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Porewater model adaption for organic/inorganic ^{14}C release

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Porewater model adaption for organic/inorganic ^{14}C release

Executive summary

Pore water chemistry of graphite is potentially affected by interaction of graphite pore surfaces with the water. This concerns principally graphite dissolution reactions. Nevertheless, graphite dissolution is very slow and only by radiolysis significant dissolution might be attained. The present work tries to assess the significance of radiolysis processes for pore water chemistry.

Radiolysis processes are of potential significance to C14 only if C14 is fixed within the graphen structure of the graphite matrix. Weakly surface bound C14, originating for example from neutron irradiation of adsorbed nitrogen, is expected to become released even without action of radiolysis.

Nevertheless, our calculations have shown that after decay of Co60 inventories, radiolysis processes will be insignificant for any additional C14 release. We conclude that radiolytic effects on C14 release are without any significance. This is true both for organic or inorganic radiolysis products. Hence, pore water chemistry is not controlled by radiolytic graphite dissolution. Instead, pore water chemistry will be similar to the composition of the external water, accessing the irradiated graphite.

The conclusion is that non-radiolytic release processes are dominant for C14 release from irradiated graphite. Since it is known that non-radiolytic graphite matrix dissolution is extremely slow we conclude that C14 is essentially released from surface sites which are easily accessible.

Revisions

Rev.	Date	Short description	Author	Internal Review	Task Leader	WP Leader
00	dd/mm/yyyy	Issue	Name, Organisation	Name, Organisation *Signature*	Name, Organisation *Signature*	Name, Organisation *Signature*
01	20/04/2010	FIRST VERSION	B. Grambow SUBATECH			Grambow
02	28/6/2011	Final	Bernd Grambow			Grambow

Introduction

Irradiated nuclear graphite is considered as waste matrix for direct disposal in shallow or deep geological formations. It will be placed in containers within an engineered barrier system which typically could consist of cement based materials. After some years groundwater will come in contact with the graphite. The porosity of the graphite is about 20%. Despite the rather hydrophobic character of the water/graphite interface, water can rather easy enter the graphite structure. In the presence of hydraulic gradients, water can easily percolate in graphite (see task 6.1 of the Carbowaste project). In the absence of such gradients in confined repository locations, groundwater will move in graphite driven by diffusive forces. Diffusion is sufficiently fast that water residence times in graphite will be few tenth of years. During the contact time water will contact the graphite pores and this can lead to change of pore water chemistry.

Additionally pore water chemistry might be influenced by the radiation field imposed by the radionuclide inventory of the graphite. Due to radioactive decay, the radionuclide inventory changes with time. Since disposed graphite is has already long interim storage times after disposal and containers will provide additional isolation functions, it is probably safe to say that first groundwater contact will not occur prior to 100 yr. Radiation fields of irradiated graphite are initially dominated by Co-60, but after 100 yr, Ni-63, C-14 and Cl-36 become dominant.

In a first step the dose rate shall be calculated for average i-graphite as time after 100 yr. Thereafter a radiolytic model for graphite dissolution developed in the Raphael project (Deliverable 2.2) will be adapted to i-graphite. In the Raphael project the model was developed for i-graphite matrices from irradiated HTR fuel. Necessary model modifications for the present project include much lower irradiation doses and the hyper-alkaline pH.

Calculation of dose rates

The evolution of the radioactivity of i-graphite with time is given in figure 1, using the inventories for the French case (presentation ANDRA/EDF at the 1st annual WP6 meeting, ITU 2009)

