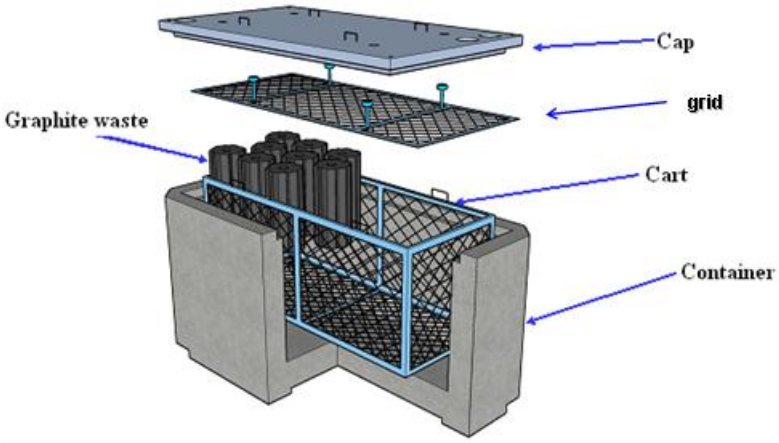

Figure 2: waste package based on CEM I concrete concept (from CEA)

In performance analyses at waste package level one needs to take into account the release properties from the waste and one needs to analyse to which degree the concrete and mortar are taking part in the safety features.

As far as release properties are concerned the question is whether and to which degree groundwater from a disposal site can enter the pore space of the graphite so that it may come in contact with the surfaces of the graphite grains and may leach out the C-14. The work in Carbowaste (deliverables 6.1.4 and 6.1.5) has shown that diffusion in graphite pore water is much faster than potentially diffusive release from graphite grains and that advective transport is only little hindered by the pore network, indicating that in the presence of even small hydraulic gradients, advective transport is dominating. Nevertheless, encapsulation of the graphite in a hydraulic cage of low diffusivity concret may block water flow across the graphite waste and may allow for dominance of diffusive water transport. But this does not mean, that radionuclides are released from the graphite with the speed of diffusive or advective water transport, since they may become retained by chemical processes such as sorption, solubility constraints or coprecipitation. In the present work, the 1 dimensional geochemical Phreeqc was used with a diffusion/advection equation constrained by the chemistry of inorganic C-14 in water and at water/solid interfaces. In principe, one would also have to consider the effect of radiation of water chemistry and C-14 release. However, radiolysis has been analysed (Deliverable 6.4.1) as not being very important neither for graphite stability, nor for C-14 release and radionuclide transport beyond 100 yr, since the dose levels will be low and concentrations of radiolytic organic species in water entering graphite pores will remain below 10^{-5} mol/L. This is not significant compared with the concentrations of other groundwater species. Therefore, focus is on inorganic C-14. Organic C-14 is not produced by radiolysis during disposal but is probably already produced during reactor operation. Also the reaction of graphite with water produces organic species (Guittonneau 2008). C-14 atoms incorporated in graphite may thus become released as well in organic from, as observed experimentally. Organic C-14 is considered in the present model as being released from the graphite grains with the same rate as inorganic C-14 but without further retention in the pore space of neither graphite nor concrete. This means, that organic C-14 is thought of being transported with the speed of water transport. A conceptual one-dimensional model for inorganic C-14 release from the waste package has been developed as given in figure 3.

