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Report on radionuclide diffusion in water saturated graphite

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Document title

Report on radionuclide diffusion in water saturated graphite

Executive summary

The focus of this deliverable is on the diffusion of C14 in graphite grains during leaching in water. Comparison is made to diffusion of other nuclides in the pore space of graphite. Diffusion coefficients derived from leaching data of C14 from powdered irradiated graphite are about 7 orders of magnitudes smaller than those for actinides and Cl36 in the water filled graphite pores. This is indicative for release control by solid state diffusion in graphite grains rather than diffusion control in pore water. This is completely different than diffusive control for Cl36 release from graphite which is fast since it appears to be controlled by diffusion in the pore water. This mechanism signifies that transport of C14 in the pore water is fast relative to the rate of transfer from the grains to the pore water. The consequence is that sample size/graphite block size will have rather little effect on release rates of C14.

Revisions

Rev.	Date	Short description	Author	Internal Review	Task Leader	WP Leader
1	2/3/2013		*B. Grambow*	C. Landesman		B. Grambow

Introduction

Irradiated nuclear graphite contains many radionuclides, formed by neutron activation of carbon and trace elements in the graphite structure. Safety analysis shall determine whether the radioactive graphite can be disposed of as nuclear waste without further treatment either in near surface or deep geological disposal. In such analyses one needs to assess the radionuclide release properties in case of groundwater access. This comprises thorough understanding of radionuclide release controlling mechanism. Graphite is a porous medium. Hence, radionuclides can be released not only from the surface but as well from the interior parts of the solid waste, provided that water can access interior pore spaces and transport processes are sufficiently rapid. A key process is molecular diffusion. We can distinguish two different diffusion processes: diffusion in the pore space of the graphite and diffusion within graphite grains. The present report is focused mainly on diffusion in graphite grains, but comparison to pore diffusion is done as well.

Diffusion and diffusion coefficients

Transfer of solute s in a porous medium is generally associated with the presence of chemical gradients. The concentration gradient is responsible for the molecular diffusion described by Fick's laws. The solutes are mobilized in the influence of Brownian motion which tends to homogenization of the distribution of solute in the medium. Molecular diffusion is described at the macroscopic scale by Fick's first law. The diffusive flux depends on the concentration gradient.

Equation 1 $$J_d = -D\frac{\partial C}{\partial x}$$ with J_d flux of solute (mol.m^{-2}.s^{-1})

D diffusion coefficient (m^2.s^{-1})

C concentration in solution (mol.m^{-3})

x diffusion length (m)

In the case of a porous medium in which the structure of the medium affects the transfer of solutes, the molecular diffusion coefficient is replaced by the effective diffusion coefficient. This includes, according to equation 2, the diffusion accessible porosity ε_{acc}, the totuosity τ (deviation of the diffusion path) and the constructiveness system δ (narrowing or widening of the diffusion path).

Equation 2 $$D_e = D\varepsilon_{acc}\frac{\delta}{\tau^2}$$

It is also conventional to use a pore diffusion coefficient, connected to effective diffusion coefficient as given in equation 3:

Equation 3 $$D_p = \frac{D_e}{\varepsilon_{acc}} = D\left(\frac{\delta}{\tau^2}\right)$$

Fick's second law taking into accounts the conservation of matter, is expressed by:

Equation 4 $$\frac{\partial C}{\partial t} = -\frac{\partial J}{\partial x} = D\frac{\partial^2 C}{\partial x^2}$$

T

his relationship is valid if the diffusion coefficient D is independent of x, that is to say, if the material is homogeneous.

In the case of a porous medium in which the structure of the medium affects the transfer of solutes, the molecular diffusion coefficient is replaced by the effective diffusion coefficient D_e The latter includes, according to the following equation, the porosity accessible to diffusion ε_{acc}, where there is no interaction between the solute and the matrix.

Équation 5 $$\frac{\partial C}{\partial t} = \frac{D_e}{\varepsilon_{acc}}\frac{\partial^2 C}{\partial x^2} = D_a\frac{\partial^2 C}{\partial x^2} \qquad \text{with } D_e = D_a\varepsilon_{acc}$$

D_a is the apparent diffusion coefficient, which is measured experimentally in the leaching tests.

The pure diffusion model is based on solving equations using Fick initial conditions and boundary conditions as follows:

$C(x)_{t=0} = cte = C_0$: the diffusing species is initially present in dissolved form and homogeneous throughout the material

$C(t)_{x=0} = 0$: the concentration is zero at the solids surface

If we place ourselves in the conditions of a semi-infinite porous matrix, then the following condition is added:

$$C(t)_{x=\infty} = C_0$$

This system had to be solved. It is possible to define the expression of the amount of material released into the leaching solution E (t) (assuming the concentration of zero at the surface of the sample):

Equation 6 $$m_i(t) = 2 \times C_{o,i} \times S \times \sqrt{\frac{D_{a,i} \times t}{\pi}}$$ where S is the sample surface

Experimentally, this relationship is expressed using the cumulative fraction leached (FCL), which is defined as the ratio of the total mass released of a species i at time t, M_i (t) and the total mass M_0 this species initially present in the sample before leaching.

Thus, we obtain the expression of F.C.L. released by diffusion, replacing $C_{0,\,i}$, the volume concentration of species i in the material studied by $M_{0,\,i}$ / V, with V the total volume of the sample. The final relationship is as follows:

Equation 7 $$F.C.L. = \frac{M_{i,t}}{M_0} = 2 \times \frac{C_{o,i}}{M_0} \times S \times \sqrt{\frac{D_{a,i} \times t}{\pi}} = 2 \times \frac{S}{V} \times \sqrt{\frac{D_{a,i} \times t}{\pi}}$$

This expression is important because it ensures that the amount of a solute is released by a purely diffusive transfer. And for such conditions, a graphical representation of cumulative fractions leached will give straight lines passing through the origin and whose slope will allow to determine the apparent diffusion coefficients.