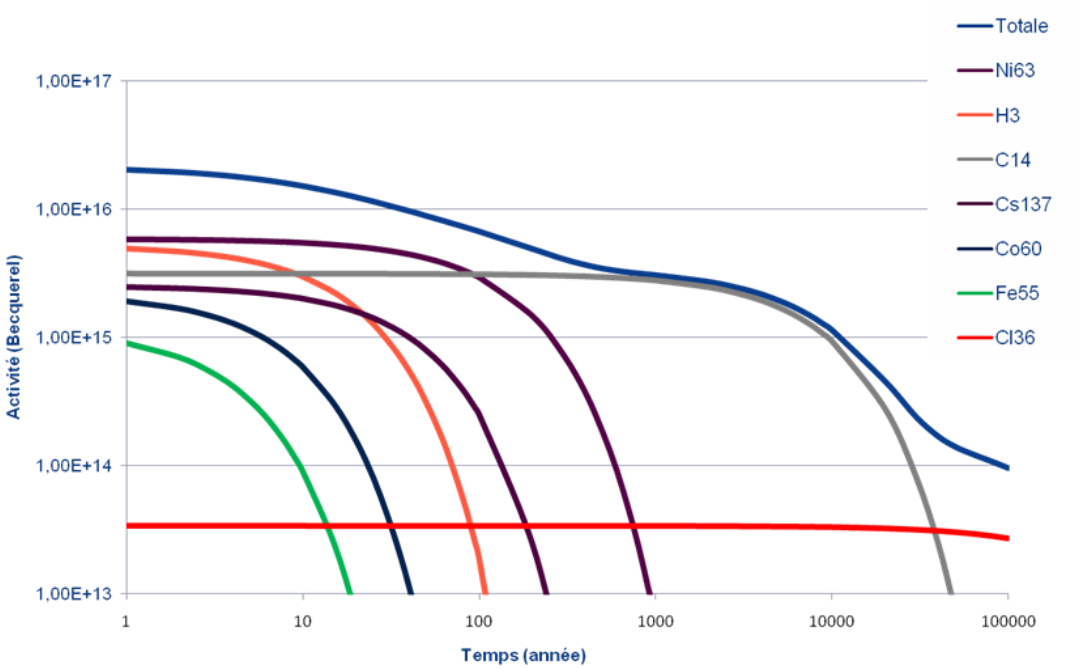

Fig. 1: evolution of total inventory of radionuclides in French irradiated graphite (data from presentation ANDRA/EDF at the 1st annual WP6 meeting, ITU 2009)

After 100 years C-13 and Ni-63 are dominant followed by Cl-36 which becomes dominant after decay of C-14. Typical specific activities and decay properties of these three nuclides are given in table 1.

Radionuclide	Specific activity	Half life	Decay mode	Decay energy	
				max	mean
	Bq/g	yr		keV	keV
C-14	10^5	5730	β^-	156	49
Ni-63	$7 \cdot 10^4$	100	β^-	65.9	17
Cl-36	100	302000	β^- 98% EC 2%	710 1144	273

Table 1 : Radionuclides of interest for dose contributions after 100 years in irradiated graphite

An average dose rate D can be calculated in units of eV/L/s from the specific activity A_s, the mean decay energy E_m and the density ρ of the graphite: $D=A_s \cdot \rho \cdot E_m$, which can be directly translated into units of Gy/h:

More detailed calculations of dose rates need to take account for the different attenuation depth of beta radiation in the graphite matrix as opposed to the water filled pores. It is essentially the dose rate in the water filled pores, which will have to be used for radiolysis calculations. The calculations of attenuation depth have not only to consider that there is there no fixed energy of beta particles but a rather large range characterized by a maximal value E_{max} and a mean value E_{mean},. Additionally, the E_{mean} values vary strongly for various nuclides, and calculations of beta dose profiles have to consider contributions from individual nuclides. To allow simplification, all following calculations are based only on the E_{mean} values of the different nuclides. Calculations are only performed for the main nuclides considered to be dominant dose contributor at a given time.

The interactions of beta particles with water or graphite a change of momentum has to be considered for collision of beta particles with the electrons of the media. Due to electrodynamics, this results in energy loss by radiation (Bremsstrahlung). This effect is important in lead or water for incident particle energies above 5 or 50 MeV respectively. Our calculations are performed with E_{mean} <1MeV, hence such radiative losses may be neglected.

