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Report on evaluation of Cl mobility as function of sample depth

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Document title
Report on evaluation of Cl mobility as function of sample depth
Executive summary
The focus of this deliverable is the development of a methodology for studying the release properties of radionuclides as a function of sample depth.

Revisions

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

1 Introduction

The inventories of irradiated graphite waste of ^{36}Cl stem mainly from neutron irradiation of impurities of ^{35}Cl of the natural chlorine introduced into the nuclear graphite in the fabrication process. Quantities of the Cl inventory as large as 80% have been reported to be already released during reactor operation (Clayton et al. 1997) . EDF/CIDEN analyses calculated from the measured ^{36}Cl inventory of irradiated graphite and from the known neutron irradiation data an initial ^{35}Cl inventory which is about 100 times lower than the measured initial ^{35}Cl inventory of non-irradiated graphite of the same type. This means that about 99% of the initial chlorine inventory has been released during reactor operation. A detailed annealing study (Vaudey et al. 2009) shows that, in the temperature range of 200 to 800°C even for a short annealing duration (4 h), chlorine is released almost athermally. At 500°C, around 20% of the initial ^{37}Cl content is released. At 800 °C, the release reaches a plateau and the loss of ^{37}Cl is around 30%. Open pores are preferential release pathways. Around 70% of chlorine is assigned to stable organic chlorine bound to aromatic carbon whereas around 30% is assigned to inorganic thermally labile oxychlorinated groups (Vaudey et al. 2010). It has also observed that implantation of Cl atoms in graphite leads to breaking of crystallites and that thermal annealing can heal these defects.

Leaching data of ^{36}Cl for irradiated graphite from literature and the Carbowaste project can be summarized as follows (Comte et al. 2012):

1) All leaching studies on i-graphite show that ^{36}Cl is released in 2 stages: a very rapid initial release controlled by diffusion of ^{36}Cl through open graphite porosity of a very labile fraction of the ^{36}Cl inventory and a very slow long-term release of the remaining rather immobile fraction. Effective diffusion coefficients are between 10^{-11} and 10^{-12} m^2/s depending on graphite porosity. Water uptake of i-graphite is faster than ^{36}Cl release, hence it does not limit release.
2) large differences were noted between the leach rates from different samples. The labile fraction is between few percent and 90% and this fraction is

probably located in open easy water accessible pores. The rather immobile fraction is either in a less leachable chemical form or it is located in less accessible parts of the graphite. Chlorine is not necessarily homogeneous distributed in the graphite but can occur as hot spots.

3) There is a clear relation between irradiation temperature (position in the reactor) and release. Higher temperatures lead to lower labile fractions of release. Different hypotheses were forwarded to explain this:
    a. the labile fraction is smaller at higher reactor temperatures since this fraction has been released to a higher extent already during reactor operation.
    b. Higher temperatures in the reactor lead to restructuring of the irradiation defects of i-graphite and associated trapping of ^{36}Cl.
    c. One should not forget that 99% of the initial inactive chlorine inventory has been released during reactor operation. Not invoked in the review of Comte et al. (2013), one may also think that a small fraction of this (1% would be sufficient) has become deposited at colder parts and may thus be more easily leachable. However, this is rather unlikely since it would not explain the diffusion dominated rate law for release.
4) One may think that the release of ^{36}Cl during reactor operation has already reduced the labile fraction and hence one might expect a relation between the remaining ^{36}Cl inventories and release properties, but experimental observations contradict this. Also, there is no clear relation between the nature of graphite coke and ^{36}Cl release.

The complicated relation between the impacts of reactor operation conditions (temperature, neutronics, release of about 99% of inactive Cl, potential redeposition at colder parts) on leaching results of ^{36}Cl from irradiated graphite makes it interesting to study the release of ^{36}Cl from different positions of a single sample at constant neutron dose and irradiation temperature in the reactor. This implies as well to account for the heterogeneity of distribution of radionuclide (RN) in irradiated graphite at millimeter scale.