Experimental

To study the behavior and speciation of radionuclides released from graphite in solution, leaching experiments were performed with irradiated graphite samples originated from French reactors SLA2 and G2. Samples were powdered and brought into contact with an alkaline solution (simulating storage conditions in cementitious materials) in a closed reactor, with constant stirring. The experiments were conducted at room temperature and different masses of graphite.

In this section, the experimental protocol is described. Leaching experiments performed on high mass of graphite, were conducted in collaboration J. Conte at CEA Cadarache.

The graphite samples were used without pretreatment. A mass m of sample is introduced into a glass reactors and a magnetic bar, through a funnel.

The reactors (Storage bottle with septum inlet stopcock with PTFE) used for these experiments are from Aldrich (Figure 1).

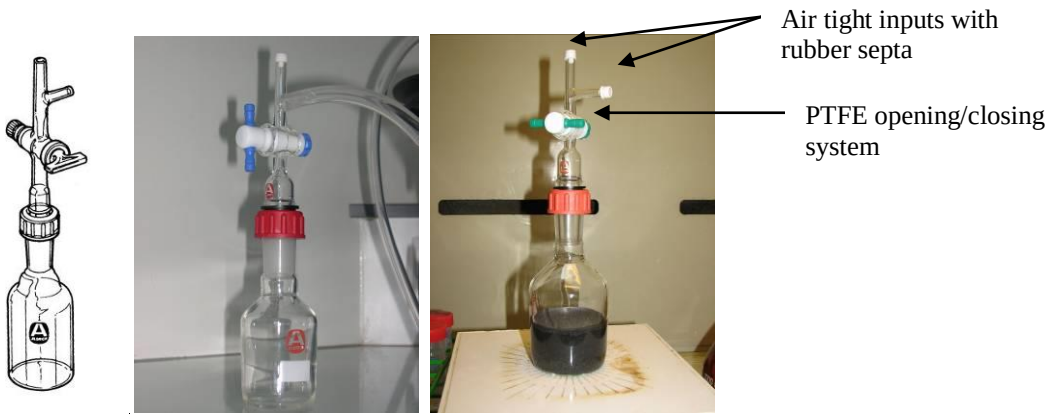

Figure 1: Schematic and photographs of a reactor

A reactor is composed of two parts: the lower part, the container and the upper part. This part is used as an opening/closing system, since it is provided with a valve sealing PTFE. This device is designed to confine the gas which may be produced during the leaching of the graphite sample. The two inputs of the reactor are sealed with rubber septa.

Leaching solutions are prepared from a NaOH Titrisol (Merck) concentrated solution diluted with ultrapure deionized water. A volume V of NaOH 0.1 mol L-1 is always added via the funnel to recover all of graphite deposited on the edges. To avoid carbonation, before closing the reactor, the mixture is placed under inert atmosphere (N_2). The input and output of the reactor are protected by rubber septa. Reactors are installed on a magnetic stir plate for a continuous stirring of the graphite suspension.

The experimental leaching conditions are summarized in table 1.

Table 1 : Experimental conditions for leaching experiments

Sample	Reference	Mass (g)	T (°C)	Sampling time (j)	Leaching volume (mL)	Gas volume (mL)	V_{sol}/V_{gas}
F10M10-102 180<x<500µm	SLA2-102	0,498 ± 0,001	22 ± 2	15, 51, 91, 133, 169, 241, 821	50	75	2/3
F10M10+F5M19-105 <180µm	SLA2-105	1,025 ± 0,001	22 ± 2	18, 51, 91, 133, 165, 241, 821	50	75	2/3
F10M10-103 500<x<1000µm	SLA2-103-1	0,350 ± 0,001	22 ± 2	3, 7, 10, 14, 28, 38, 51, 680	50	75	2/3
F10M10-103 500<x<1000µm	SLA2-103-2	0,356 ± 0,001	22 ± 2	4, 9, 15, 18, 30, 39, 51, 680	50	75	2/3
F10M10+F5M19-107 500<x<1000µm	SLA2-107	0,710 ± 0,001	22 ± 2	3, 7, 10, 14, 28, 38, 51, 680	50	75	2/3
F10M10-104 >1000µm	SLA2-104	1,513 ± 0,001	50 ± 2	56, 106, 438	75	50	3/2
F10M10+F5M19 180<x<2000	SLA2-15	15,192 ± 0,002	22 ± 2	1, 4, 8, 13, 27, 50, 95, 347, 512	50	75	2/3
F4M10* 50<x<2000	SLA2-25	24,97 ± 0,01	22 ± 2	4, 11, 21, 53, 90, 132, 179, 280	100	150	2/3
G2-27* 50<x<2000	G2-50	50,29 ± 0,01	22 ± 2	1, 5, 12, 21, 50, 90, 132, 180	200	300	2/3

Diffusion controlled C14 release from nuclear graphite

A) Interpretation by diffusion control of leaching data of French graphite obtained at SUBATECH

Leaching results of C14 from powdered French graphite (SLA2 and G2) can be interpreted either a fast initial release followed by a much slower one or they can alternatively be interpreted by a diffusion process (Vendé 2012).

Our experiments are conducted on powders, not blocks. This makes diffusion distances much smaller allowing that even very small solid state diffusion coefficients can be studied.