The mechanism for energy loss of beta particles in water and graphite is similar than for alpha particles, but one has to consider that the particle changes its direction on its trajectory and hence, the parallel component of its momentum cannot anymore be neglected. Beta particles are typical relativistic particles already at energies >0.5 MeV. To consider these effects Bethe has derived the following equation to describe the energy loss:

$$\frac{dE}{dx} := -\left[\frac{e^4 \cdot n_e}{8 \cdot \pi \cdot \varepsilon_0^2 \cdot m_e \cdot v(E)^2} \cdot \ln\left[\frac{v(E)^2 \cdot m_e \cdot E_e}{E_i^2 \cdot 2 \cdot \left(1-\beta(E)^2\right)} + 1 - \beta(E)^2 - \frac{2 \cdot \gamma(E) - 1}{\gamma(E)^2} \cdot \ln(2) + \frac{1}{8}\left(\frac{\gamma(E)-1}{\gamma(E)}\right)\right]\right]$$

where "E" is the average kinetic energy and $E_e = m_e c^2$ of the beta particle (electron) of masse m_e and e the charge of the électrons, n_e is the electron density of the media (graphite or water filled graphite pore) v(E) is its velocity, β(E)=v(E)/c and

$$\gamma(E) := \frac{E + E_e}{E_e}$$

and ε_o is the permittivity of the vacuum.

Using this equation the attenuation depth x_A can be calculated by

$$x_A = \int_E^0 \frac{1}{(dE/dx)_E} dE$$

Table 2 contains calculated average dose rates, attenuation depth in graphite and graphite pore water as well as local dose rates both for the graphite matrix and the water filled pores

Radionuclide	Average dose rate		Average attenuation depth		Dose rate	
			water	graphite	water	graphite
	eV/L/s	mGy/h	µm	µm	mGy/h	mGy/h
C-14	$8.9 \cdot 10^{12}$	5.14	32	21	3.6	5.5
Ni-63	$2.2 \cdot 10^{12}$	1.24	4.3	3	0.92	1.3
Cl-36	$4.9 \cdot 10^{10}$	0.028	620	400	0.020	0.031

The data in table 2 allow assessing the evolution of dose rates in water filled graphite pores with time. Up to about 10000 years the dose rate is governed by the C-14 contribution, thereafter by Cl-36.

Radiolysis model for graphite/water interfaces

Graphite/water reactions (dissolution, hydration) depend on the presence of oxidants and even in presence of oxidants the reaction is very slow. In order to know how much oxidants are available for graphite oxidation/dissolution, one needs first to assess water radiolysis. A water radiolysis in presence of graphite surfaces has been developed in the European project Raphael (deliverable BF 2.2). The model calculates a steady state concentration of hydrogen peroxide as a function of apha, beta and gamma dose rate. The rate constants for interaction of H_2O_2 with the graphite surface were obtained by calibration with experimental data from FZ Jülich on H_2O_2 dependency of graphite dissolution rates. For the calculations the radiolysis code MAKSIMA chemist has been used.

Surface sorbed H_2O_2 may lead to a chemical reaction between the carbon from the graphite leading to CO_2 and H_2 formation.

$$S\text{-}H_2O_2 = S + CO_2 + H_2 \qquad K = 1.300E\text{-}04 \qquad (1)$$

Bicarbonate ions are formed in equilibrium from initially produced CO_2 (the latter is formed via reaction 1).

Once bicarbonate species are formed, their irradiation will lead to the formation of CO_2^- or CO_3^- radicals from which organic molecules can be formed by reactions such as

$CO_3^- + CO_3^- = C_2O_6^{-2}$	k=1.400E07
$CO_2^- + CO_2^- = C_2O_4^{-2}$	k=6.500E08
$CO_2^- + HCO_3^- = HCOO^- + CO_3^-$	k=1.000E03
$CO_3^- + C_2O_4^{-2} = C_2O_4^- + CO_3^{-2}$	k=3.000E03

Table 3: Radiolysis reactions leading to organic matter production from irradiation of carbonate containing solutions. Data from the European SFS project.