Our first intention was to determine the distribution profile of ^{36}Cl in an irradiated graphite sample with a depth resolution of few hundreds of microns. The basic idea was to cut thin slices from an irradiated graphite sample and to perform leaching experiments in several aqueous media (water and alkaline solution simulating the cement environment chosen for the storage of graphite wastes) in order to collect data on both mobile released and sorbed/incorporated fractions. Indeed, as the sizes of the graphite samples are small, total activities for each RN are very low and their analysis would require very sensitive analytical techniques such as Accelerator Mass Spectrometry (AMS) for ^{36}Cl for example. In the case of beta emitters (^{3}H, ^{14}Cl or ^{36}Cl), the detection limits of liquid scintillation counting would certainly not be sensitive enough (LQ ranges from 0.1 to 0.5 Bq/L).

2 Installation of the experimental setup

The next step was to settle the cutting device in a protective space (glove The first stage of this study was to choose the best fitted cutting device. In order to reach the required precision, various precise cutting devices were tested (microtome, rotary and wire saws) on virgin graphite samples. Each of the apparatus was specifically fitted for working on graphite sample (modified sample holder for example) and cutting conditions had to be optimized. Thin slices of graphite were then cut with each device and checked visually and with a magnifying binocular. As a result, it was noticed that slices cut with microtome were thin enough only when the direction of cutting was parallel to graphite planar layers. If not, samples were folded and coarsely cut. Thickness of slices was irregular ranging from 150 to 300 microns for one sample. Because of all these drawbacks, it was decided to choose a diamond wire saw as the cutting device. Wires of different diameters had been tested. It appeared that a diameter of 150 µm with diamond grains size of 30 µm was a good technical solution combining a low loss of matter and a well thickness regularity (few hundreds of microns). However, since for the tested saw the cutting plan was vertical, the surface of cut samples showed some ripples due to the vertical back and forth movement of the wire. In order to reduce this phenomenon, a diamond wire saw with a horizontal cutting plan (ESCIL Well 3032) had been finally chosen.

box) in order to be able to work with radioactive materials in a safe environment. Figure 1 show the experimental set up in which the diamond wire saw is located into a plexiglass box. Generally, for many applications, a diamond wire operates in water to reduce the heating of the sample and also to avoid the emission of dust during the

cutting process. In our case, this was not possible since in presence of water, sample would have started to be leached. Thus, specific drawing-in devices (black pipes on figure 1) had been installed in order to suck up radioactive dust originated from the cutting. For all these reasons, installation and tests stages lasted more than a year and a half.

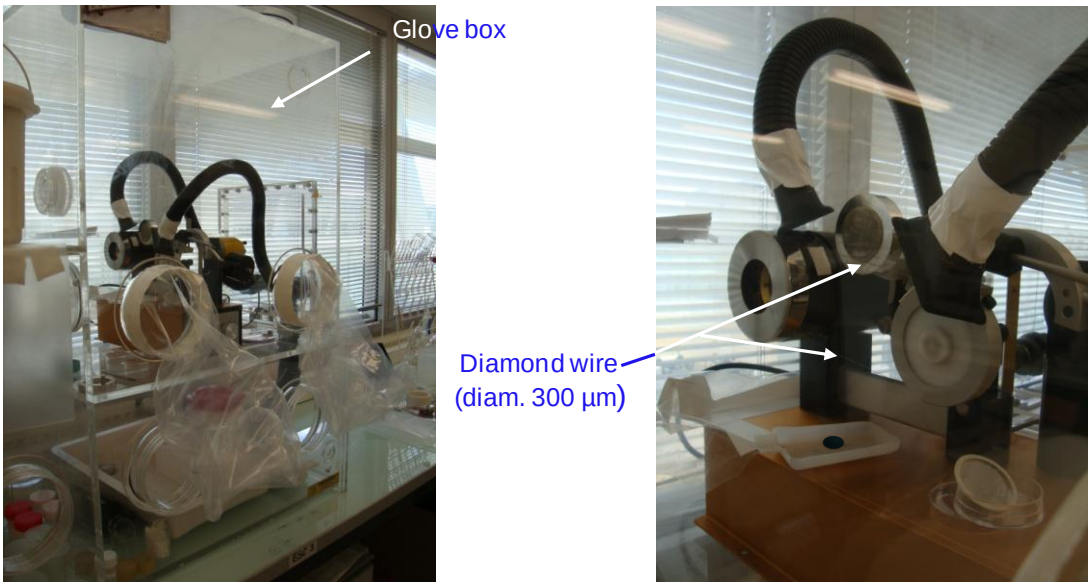

Figure 1 : Diamond wire saw cutting devices installed in its protection glove-box

3 Description of leaching experiments

The selected samples for these experiments are originated from Saint-Laurent A2 EDF reactor (France) and were sent to Subatech by J. Comte (CEA Cadarache/LARC).