Fractions of inventories of C14 from different leaching tests were plotted against the square root of time. For each data set, the linear regression curves were calculated according to Eq. 7. The data sets obtained during experiments on samples SLA2 on low masses at room temperature (Figure 2) show a linear trend with square root of time. However, no conclusion can be drawn: the measurement uncertainties are too high.

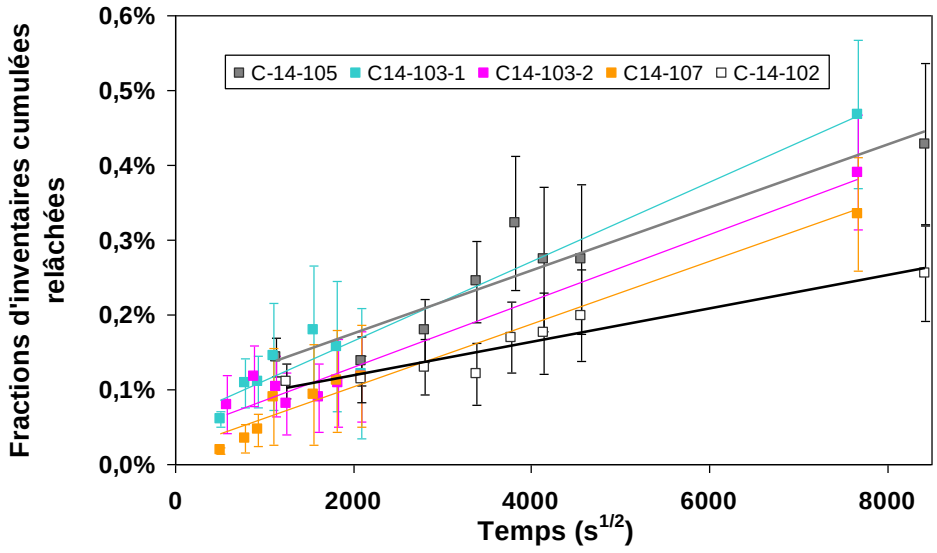

Figure 2: Evolution of C-14 cumulative fractions of inventory released *vs* the root function of time for experiments SLA2-102-105 SLA2, SLA2-103-1-103-SLA2 2 SLA2-107

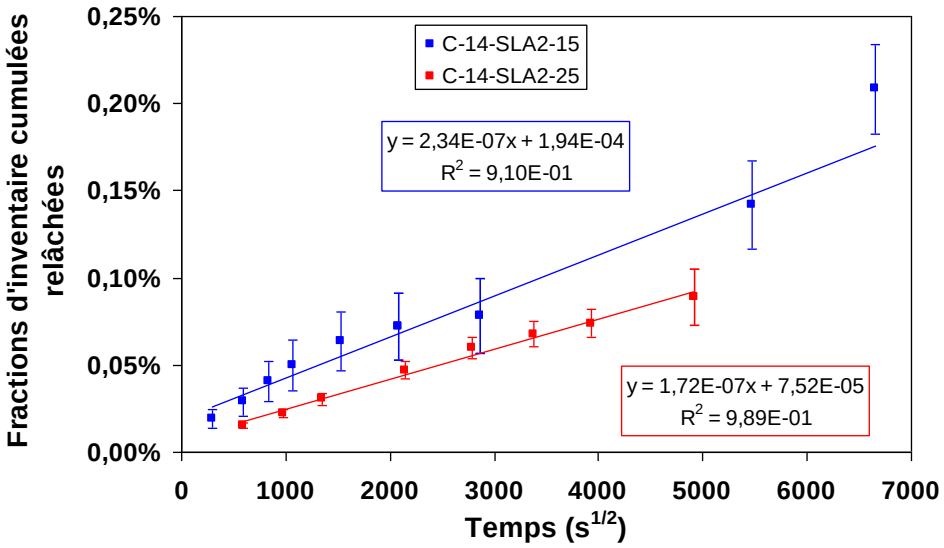

Figure 3: Evolution of C-14 cumulative fractions of inventory released *vs* the root of time for experiments and SLA2 SLA-15-25

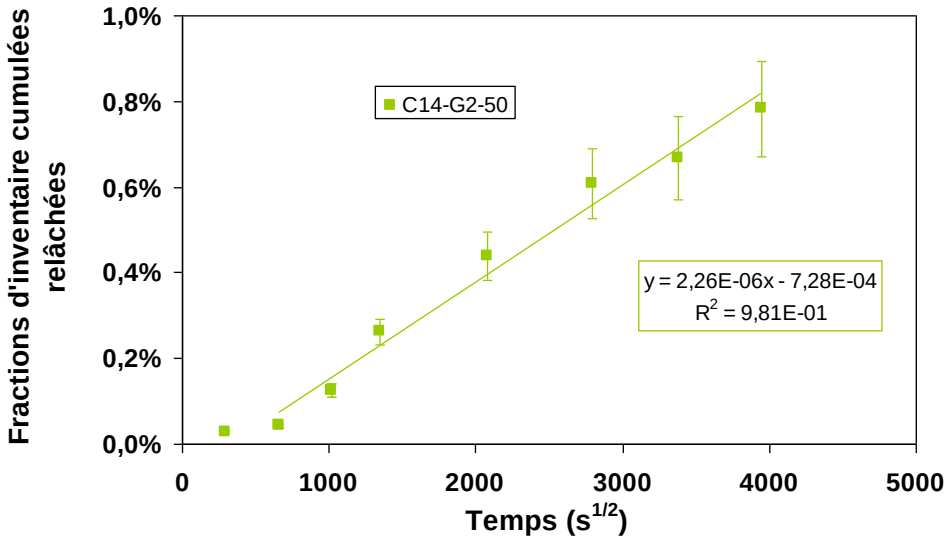

Figure 4: Evolution of C-14 cumulative fractions of inventory released *vs* the square root time for experiment G-50

The results of leaching tests SLA2-15 and SLA2-25 (Figure 3) is a linear function of the square root of time: for short times SLA2-15 (t <27 days), and throughout the experience SLA2-25. The results obtained in the experiment G2-50 (Figure 4) are linear with respect to

the square root of time from t = 5 days on. The results indicate that a diffusion mechanism seems to be involved in the release of carbon-14 solution for all experiments. It is therefore useful to calculate an apparent diffusion coefficient.