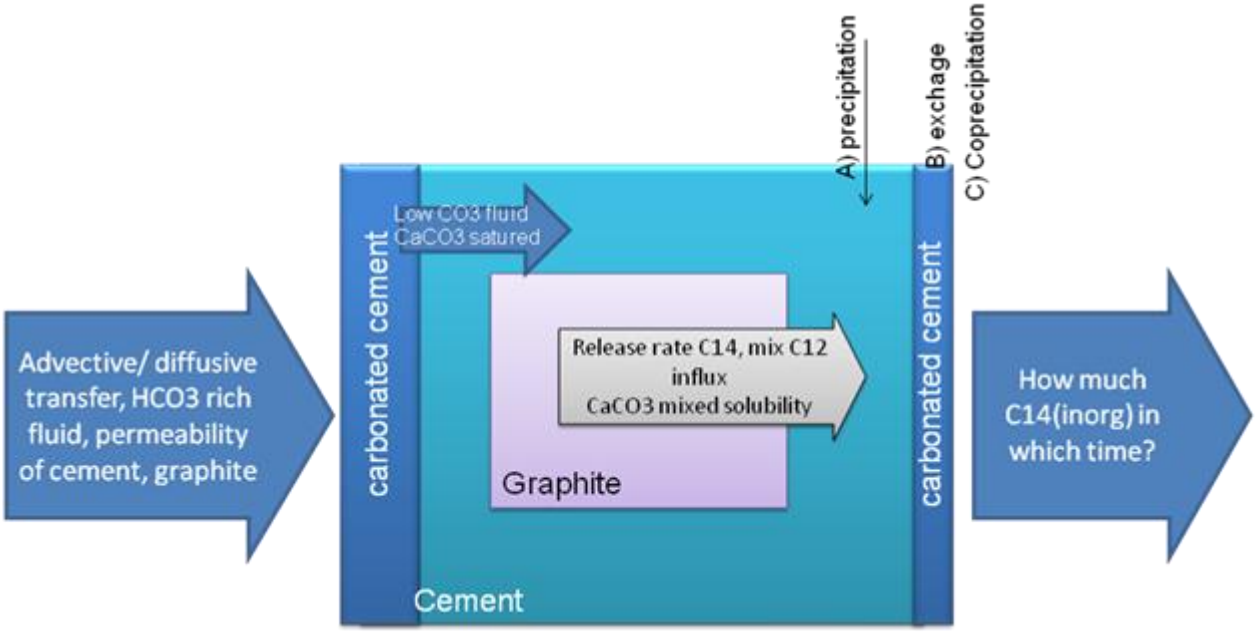

Figure 3: conceptual model for C-14 release and transport in a cemented graphite waste package.

This one-dimensional geochemical/transport model has been implanted in the geochemical code PHREEQC both for advective/diffusive and for pure diffusive transport of reactants and dissolved C-14. Conservative effective diffusion coefficients used are 10^{-11} m^2/s for water molecules, dissolved aqueous species as well as for inorganic and organic C-14. This is a conservative assumption since organic molecules are larger than inorganic ones implying lower diffusion coefficients. Also conservatively, no sorption of C-14 on cement is considered.

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 20 cm CEM I concrete is considered. The diffusion path is simulated by 61 equal cells of 2 cm lenth: 1 cell representing pore water outside the waste package, 10 cells representing the concrete and 50 cells representing the graphite. No difference in diffusivity between graphite and concrete has been considered.

3 Model results for graphite waste inside a concrete container

Once the carbonate rich clay water (pH 7.1, dissolved carbonate concentrations are 3.3 mMol/L) enters the concrete, the pH increases by dissolution of the cement phase portlandite ($Ca(OH)_2$). Calculated initial cement pore water pH is 12.46 and dissolved Ca concentrations are 21 mMol/L. Diffusion and/or advection of carbonate rich clay pore water into the cemented waste package leads to further dissolution of portlandite and a reduction of Ca concentrations and pH to values between 11 and 12 (see figure 4). While at the outer surface of the concrete the pH decreases with time, it stays constant inside the waste package at a value of 12.46 for > 10000 years.

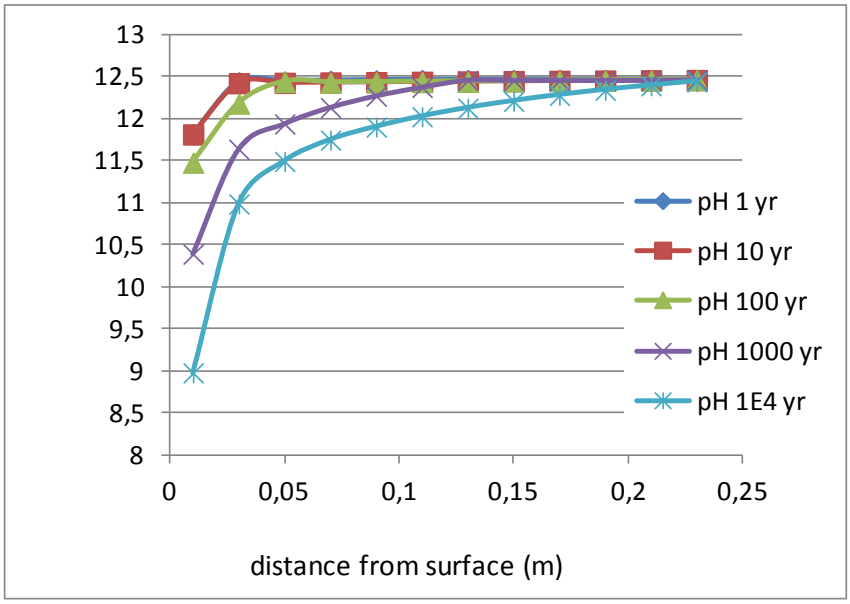

Figure 4: Evolution of cement pore water pH during diffusion of clay water into the cement

The reduction of pH in the outer parts of the concrete at the concrete/clay rock interface is conditionned by the complete dissolution of portlandite and by the carbonatisation of a few outer centimeters of the concrete. Calculation results are given in figure 5.