Two specific samples were chosen SLA 82 and SLA 120. Their characteristics are reported in Table 1.

Moreover, the stacking of Saint-Laurent A2 reactor is reported on figure 2. Localization of the two samples used is marked with red spots.

Table 1 : Data for the two Saint Laurent A2 reactor irradiated graphite samples

Sample	Mass (g)	Location in the reactor	Height (mm)	Diameter (mm)	Average thickness (mm)
SLA 82	0,4857	F7M5 – c17	1080	18	1.5
SLA 120	1,0126	F4M10 – c19	9260	18	2

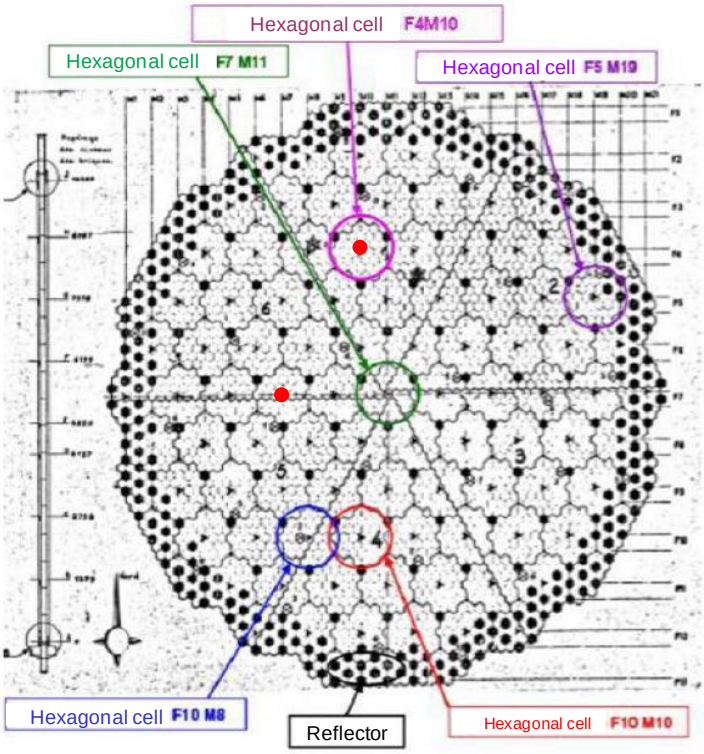

Figure 2 : Localization of the samples (red spots) inside the stacking of Saint-Laurent A2 EDF reactor [adapted from VENDE 2012]

Before starting the leaching experiment, each sample was quickly immersed in an ultrasonic bath during 30 to 45 seconds in order to eliminate the residual dust that would have adhered on the surface after the cutting stage. Then the samples were rinsed with aceton and put into a HDPE flask containing 200 mL of either ultrapure deionized water (MilliQ®; 18.2 Mohm.m) or 0.1 mol/L NaOH solution. Solutions were stirred on a magnetic stirrer A small basket (like a tea bag) was specifically designed to avoid that samples were damaged by the rotation of the magnetic bar during the

experiments. At each sampling time, the whole solution was changed and replaced with a fresh solution (water or NaOH). Then solutions were analyzed by gamma spectrometry (hyperpure Ge detector P type, Amtek) in SG 50 geometry (50 mL) and liquid counting scintillation (Tricarb 3170 Packard).

4 Results

The results are defined in term of the cumulative released fraction F (in percentage). F is defined for each radionuclide by the following equation (1)

$$F(\%) = \frac{\sum_{i=0}^{t} a_i}{A_0} \times 100 \quad (1)$$

where a_i : mass activity released in solution at t in Bq/g
A_0 : initial mass activity in Bq/g

Leaching of the SLA 120 sample was performed during 218 days. The evolution of the cumulative released fraction for gamma emitters (^{60}Co and ^{137}Cs) and tritium are reported in Figure 3 and table 2 summarize the results obtained.