Our samples are in the form of powder with a known particle size range. Because of their radioactivity, no specific surface area measurements could be made. However, it is necessary to know the S/V ratio to calculate the apparent diffusion coefficients. For this purpose the assumption was made that the graphite grains in our powders are spherical and consists of n spheres: in this case a surface and a volume can be estimated, and this for different macroscopic size fractions.

The macroscopic grain size of our samples is variable. We therefore consider that our sample is a set of n identical spheres: a coefficient is calculated for a mixture with the smallest size and highest coefficient. Two apparent diffusion coefficients are calculated from equation 7 for each sample (Table 2) we obtain an interval in which is contained the true apparent diffusion coefficient.

Table 2: Interval for apparent diffusion coefficients derived for the experiments SLA2-103-1, 103-2, SLA2, SLA2-107-15 SLA2, SLA2-25 and G2-50

	SLA2-15		**SLA2-25**		**G2-50**	
Grain size range (µm)	180	2000	50	2000	50	2000
Slope (Fraction.$s^{-1/2}$)	$2{,}3.10^{-7} \pm 0{,}2.10^{-7}$		$1{,}7.10^{-7} \pm 0{,}1.10^{-7}$		$2{,}3.10^{-6} \pm 0{,}1.10^{-6}$	
Intersection with y-axis	$2{,}1.10^{-4} \pm 0{,}4.10^{-4}$		$7{,}5.10^{-5} \pm 2{,}1.10^{-5}$		$-7{,}3.10^{-4} \pm 3{,}5.10^{-4}$	
V_e/S_e (m)	$3{,}1.10^{-12}$	$4{,}2.10^{-9}$	$6{,}5.10^{-14}$	$4{,}2.10^{-9}$	$6{,}5.10^{-14}$	$4{,}2.10^{-9}$
Da ($m^2.s^{-1}$)	**$3{,}9.10^{-23}$**	**$4{,}8.10^{-21}$**	**$1{,}6.10^{-24}$**	**$2{,}6.10^{-21}$**	**$2{,}8.10^{-22}$**	**$4{,}5.10^{-19}$**

The true values of apparent diffusion coefficients are within the ranges calculated. The calculated values are low, with D_a values varying from 10^{-23} to 10^{-19} m^2/s. This reflects a very slow diffusion, consistent with small fractions of carbon-14 released into solutions. The upper boundary of D_a, for sample G2 is higher than for samples SLA2, this reflects a greater reactivity of the sample. These coefficients were calculated from the slope of the linear regression lines. The lines for experiments SLA2-15 and SLA-25 have a positive intercept,

unlike G2-50. The positive ordinate for these two experiments indicate a relaxation of the initial irradiated graphite. Our samples are in powder form, and have not been treated before leaching. The possibility of an initial release of carbon 14 from the surface of our grain graphite is not excluded. In experiment G2-50, the y-intercept of the line is negative. This reflects a process preceding the diffusion phenomenon. This phenomenon could be related to the impregnation of the water within the grains of graphite. Indeed, if the kinetics of impregnation is slower, the phenomenon of diffusion will be delayed.

The results for experience SLA2-15 show a diffusion phenomenon in the short term. But at longer time: fraction inventory increases over time. This may be explained as follows: In our experiments, a decrease in particle size with time is observed. The ratio S_e / V_e is inversely proportional to the grain radius by:

Equation 8 $$\frac{S_e}{V_e} = \frac{4 \times \pi \times r^2}{4/3 \times \pi \times r^3} = \frac{3}{r}$$

If the particle size decreases, the grain radius r decreases, then the ratio S_e / V_e increases. This therefore leads to an increase in the fraction of inventory, if the coefficient D_a is constant. In addition, the diffractograms of graphite have shown that leaching has no influence on the structure of graphite crystallites. A decrease in grain size can explain the increased release of carbon 14 total long term. Samples SLA2 and G2 exhibit different leaching behaviors and release of carbon 14.

The released Carbon 14 has been observed to be the total sum of the fractions of organic and inorganic forms. The same method is applied to data sets of these two forms. During the experiment SLA2-15, inorganic and organic carbon-14 have different release rates (Figure 5). The release of organic form is like the inorganic carbon for early time a linear function of the square root of time throughout the experiment: this indicates that the release mechanism is similar.

