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Report on results of hydrodynamic properties of UNGG graphite

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Document title
Report on results of hydrodynamic properties of UNGG graphite

Executive summary

The focus of this deliverable is on the hydrodynamic properties of unirradiated nuclear reactor graphite. Open and closed porosity were determined as well as permeability and dispersivity. The experimental results show that water accessible porosity of unirradiated G2 reactor graphite is very high. Due to the high average pore size of 3,75 µm and a continuous connected pore network the resistance of the graphite against water flow is very small. This means for geological disposal that even very small hydraulic gradients in disposal cells will lead to advective flow across the graphite blocs, leading to washing out the dissolved radionuclides in graphite pores. Only in absence of hydrological gradients, molecular diffusion in the graphite pore space will govern the release rates of soluble radionuclides.

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

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 the rates by which water can contact the disposed graphite. Since graphite is a porous medium the question is also 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 radionuclides. One needs to understand the mechanism of this water access: transport of water can either be controlled by molecular diffusion or by advection (transport in hydraulic gradients). To assess these transport processes, both porosity and hydrodynamic parameters were assessed in an experimental program and by modeling.

2 Virgin graphite sample

Subatech received from CEA Cadarache, a non-irradiated graphite brick from G2 reactor. This brick was a lamella of about 3 cm in thickness originated more precisely from the G2 moderator graphite [COM2010]. Figure 1 shows the localization of the lamella assigned to Subatech with regard to the distribution of virgin graphite samples to the other laboratories implied in Carbowaste

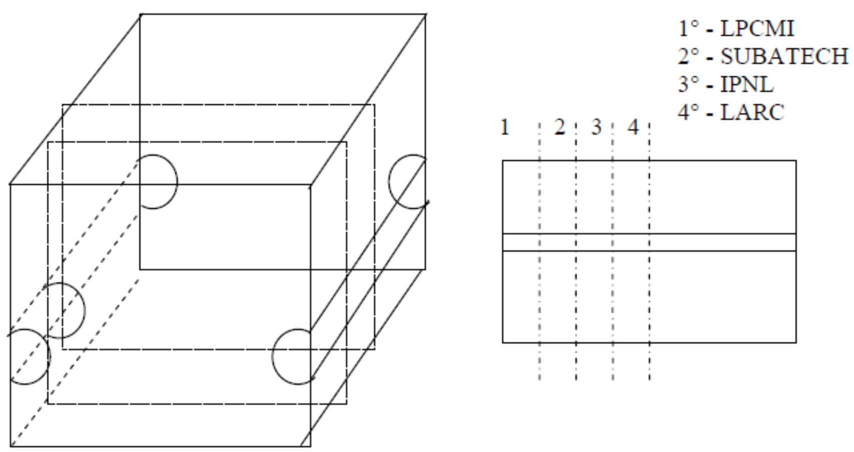

Figure 1: Localization of the G2 moderator graphite sample

3 Porosity determination

In order to assess the hydrodynamic properties of nuclear graphite G2, the open and closed porosity of non irradiated graphite has been determined comparing mercury porosimetry (MIP) and helium pycnometry.

Mercury Intrusion Porosimetry (MIP)

Figure 2 shows the apparent pore distribution obtained by MIP. Tests were performed in triplicate on 5g of graphite powder.