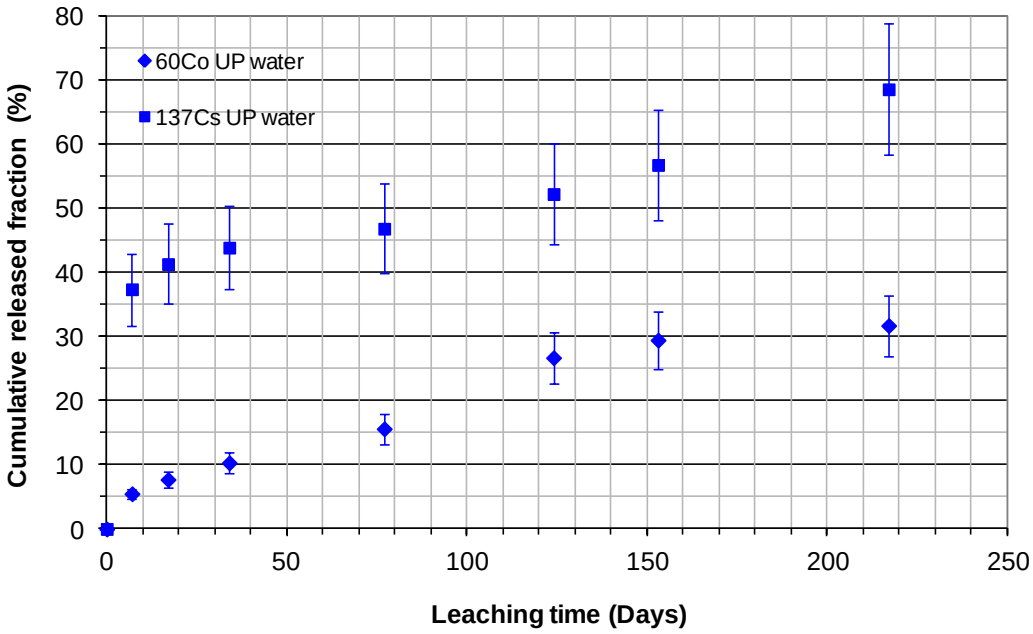

Figure 3 : Evolution of the cumulative released fraction for gamma emitters in pure water (sample SLA 120)

Table 2: Results for ^{60}Co and ^{137}Cs after 218 days of leaching (SLA 120 sample)

Sample	V_L/S (cm)	V/S (cm)	$A_0(^{60}Co)$ kBq/g	F(%) ^{60}Co	$A_0(^{137}Cs)$ kBq/g	F(%) ^{137}Cs
SLA 120	40	0.2	0.4	32	0.02	69

V_L = leachant volume ; V= geometrical volume ; S= surface exposed to leaching

Literature data are very scarce but these results can be compared with the date reported by J. Comte [COM11] in the framework of CARBOWASTE project. Table 3 summarizes the results obtained on SLA2 sleeves, Bugey 1 blocks and powder in water at 20°C after 90 days of leaching.

Table 3 : Leaching data from SLA2 sleeves and Bugey 1 (blocks and powder) samples (leaching time : 90 days) from [COM11]

Reactor	Sample	V_L/S (cm)	V/S (cm)	$A_0(^{60}Co)$ kBq/g	F(%) ^{60}Co	$A_0(^{137}Cs)$ kBq/g	F(%) ^{137}Cs
SLA2 sleeves	01	11.9	0.27	2.8	0.4	21.6	36
	07			2.6	2.3	11.4	69
	24			1.4	1.4	2.7	87
Bugey 1 blocks	N55	1	0.33	9.6	30	-	-
	N58			131	2.3	-	-
	N75			3.5	17.8	-	-
Bugey 1 powder	N87	-	-	39	9	107	33
	N67+N68	-	-	9.1	59	-	-
	N88	-	-	3.6	37	-	-