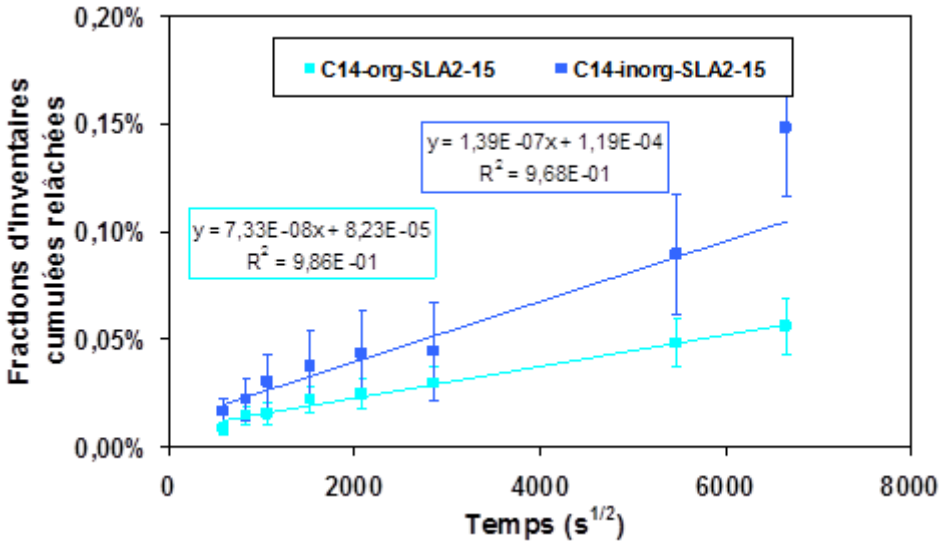

Figure 5: Evolution of the fraction of inorganic and organic carbon-14 inventory in solution plotted *vs* the square root of time for SLA2-15

The release of two forms of carbon-14 during the experiment SLA2-25 (Figure 6) is a linear function of the square root of time throughout the experiment, indicating control by a diffusion mechanism.

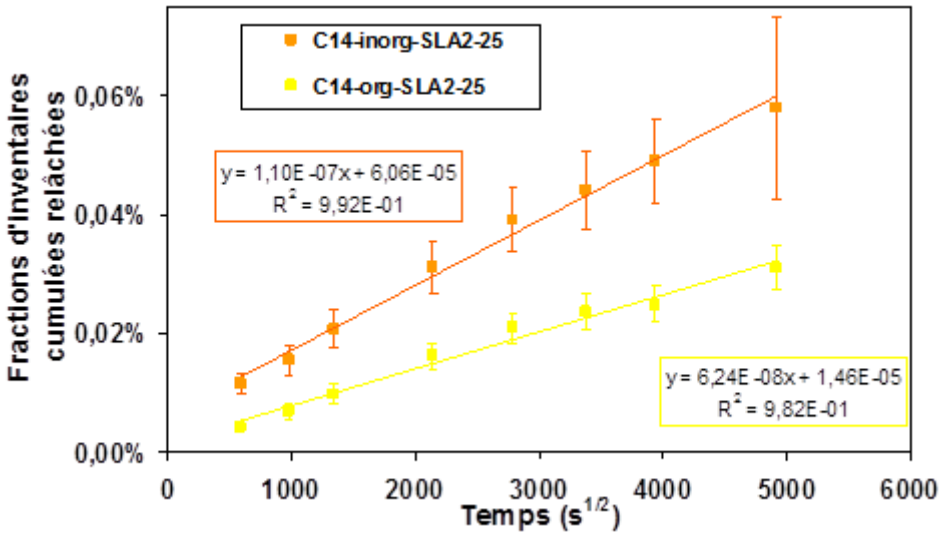

Figure 6: Evolution of the fraction of carbon-14 inventory released in organic and inorganic form into solution *vs* the square root of time for SLA2-25

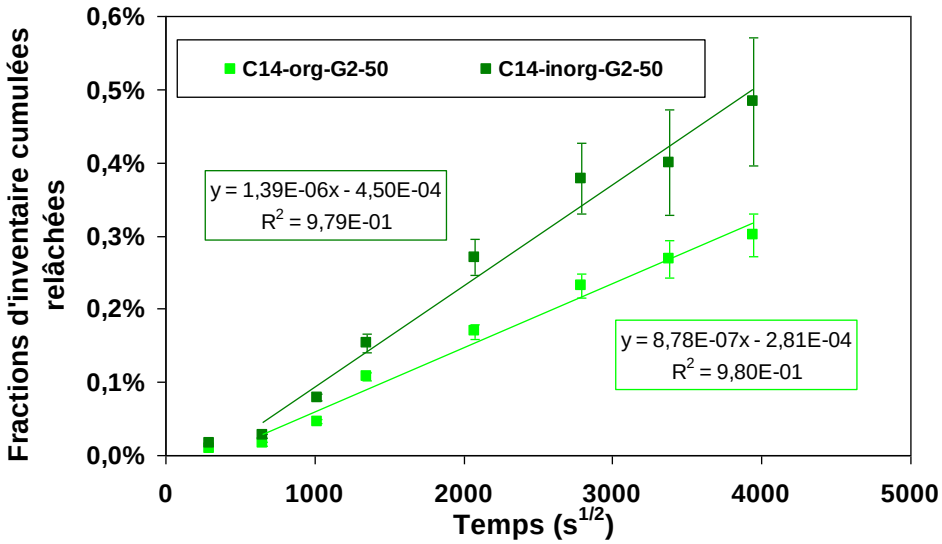

Figure 7: Evolution of the fraction of carbon-14 inventory in organic and inorganic form released into solution plotted *vs* the square root of time for G2-50

The results obtained during the experiment G2-50 (Figure 7) are linearly dependent on the square root of time from t = 5 days, both organic and inorganic form. Calculated diffusion coefficients (according to Eq. 7) are reported in Table 3.