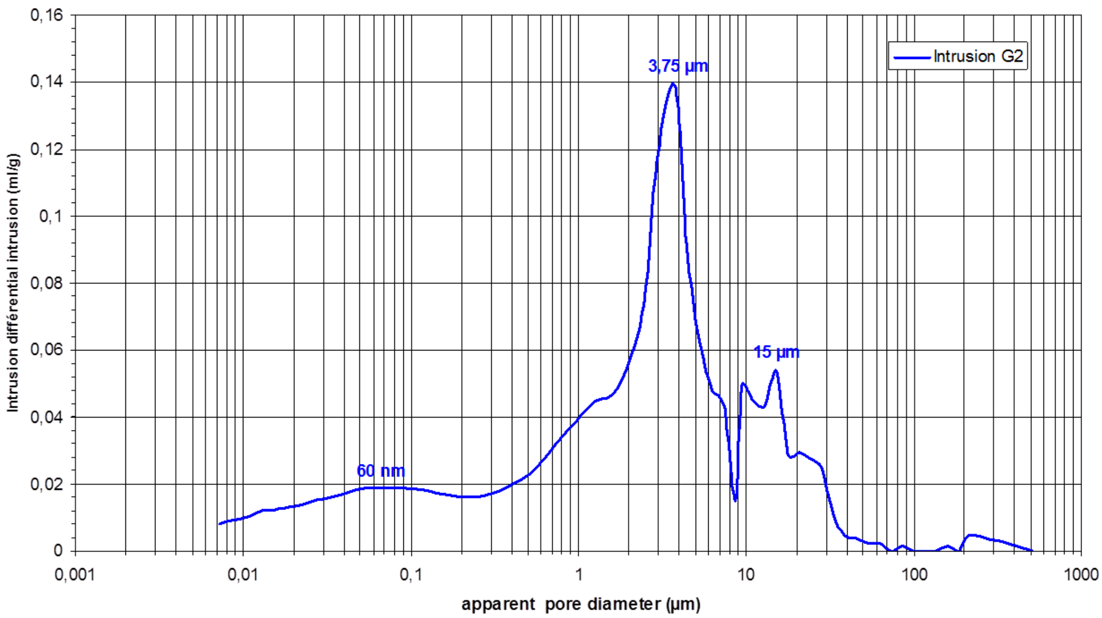

Figure 2: Apparent pore diameter distribution of G2 reactor non irradiated graphite (in mL/g)

The results show that a large part of the porosity lies in the range between 1 µm to 30 µm with an average pore size of about 3.75 µm. It should be noted that results for pore diameter smaller than 0.1 µm are questionable because of the potential destruction of the porous structure by intrusion of mercury at pressure (around 300-400 MPa) much higher than the mechanical resistance of the graphite network. This means that finest could be crushed and the pore network modified. So the small peak at 60 nm is probably not representative of a real graphite network.

Helium Pycnometry

He pycnometry gave a powder density of 2,197 g/cm^3. Table 1 summarizes the results obtained from the two techniques

Table 1 : Summary of porosity data for G2 non irradiated graphite samples

	$\rho_{skeleton}$ (kg/m^2)	$\rho_{apparent}$ (kg/m^2)	Open porosity (%)	Close porosity (%)
MIP	2.21 +/- 0.02	1.73 +/- 0.08	21.7 +/- 0.8	2.9 +/- 0.4
Pycnometry	2.20 +/- 0.08	1.71 +/- 0.05	22.2 +/- 1.2	3.6 +/- 1.5
Average	2.20 +/- 0.04	1.72 +/- 0.06	21.9 +/- 0.4	3.3 +/- 0.9

These results are consistent with the results obtained by Comte and coworkers on a much larger quantity of samples [COM2010]. Virgin graphite is macroporous material with an open porosity of about 22 %. So water during leaching experiment can easily enter the porous network despite the hydrophobic character of the non irradiated graphite surface.

4 Hydrodynamic parameters

In order to perform percolation tests, virgin graphite samples were precisely machined as cylinder core (diameter = 32,0 +/- 0.1 mm ; length = 25,0 +/- 0,1 mm). These core were then embedded in a epoxy resin inside a stainless steel reactor (figure 2). This percolation reactor allows pushing high purity water (MilliQ® ; 18.2 MΩ.cm^{-1}) across the sample by means of an HPLC pump. Due to the high permeability of the sample a counter pressure (PEEK® capillary tube + a HPLC column) has to be integrated in the system. An injection loop allowed to inject pulses of tritiated water at a given time step. Flow rates are measured at the outlet by weighting the mass of water, as the function of the inlet pressure. The experimental set-up is shown figure 3.

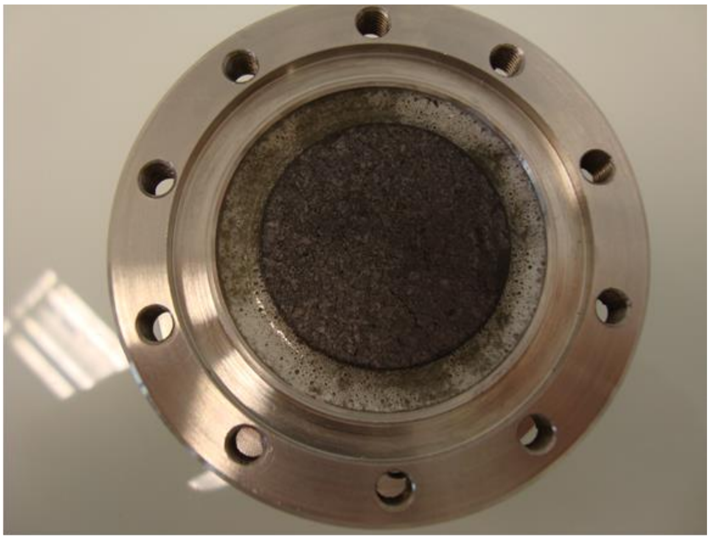

Figure 2 : Non irradiated G2 graphite sample embedded in the percolation reactor (D = 42 mm ; l = 25 mm)