Results from SLA2 sleeves and Bugey 1 samples show that the release of gamma emitters such as ^{60}Co and ^{137}Cs can vary over the large range from fractions of percent to tens of percent. For every sample, ^{137}Cs is much more released than ^{60}Co. The same trend was obtained with our samples: 69% of release for ^{137}Cs and 30% for ^{60}Co. This could be explain by the origin of these two radionuclides: ^{137}Cs is the fission product and is mainly found on graphite surface due to contamination from fuel assemblies during storage process [COMTE 2011] while ^{60}Co is an activation product and should be hardly released as it is shown in J. Comte's work because of its localization inside the graphite matrix. In our case, the small size, with a higher V_L/S ratio of SLA 120 sample have probably promoted the release of ^{60}Co by exposing more surface to the leachant.

5 Tritium

The evolution of the cumulative released fraction for tritium is reported in Figures 4 and table 4 summarizes the results obtained for this radionuclide.

Table 4 Results for tritium after 218 days of leaching (SLA 120 sample)

Sample	V_L/S (cm)	V/S (cm)	$A_0(^3H)$ kBq/g	F(%) ^3H
SLA 120	40	0.2	93	5.25

V_L = leachant volume ; V= geometrical volume ; S= surface exposed to leaching

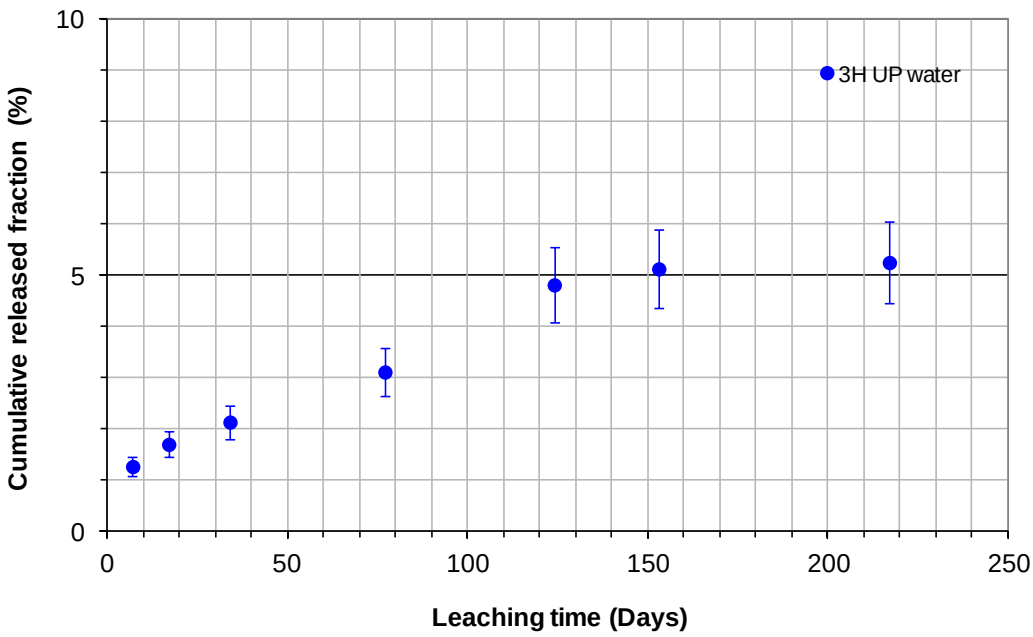

Figure 4 : Evolution of the cumulative released fraction for tritium in pure water (sample SLA 120)

The release of tritium in water increases progressively over the leaching period. The final cumulative released fraction after 218 of leaching is around 5%. Comparing to the literature data (table 5), this value appears to be high.

Table 5 : Leaching data from SLA2 sleeves and Bugey 1 (blocks and powder) samples (leaching time : 90 days) from [COM11]

Reactor	Sample	V_L/S (cm)	V/S (cm)	$A_0(^3H)$ kBq/g	F(%) ^3H
SLA2 sleeves	01	11.9	0.27	221	0.034
	07			580	0.014
	24			289	0.022
Bugey 1 blocks	N55	1	0.33	141	0.59
	N58			25	0.12
	N75			6.3	0.27
Bugey 1 powder	N87	-	-	36	0.07
	N67+N68	-	-	22	< 0.06
	N88	-	-	6.8	< 0.2

Nevertheless, if the cumulative released fraction is plotted *vs* the square root of the time (figure 5), a linear correlation is obtained meaning that tritium could be released through a diffusion process. The calculation of the apparent diffusion coefficient (D_a) from the slope gives 5 10^{-12} m^2/s that is in very good agreement with literature data for other reactor, 6 10^{-12} m^2/s for G2 and 10^{-11} m^2/s for Bugey [COM11].