Indeed at SUBATECH laboratory, experiments of gamma irradiation of carbonate containing solutions were performed. The cumulative dose was 68480 Gy corresponding to a cumulative time under graphite irradiation conditions of about 3000 yr. About 100 ppm of organic matter were produced. The experiments were conducted in another context but the results show how relevant the calculations below are.

The calculations for graphite pore water were performed using MAKSIMA-Chemist with a dose rate of 3.6 mGy/hr given for irradiation of pore water by the C-14 inventory of irradiated graphite in table 2. Using the measured G2 graphite density of 1.72 g/cm^3, a porosity of 22 Vol.% and a specific surface area of 5 m^2/g one obtaines a ratio of graphite surface to the irradiated pore water volume of $3.9 \cdot 10^6$ dm^{-1}. Chemical conditions were considered to be hyperalkaline at pH 11, as imposed by the degraded beton of the engineered barrier materials. Under such conditions solution concentrations of CO_3^{-2} in water are typically controlled at a low value by calcite formation. In a first calculation, this effect was conservatively neglected, assuming that all produced CO_2 will be available for formation of organic matter.

Results for zero initial bicarbonate concentrations are given in figure 2, considering a static irradiation system, allowing no exchange with the environment. The principal results are the rise of concentrations of oxalate, acetate and dissolved carbonate.

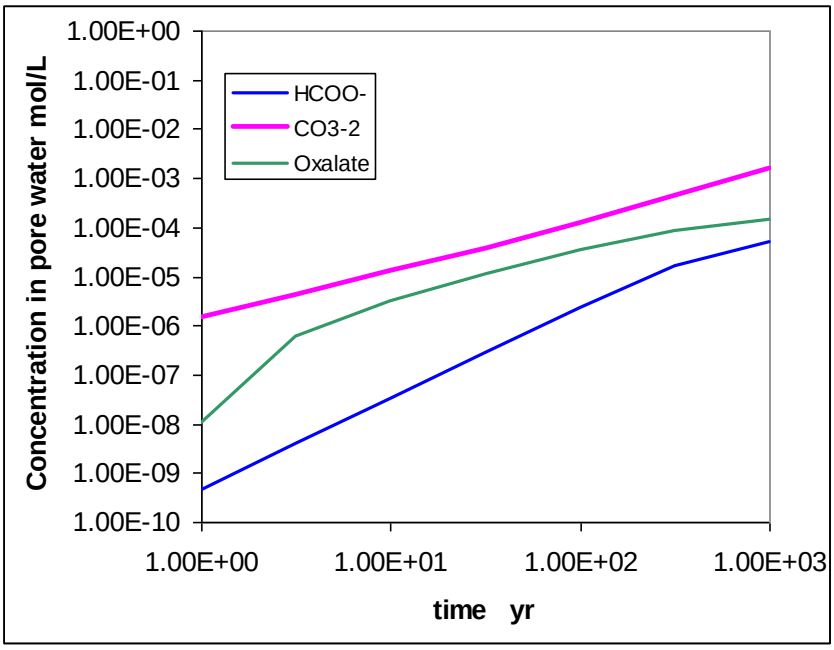

Figure 2: Effect of a long term dose of 0.003 Gy/hr on the irradiation of graphite pore water, under static conditions at pH 11 and 25°C, assuming no exchange with the environment. For more details on calculation conditions see text.

A second calculation was performed assuming that the concentrations of carbonate in the pore water solution were fixed at a low value by the solubility of calcite at pH 11. This implies exchange of Ca with the environment. Figure 3 presents the results. Comparison of Figures 2 and 3 show eventently that carbonate concentrations remain indeed lower in the second case, and this is true as well for acetate concentrations, but in contrast production of oxalate is predicted to increase under these conditions when compared to Figure 2. Nevertheless, organic matter concentrations are in all cases rather low.