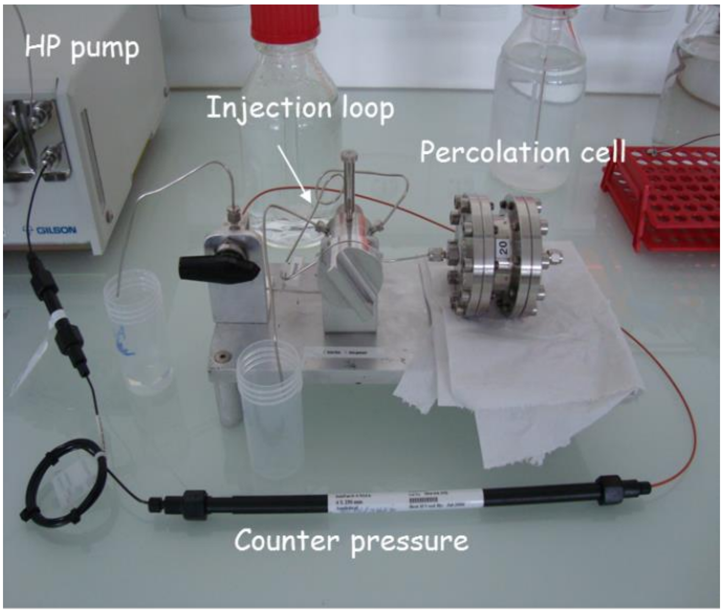

Figure 3 : Percolation experimental set-up

For each sample, the Darcy law expresses by equation below, has been tested by varying pressure either by stepwise increasing or decreasing pressure.

$$Q = \frac{A \times \cdot \Delta P \times \cdot k}{L \cdot \times \mu}$$

where

Q: Flow rate ($m^3.s^{-1}$)
A: Cross section area (m^2)
ΔP: Hydrostatic pressure gradient (Pa)
k: Graphite intrinsic permeability (m^2)
L: Sample length (m)
m: Water dynamic viscosity (Pa.s)

The results are shown figure 4.