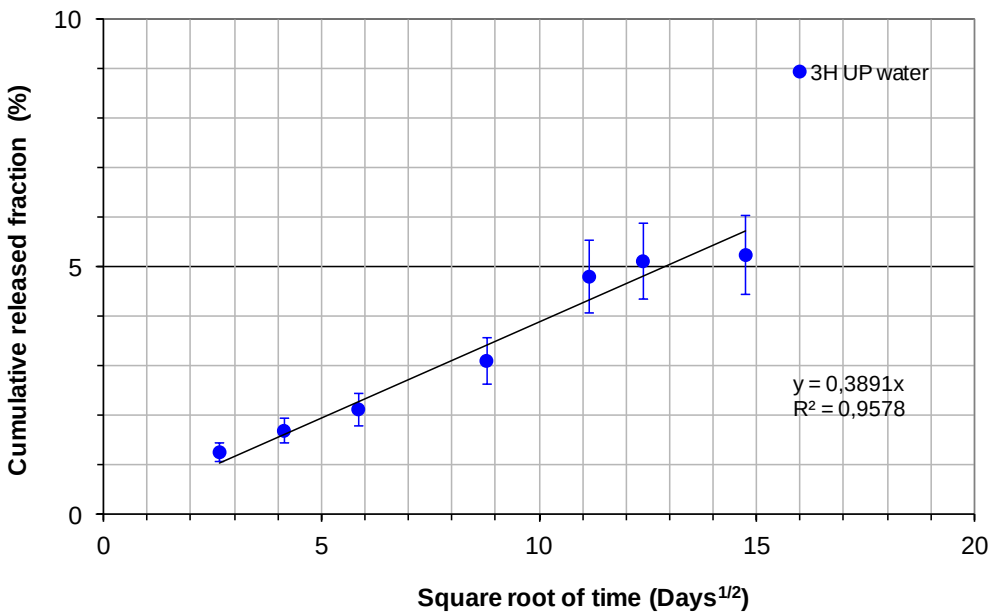

Figure 5 : Cumulative released fraction for tritium in water *vs* square root of time (SLA 120 sample)

6 Alkaline solution (NaOH 0.1 mol/L)

Leaching of the SLA 82 sample was performed during 84 days. The evolution of the cumulative released fraction for gamma emitters (^{60}Co and ^{137}Cs) and tritium are reported in Figure 6 and table 6 summarize the results obtained.