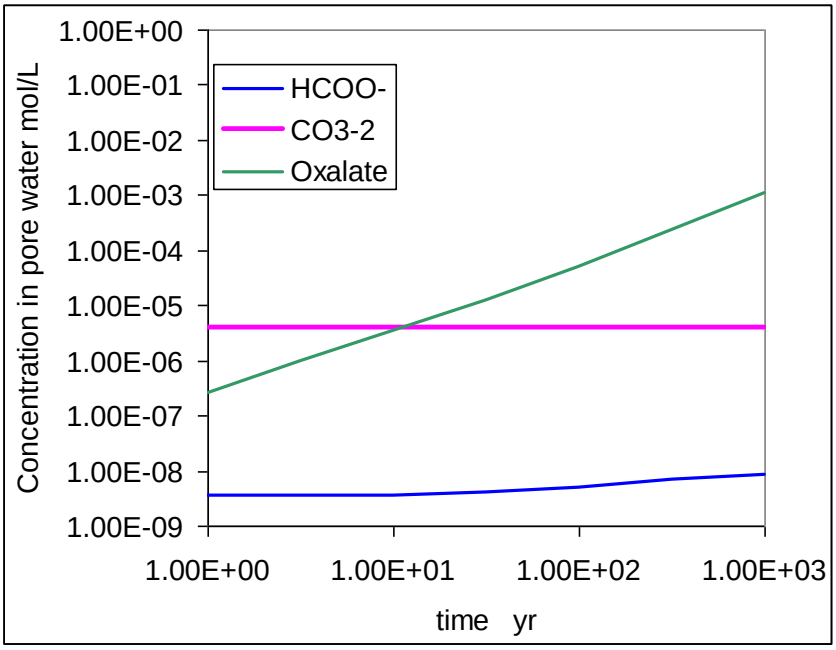

Figure 3: Effect of a long term dose of 0.003 Gy/hr on the irradiation of graphite pore water, under static conditions at pH 11 and 25°C, assuming carbonate concentrations being controlled by calcite. For more details on calculation conditions see text.

Significance or γ radiolysis for disposal conditions

The radiolysis field in the graphite pore water is very weak but the ratio of surface area to solution volume is high in the pores, so that even slow reactions might in principal lead to a significant contribution to pore water composition. Nevertheless, the results of our calculations in figures 2 and 3 show very low concentrations of dissolved organic and inorganic carbon species. To upscale the information in the diagram to realistic repository conditions, the time values for these static case calculations signify under dynamic exchange conditions water residence times. Water residence times in graphite depend on the hydraulic gradient. The hydraulic conductivity is very high. A permeability coefficient K of about 10^{-9} m/s has been measured by SUBATECH's contribution to CARBOWASTE. Under such conditions even small hydraulic gradients lead to short water residence times. But even in absence of hydraulic

gradients, diffusion will be fast, leading to water residence times of few tens of years as has been shown in the Raphael project. A water residence time of 10 yrs might be considered. Under such conditions concentration of radiolytically produced organic and inorganic carbon species are well below 10^{-5} mol/L. This is rather low when compared to natural water compositions. Hence, radiolysis does not seem to be of significance for creating complexing carbonic ligands, which might influence radionuclide mobility. A concentration of 10^{-5} mol carbonic species per liter of pore water solution correspond to only 10 Bq/L of C14 if C14 would have the same behavior than C12.

From the accumulation rate of radiolytic carbon species in the pore water we can calculate radiolytic graphite dissolution rates. The accumulation rate is about 10^{-5} mol/L/yr. Using a surface to volume ratio of $3.9 \cdot 10^{6}$ dm^{-1} this correspond to a very low dissolution rate of $3 \cdot 10^{-10}$ g/m^2yr leading to graphite life times of a billion of years. Hence, also from the point of view of graphite dissolution rates, radiolytic effects can be ignored.

Conclusions

Our calculations have shown that under disposal conditions after decay of Co60, radiolytic processes are insignificant for C14 release. This is true both for organic or inorganic radiolysis products.
The consequence is that non-radiolytic release processes are dominant for C14 release from irradiated graphite. Since it is known that non-radiolytic graphite matrix dissolution is extremely slow we can conclude that only that fraction of C14 can be released which is located on easily accessible surfaces outside the graphenes. For safety analysis it is important to identify this fraction.