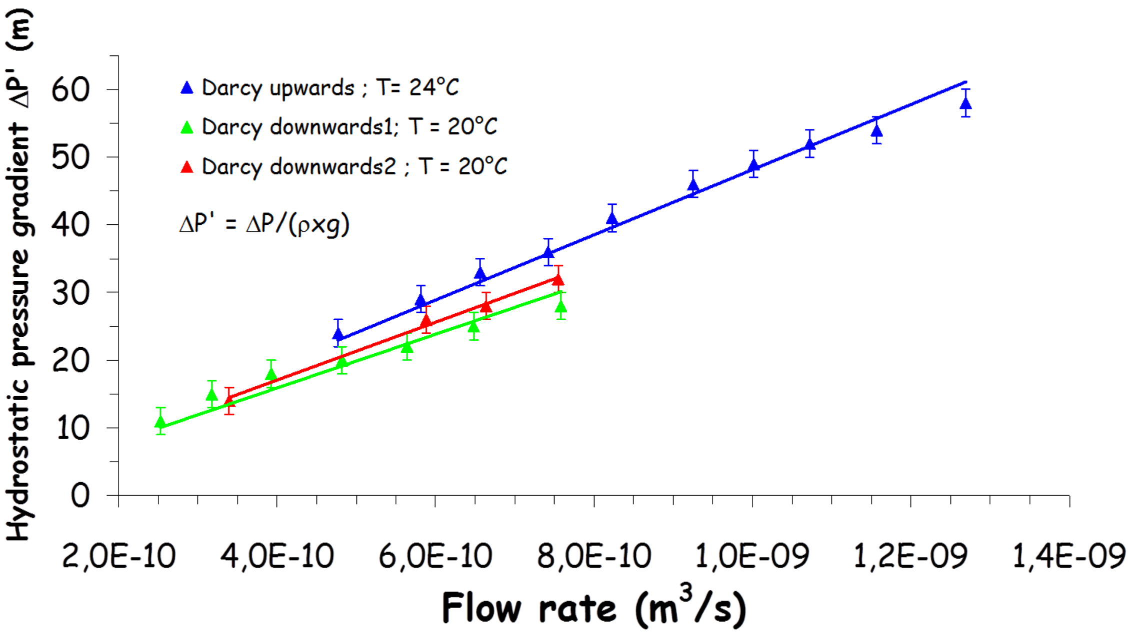

Figure 4 : Validation of Darcy law for G2 graphite sample

Straight lines are observed both with increasing and decreasing pressure, thus validating the Darcy's law with a permeability coefficient K of $1 \cdot 10^{-9}$ m/s. The permeability coefficient can be related to the intrinsic permeability k=K/μ where μ is the viscosity of pure water. An intrinsic permeability of $k=(8\pm2)\times10^{-17}$ m^2 was obtained. In comparison, irradiated graphite permeability should even be higher due to irradiation damages. This high permeability is consistent with the high open porosity and the large average pore diameter. The permeability of the graphite is so high that even small hydraulic gradients will lead to short water residence times in the sample and it is likely that water transport is advection and not diffusion controlled. It is interesting to note an effect of hysteresis: for a given pressure, flow rates are higher when the pressure is increases than when it is decreased. Obviously, the structure of the flow path in the graphite sample has been modified by increasing the pressure.

Experiments for migration of tritiated water (HTO) in the graphite core have been performed for three different water flow rates. HTO was added by the pulse injection technique: 50 Bq in case of a water flow rate of 25 µL/min and 500 Bq in case of a water flow rate of either 9 or 15 µL/min. Typical results are given in the following figure 5.

The experimental results were modeled using the geochemical code PHREEQC for one dimensional transport simulation. This code solves the diffusion advection equation (equation 2) in x-direction (v is water velocity and D_{disp} is the dispersion coefficient).

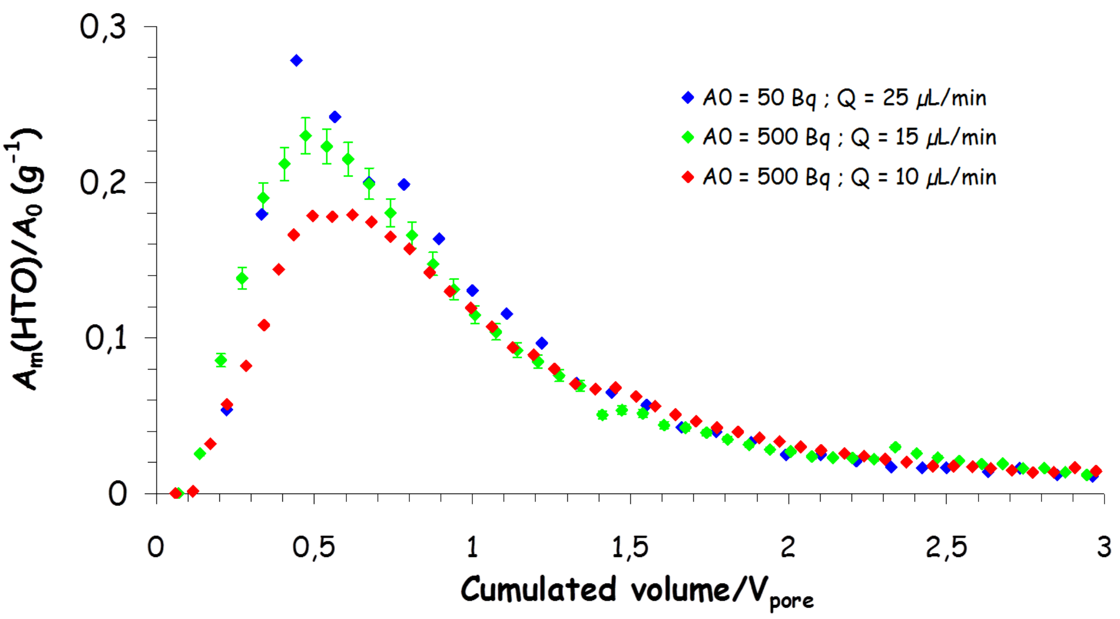

Figure 5 : Breakthrough curves of HTO as a function of flowrate

$$\frac{\partial C}{\partial t} = -v\frac{\partial C}{\partial x} + D_{disp}\frac{\partial^2 C}{\partial x^2} \quad \text{(Equation 2)}$$

The dispersion coefficient is defined as $D_{disp} = D_e + \alpha_n$ where De is the effective diffusion coefficient and α_n is the dispersivity of the porous medium. The simulation of the experimental set-up is shown in the following figure 6