The apparent diffusion coefficients of organic and inorganic carbon 14 are similar. The release of organic carbon 14 is slower. One might think that the reactivity of organic molecules is lower since these molecules are larger than carbonates, and therefore have a higher steric hindrance and slower diffusion rate. But it can also be the case that carbon is released from the graphite in elementary form and only at the interface to water fractions transforms into organic carbon, another to inorganic one. The results obtained in these experiments indicate that the release of carbon-14, inorganic and organic, can be related to a diffusion mechanism, with either initial release, a delay effect. Other processes are therefore involved. So there are two release mechanisms that can be associated with the experimental data: a first mechanism involving more or less labile fractions, or a diffusional release mechanism.

Table 3: Apparent diffusion coefficients for organic and inorganic species of carbon-14 in experiences SLA2-15, SLA2-25 and G2-50

	Carbone 14 (organic)							
sample	SLA2-104		SLA2-15		SLA2-25		G2-50	
Grain sises (µm)	500	1000	180	2000	50	2000	50	2000
slope (Fraction.$s^{-1/2}$)	$1,4.10^{-7} \pm 0,2.10^{-7}$		$7,3.10^{-8} \pm 0,4.10^{-8}$		$6,2.10^{-8} \pm 0,3.10^{-8}$		$8,8.10^{-7} \pm 0,6.10^{-7}$	
Intersection ordinate	$5,2.10^{-5} \pm 0,9.10^{-5}$		$8,2.10^{-5} \pm 1,2.10^{-5}$		$1,5.10^{-5} \pm 0,9.10^{-5}$		$-2,8.10^{-4} \pm 1,4.10^{-4}$	
V_e/S_e (m)	$1,67.10^{-4}$	$3,33.10^{-4}$	$3,1.10^{-12}$	$4,2.10^{-9}$	$6,5.10^{-14}$	$4,2.10^{-9}$	$6,5.10^{-14}$	$4,2.10^{-9}$
Da ($m^2.s^{-1}$)	**$4,2.10^{-22}$**	**$1,7.10^{-21}$**	**$3,8.10^{-24}$**	**$4,7.10^{-22}$**	**$2,1.10^{-25}$**	**$3,4.10^{-22}$**	**$4,2.10^{-23}$**	**$6,7.10^{-20}$**

	Carbone 14 (inorganic)					
sample	SLA2-15		SLA2-25		G2-50	
Grain sizes (µm)	180	2000	50	2000	50	2000
Slope (Fraction.$s^{-1/2}$)	$1,4.10^{-7} \pm 0,1.10^{-7}$		$1,1.10^{-7} \pm 0,1.10^{-7}$		$1,4.10^{-6} \pm 0,1.10^{-6}$	
Intersection ordinate	$1,2.10^{-4} \pm 0,3.10^{-4}$		$6,1.10^{-5} \pm 1,2.10^{-5}$		$-4,5.10^{-4} \pm 2,2.10^{-4}$	
V_e/S_e (m)	$3,1.10^{-12}$	$4,2.10^{-9}$	$6,5.10^{-14}$	$4,2.10^{-9}$	$6,5.10^{-14}$	$4,2.10^{-9}$
Da ($m^2.s^{-1}$)	**$1,4.10^{-23}$**	**$1,7.10^{-21}$**	**$6,6.10^{-25}$**	**$1,1.10^{-21}$**	**$1,1.10^{-22}$**	**$1,7.10^{-19}$**

B) Study of literature data: Results for samples of Hanford reactor

Gray and Morgan [GRA88] studied the release of carbon-14 from graphite samples originated from the C reactor C at Hanford. The table 4 summarized the experimental conditions of the leaching experiments. This allows to plot the values of the cumulative fractions released into solution with time (Figure 8).

Leached fractions of C14 are low and appear to be linear function of time. Fractions leached inventory after 56 days ranged from 0.004% (groundwater at 25 ° C) to 0.050% (ultra pure UP water to 90 ° C) . In both experiments at 90 ° C, the leached fractions are higher (both in UP water in groundwater). The temperature is a factor influencing the release. According to Gray and Morgan this dependence is not related to oxidation kinetics.

Table 4 : Experimental conditions of leaching experiments and C-14 cumulative released inventory fractions on Hanford C-reactor (adapted from [GRA88])

	Sample.	Leaching solution	Mass (g)	Temp. °C	Leaching volumet (mL)	Duration (day)	Initial activity (Bq/g)	Cumulative released inventory fraction (%)
Hanford (PNL)	HGW-25	Hanford site water pH = 8,3	36,0	25	406	56	$2,59.10^5$	0,004
	HGW-90	Hanford site water pH = 8,3	36,7	90	406	56		0,026
	DIW-25	UP water*	36,6	25	406	56		0,009
	DIW-50	UP water	36,5	50	406	56		0,018
	DIW-90	UP water	36,6	90	406	56		0,050

* UP water = ultra pure water

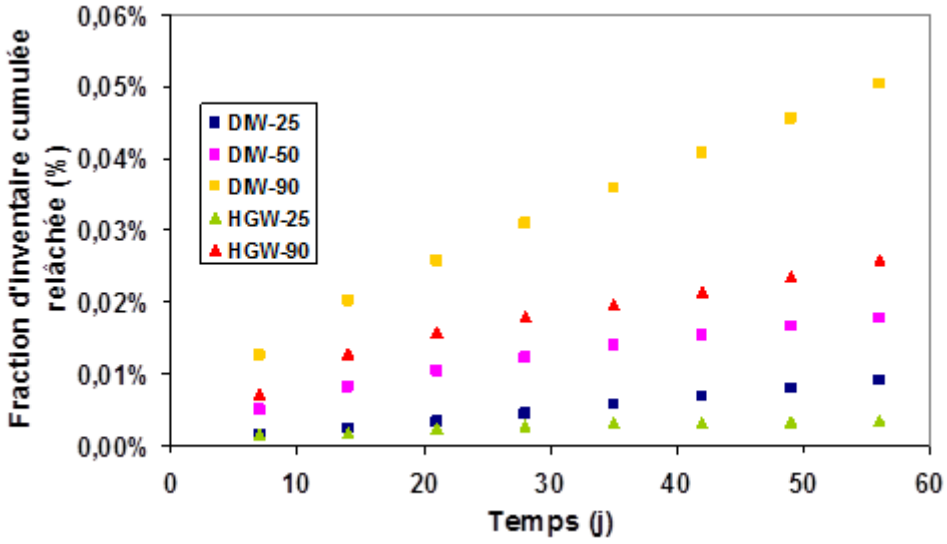

Figure 8 : Evolutions of the released inventory fractions as function of time for samples from Hanford (results PNL)