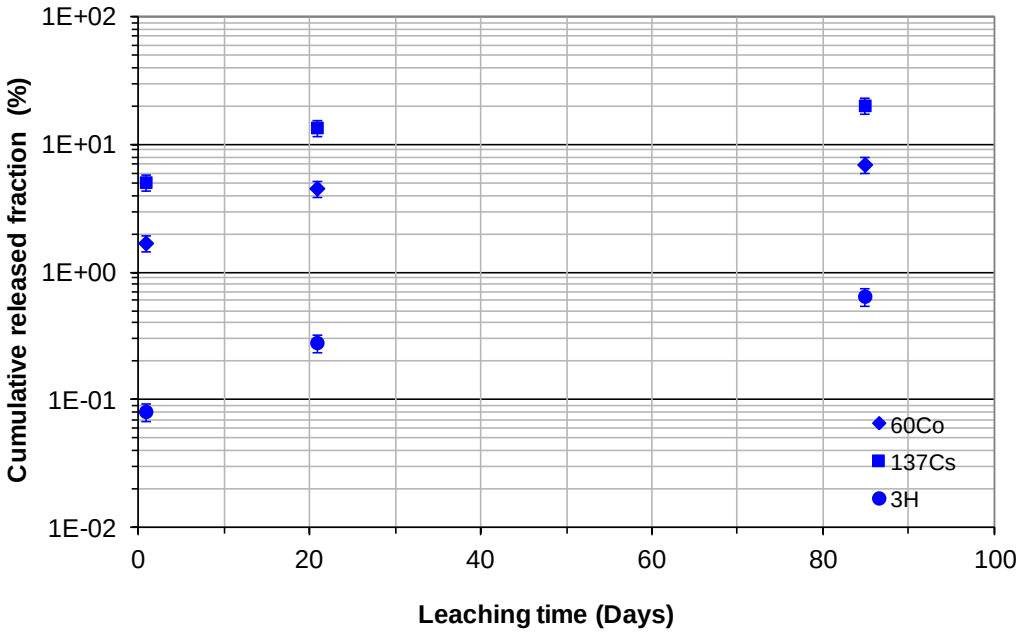

Figure 6 : Evolution of the cumulative released fraction for ^{60}Co, ^{137}Cs and tritium in alkaline (sample SLA 82)

Table 6 Results for gamma emitters and tritium after 85 days of leaching (SLA 82 sample) from [COM11]

Sample	V_L/S (cm)	V/S (cm)	A_0(^{60}Co) kBq/g	F(%) ^{60}Co	A_0(^{137}Cs) kBq/g	F(%) ^{137}Cs	A_0(^{3}H) kBq/g	F(%) ^{3}H
SLA 120	40	0.2	2.0	7.0	29.3	20.3	54	0.65

V_L = leachant volume ; V= geometrical volume ; S= surface exposed to leaching

For the three radionuclides, the results obtained in alkaline solution, are lower than those obtained in pure water. There are very few data in literature for leaching graphite in alkaline solution. J. Comte reported leaching experiments performed on Bugey blocks in lime solution ($Ca(OH)_2$; pH = 12,4) [COMTE 2011] and L. Vendé performed her leaching experiments in NaOH 0.1 mol/L either on SLA2 powder samples originated from the same position as SLA 120 and on G2 CEA reactor powder sample [VENDE 2012]. Those data are reported in table 7.

For the three radionuclides, values of F(%) are very low and lower than those obtained in our study. On the contrary, L. Vendé's data on powder are very close.

These differences are surely not due to the difference of chemistry between lime water and soda solution. RN are present in solution at extremely low concentrations (< 10^{-10} mol/L), so their behaviours are not controlled by solubility/precipitation processes and the chemical composition of the leachant is not determining. These differences may most probably be due to the V_L/S ratio that is favorable to SLA 82 sample and lead it to behave like a powder sample during leaching experiments in increasing the F(%) values.

Table 7 : Leaching data from Bugey 1 blocks and SLA2 powder samples in alkaline media (leaching time : 90 days)

Reactor	Sample	Leachant	V_L/S (cm)	V/S (cm)	$A_0(^{60}Co)$ kBq/g	F(%) ^{60}Co	$A_0(^{137}Cs)$ kBq/g	F(%) ^{137}Cs	$A_0(^{3}H)$ kBq/g	F(%) ^{3}H
Bugey 1 Blocks [COM11]	N57	Lime Water pH= 12.4	1	0.33	79.2	0.15	143	0.002	21	0.06
	N58				1.9	0.045	-	-	270	0.004
	N98				61	0.004	-	-	80	0.184
SLA2 [VEN12]	Powder F4M10	NaOH 0.1 mol/L	-	-	10.8	3.6	0.025	25	116	0.7

7 Conclusion

Leaching experiments on very small size irradiated graphite samples were performed in either ultrapure water and alkaline solution simulating the pore water of cementitious material which could be a potential host environment for the irradiated graphite wastes. In both media, the cumulative released fraction values obtained for three radionuclides (^{60}Co, ^{137}Cs and ^{3}H) are higher (some percents) compare to available literature data (fraction of percent) obtained on large blocks of i-graphite. Our results appear to be more comparable to those obtained on powder sample probably because of the high V_L/S ratio of our sample.

For ^{36}Cl, our intention to determine a profile distribution of this radionuclide inside small size samples has failed because of experimental difficulties which prevent us to realize specific samples ready for ^{36}Cl AMS analysis.

8 References

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