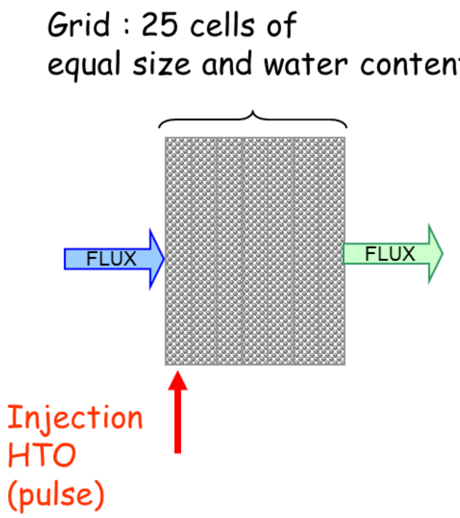

Figure 6 : Simulation of the experimental set-up with PHREEQC geochemical code

Modeling results (solid lines in figure 7) have provided both dispersivity and dispersion coefficients in non-irradiated graphite as well as cinematic porosity. Cinematic porosity varied from w= 18.2 vol.% at a water flow rate of 25µL/min to w = 19.7 vol.% at 15 µL/min and w = 23.4 vol.% at the lowest flow rate of 9 µL/min. The dispersivity α_n was 8 mm. Typical value for D_{disp} is 1;4 10^{-8} m^2s^{-1} which is much higher than D_e. This expresses that the flow is dominated by the advection as expected.

It is interesting to note that cinematic porosity increases with decreasing water flow rate. This was explained by the fact that at high water flow rates not all water filled pores contribute in an equal manner to water transport. At the lowest flow rates, cinematic porosity comes close to total open porosity, indicating that the total open pore space contributes equally to water transport.

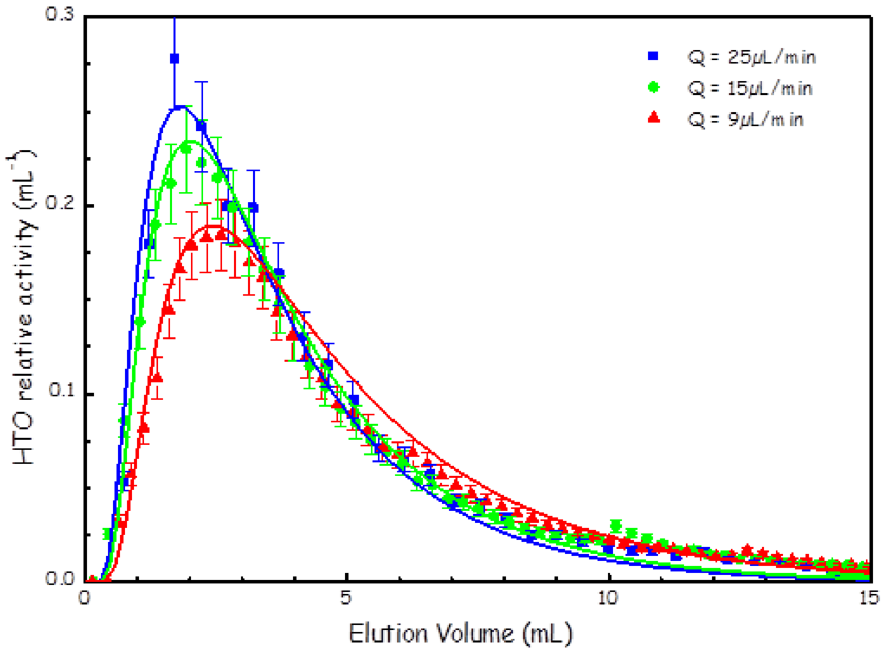

Figure 7 : Modelling of HTO breakthrough curves

5 Conclusions

The experimental results show that water accessible porosity of unirradiated G2 reactor graphite is very high. Due to the high average pore size of 3,75 µm and a continuous connected pore network the resistance of the graphite against water flow is very small. This means for geological disposal that even very small hydraulic gradients in disposal cells will lead to advective flow across the graphite blocs, leading to washing out the dissolved radionuclides in graphite pores. Only in absence of hydrological gradients, molecular diffusion in the graphite pore space will govern the release rates of soluble radionuclides.

6 References

[COM2010] Comte, J., Gosmain, L., Guy, C., Characterisation of G2 pile graphite before and after irradiation, Carbowaste Technical Report WP3 Task 3.2, October 2010