The rate of release of carbon-14 in solution as a function of time decreases with time. To explain this trend, Gray and Morgan propose two mechanisms: either a depletion of the carbon source 14, or release is diffusion limited by the transport of reactants or products.

Since the total release is low (Fig. 8) the source does not seem to be depleted. But it is possible that part of the C14 inventory is more reactive or more accessible to the leachate. If

diffusion is the limiting mechanism, then the cumulative released fraction is linear as a function of the square root of the time (Eq. 7). The authors observed such a linearity is observed but refrained from taking a final conclusion since a diffusion control was not observed for Cl-36 and they believed that carbon-14 and chlorine-36 should have the same behavior.

We decided to reinterprete the results presented by the PNL to verify the assumption of a diffusion mechanism. For each set of data, a linear regression line is plotted (Figures 9 and 10).

The regression curves have a negative intercept, but are linearly dependent on the root of the time. This indicates that there is a process which precedes the diffusion step. Graphite is a hydrophobic material. It is therefore possible that the delay (zero offset) is the time required for water infiltration graphite. In HGW-25 experiement, the intercept is positive (4.39 ± 1.37) $.10^{-4}$%. This could be due to initial relaxation.

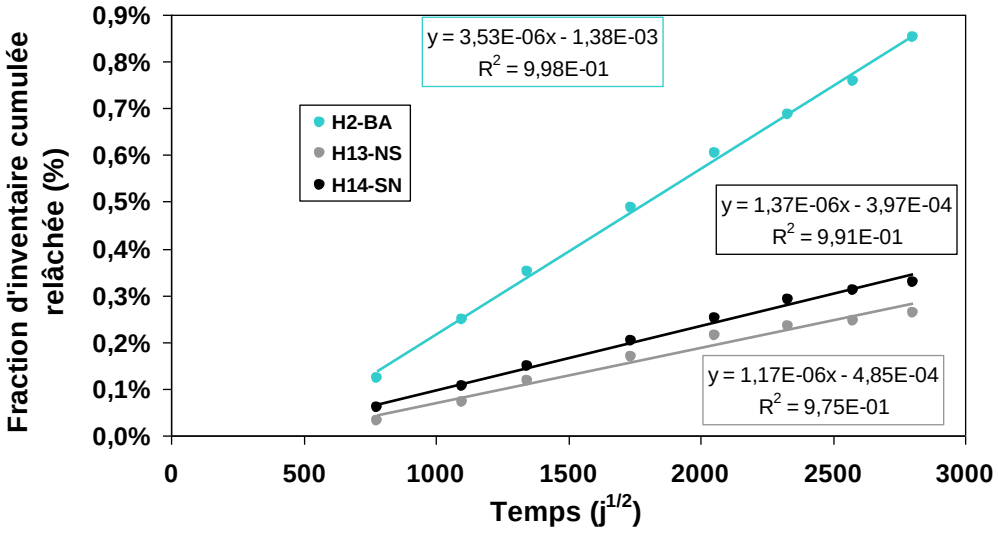

Figure 9: Evolution of cumulative fractions inventory of C14 released as function of the square root of time for samples of Hanford

From Equation 7 and the slope of the regression line, we determined the apparent diffusion coefficients. The results are presented in Table 5.

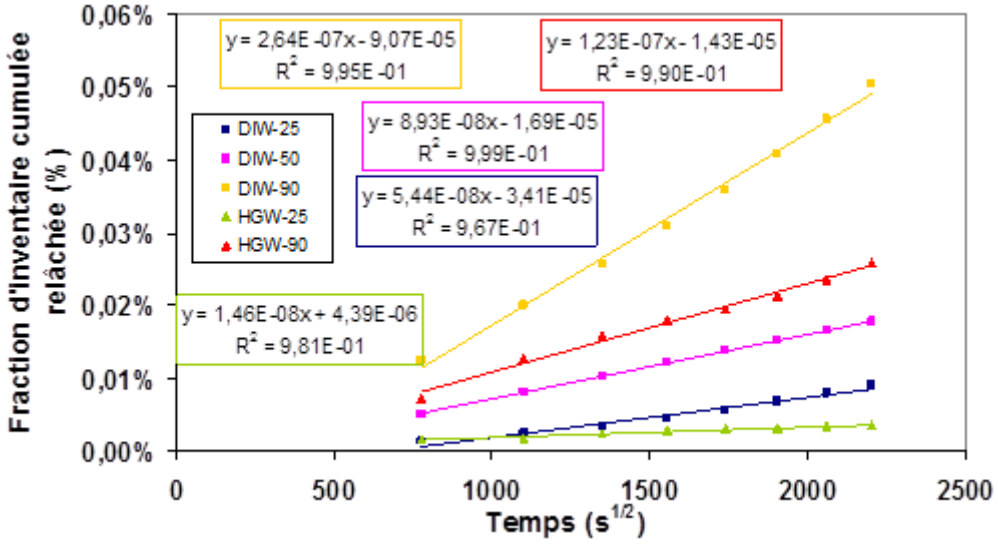

Figure 10: Evolution of cumulative fractions inventory of C14 released as function of the square root of time for samples of G2 analysed by PNL.