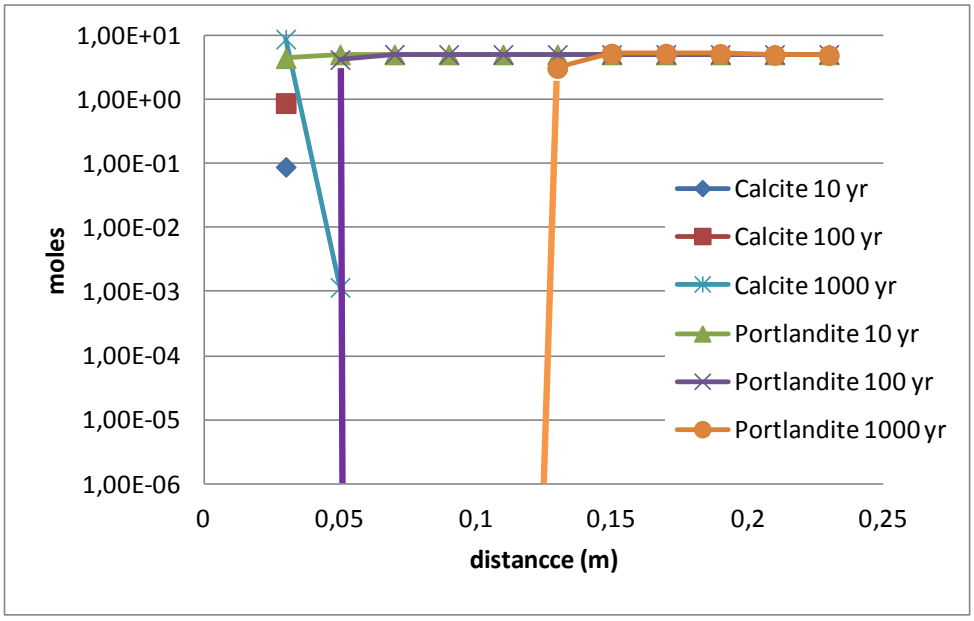

Figure 5: Evolution of carbonatization (calcite formation) and portlandite content during diffusion of clay water in CEM I concrete

Full carbonatisation of the cement is calculated to take well beyond 100000 yr.
If the C-14 concentration in the pore water in the graphite were considered constant to assess (constant source), it takes less than 10 yr to establish a constant diffusion gradient of species across the cement barrier (see figure 6).

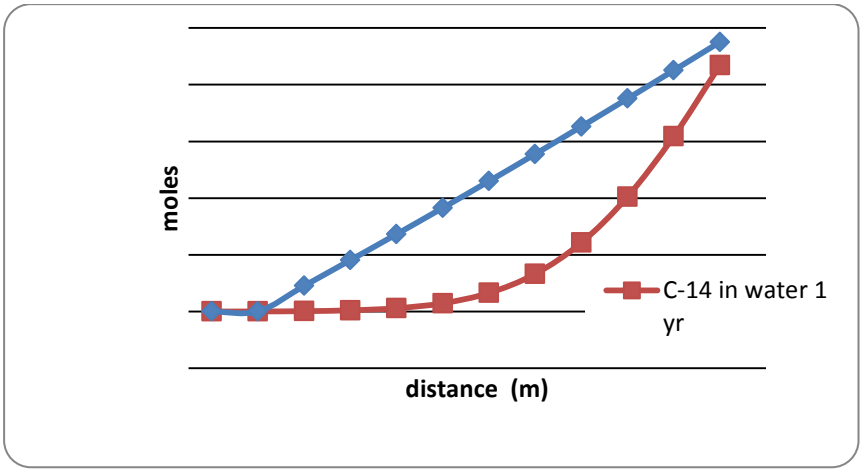

Figure 6 : concentration profile of C-14 in cement pore water as a function of distance from the surface considering a constant concentration of 10^{-10} M inside the waste package.

While no interaction of organic C-14 with the cement is considered along the transport path, coprecipitation (isotopic exchange of C-14/C-12 is considered during carbonatisation (calcite formation) 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 as indicated in table 1 but even after 10000 yr more than 99.5% of inorganic C-14 released from the graphite is retained in the calcite (see Table 1). All retention of inorganic C-14 is calculated to occur in the few centimeters of carbonatized cement at the interface to the clay rock (see figure 5).

Table 1

Time [yr]	Ratio of C14 retained in precipitating calcite to inorganic C14 released from the waste package
10	758
100	360
1000	286
10000	190

The effect of a concrete barrier on organic and inorganic C-14 release from the waste package can be seen in figure 7. C-14 activities in the graphite were considered as 10^4 Bq/g. Considering a graphite

density of 1.7 g/cm^3 and a porosity of 20%, this was transformed to a hypothetical pore water activity . In accordance to experiments done with SLA2 graphite at SUBATECH (Vendé 2012), 1/3 of the released C-14 was analysed as being in organic form, 2/3 in inorganic form.

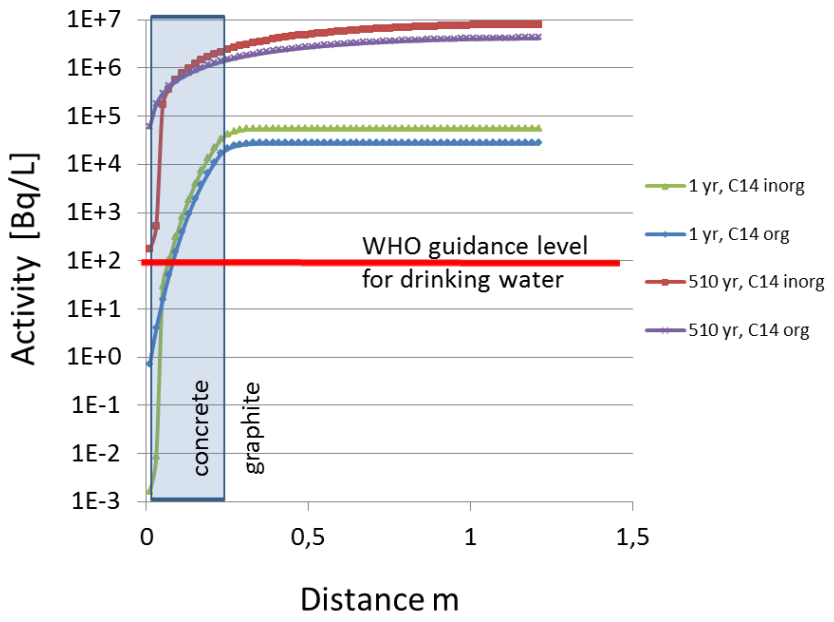

Figure 7: Modeling of organic and inorganic C-14 release from a graphite containing waste package (see text for details)

A simple 2 step release model was used: instant release of 0.045% of the C-14 inventory and slow long term release with a constant rate of 5.10^{-4}/yr again obtained from experimental data from SUBATECH using SLA2 graphite. The hypothesis was made that the release ratio organic/inorganic dose not changes in time. Activities after one year in the graphite pore water are largely goverened by the initial release. Activities in the pore water increase with time due to the slow long term release term. No steady state concentrations for C-14 were obtained in the waste package.

It is interesting to note that inorganic C-14 activities at the outside of the waste package are very low, after 510 yr being similar to WHO guidance levels (WHO 2006) for C-14 activities in drinking water. However, this cannot be generalized since release rates of C-14 form other irradiated graphite can vary largely: in the case of G2 graphite, release rates of C14 were observed to be about ten times faster than for the SLA2 graphite (Vendé 2012).

4 Other carbonaceous waste products

For other carbonaceous waste products like SiC, task 6.3 of carbowaste has shown that the C-14 release rates for powdered SiC are much lower than for powdered graphite. Nevertheless, no

detailed release law has been derived so that PA calculations of waste package performance could not be made. For detailed modeling, also the porosity of the final waste product must be known. It is expected that SiC can be produced as solids with much lower porosity than graphite, indicating further reduction of release rates (higher waste form stability) compared to graphite.

Work in task 6.3 has also shown that graphite pore volumes can effectively be reduced by vitrification. This will strongly reduce the diffusion coefficient of water and of C-14 species in the graphite. It is clear from the present model that this leads to a strong reduction of C-14 activities at the outside of the waste package. Nevertheless, the glass filling the pores of the graphite is not stable in hyperalkaline solutions expected to prevail inside the waste package. The glass will be transformed into a number of secondary alteration products which may remain in the graphite pores. A detailed model for transport of C-14 in glass filled pores of graphite would have to model as well these alteration properties of the glass. Corresponding model development would require detailed analyses of the glass alteration process, which is outside the scope of carbowaste project.

5 Conclusions

A one dimensional coupled geochemical/transport model has been developed to assess the performance of concrete based waste packages for graphite. The model considers the diffusive access of clay pore water to the pore space in concrete and in graphite, kinetics of release of C-14 from the graphite grains, alteration of the concrete by clay pore water including carbonatisation of concrete and incorporation of inorganic C-14 in the carbonated concrete. The model shows that concrete is a very effective chemical barrier against inorganic C-14 release leading to inorganic C-14 activities outside of the waste package hundreds times lower than those of organic C-14. In the case of SLA2 graphite, for 500 yr, inorganic C-14 activities outside the waste package meet WHO guidance levels for drinking water. More detailed modeling is necessary to allow drawing some general conclusions: one needs to consider 3 dimensional geometry and variability of types of graphite. Also fracturing of the concrete barrier may not be entirely excluded, leading to potential advective path ways across the concrete barrier. But the data clearly indicate that in the presence of carbonate rich clay pore water, the source term for C-14 release from the waste package to the surrounding repository is essentially governed by organic C-14.

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