These values are low: they ranges from 10^{-18} to 10^{-21} m^2s^{-1}. The influence of temperature is significant: D_a increases with temperature (under similar leaching conditions). The apparent diffusion coefficient is fourteen times higher in deionized water than in Hanford groundwater at 25 ° C. No explanation is available, but one may speculate that the carbonate content of the groundwater decreases diffusion gradients and consequently release rates.

Table 5: Apparent diffusion coefficients derived from the release of carbon-14 in solution

	Graphite from Hanford					Graphite from G2		
Sample	HGW-25	HGW-90	DIW-25	DIW-50	DIW-90	H2-BA	H13-NS	H14-SN
Ratio S/V (cm)	0,51	0,51	0,51	0,51	0,51	0,48	0,48	0,48
Slope (%/$s^{-1/2}$)	$1,46.10^{-8}$	$1,23.10^{-5}$	$5,44.10^{-8}$	$8,93.10^{-8}$	$2,64.10^{-7}$	$3,53.10^{-6}$	$1,17.10^{-6}$	$1,37.10^{-6}$
D_a (m^2/s)	$4,4.10^{-21}$	$3,1.10^{-19}$	$6,0.10^{-20}$	$1,6.10^{-19}$	$1,4.10^{-18}$	$2,3.10^{-16}$	$2,5.10^{-17}$	$3,4.10^{-17}$

D_a values calculated for samples G2 are higher than those obtained for samples from the C reactor of Hanford. G2 samples are more reactive. The reactor is cooled by light water [IAEA06]. The type of coke and conditions of use of graphite (coolant, neutron flux, ...) can

be parameters influencing this difference in reactivity, but due to lack of data we can not specify which of these parameters are prevailing.

Results of these reinterpretations of literature date are consistent with the interpretation of SUBATECH data by a diffusion process. The apparent diffusion coefficients of samples G2, both during experiments conducted by the PNL in our experience, are higher than those of SLA2 and Hanford. The total release of carbon-14 is also associated with higher: graphite G2 seems more susceptible to leaching.

Discussion and conclusions

Two mechanism are proposed to explain C14 release from graphite: First, it can be seen that the release occurs in two stages: a first stage where a labile fraction is released, and the kinetics is fast, then a second step with a more moderate release rate of a less labile fraction. The second mechanism is following a diffusion law. It is not possible to decide between these two mechanisms controlling potentially the long-term behavior of carbon-14 in solution in view of our experimental results. Indeed, none of the two mechanisms may be privileged, and the release mechanism is probably more complex.

However, these two mechanisms do not have the same impact in the long term if they are applied to the context of storage. Estimated linear release rates for total carbon-14 range from 0.05 to 0.9% / year. In case of validity of a linear long term -release model this would mean that in our experimental conditions, 100% of carbon-14 in the graphite would be released in a period of 100 to 2000 years. In case of the validity of a diffusional rate law release rates will become rapidly extremely low. This is the case in particular for the fact that diffusion constants were derived from powdered samples with very small diffusion distances. In real bulk graphite samples, diffusion rates will be many orders of magnitude smaller so that C14 release in a repository from graphite containing waste will become rapidly insignificant. It is therefore extremely important to further analyze the governing mechanism.

Interpreting C14 release data from powdered graphite indicates that a diffusion mechanism might control release. Diffusion coefficients are very low. They are in the range of solid state diffusion and are much lower than expected for diffusion in aqueous phase. This indicates that

the rate limiting step is the release of C14 from graphite grains and that the transport of C14 species in the pore water of the graphite is much faster.

Indeed the diffusion coefficients measured A. Bukaemskiy in FZ Jülich in diffusion cells for the much larger actinide ions are about 7 orders of magnitude larger (diffusion coefficients around 10^{-13} to 10^{-14} m^2/s, see deliverable D 6.1.5.a). In this case, transport in pore water is controlling the rate of transfer through the graphite and not the release from solid graphite grains.

Diffusion tests have been also been carried out by CEA in the carbowaste project in order to check whether chlorine release might be a diffusion driven process (see Deliverable 6.1.6).

Results have been compared to diffusion coefficients fitted on leaching plots. Diffusion tests were performed on virgin graphite samples by monitoring chlorine-36 transfer kinetics through the samples. The effective diffusion coefficient of chlorine-36 was found to be about 4.10^{-12} $m^2.s^{-1}$ for G2 graphite moderator samples. Like in the present work, the diffusion coefficient of chlorine-36 was fitted from leaching data. In Table 4 3 of deliverable 6.1.6 the apparent diffusion coefficients (D_a) for G2 moderator samples are close ([$1,3.10^{-11}$ - $4,6.10^{-11}$] $m^2.s^{-1}$). The mean value is 3.10^{-11} $m^2.s^{-1}$ which accounts for an effective diffusion coefficient (D_e) of 6.10^{-12} $m^2.s^{-1}$. Compared to the potentially diffusion controlled C-14 release from grains to pore water described in the present report, the release of Cl-36 seems to be controlled by the much faster transport in the graphite pore water and not be the very slow diffusional release from solid grains.

The proposed mechanism signifies that transport of C-14 within the pore water is fast relative to the rate of transfer from the grains to the pore water. The consequence is that sample size/graphite block size will have rather little effect on release rates of C-14 in contrast to behavior of Cl-36

References:

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