EUROPEAN COMMISSION

Community Research

SEVENTH FRAMEWORK PROGRAMME

CARBOWASTE

Treatment and Disposal of Irradiated Graphite and Other Carbonaceous Waste

Grant Agreement Number: FP7-211333

- Technical Report (WP 6 Task 1) –

- BEHAVIOUR OF ^{36}CL IN IRRADIATED GRAPHITE SAMPLES FROM UNGG G2 REACTOR – FIRST RESULTS

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Date of issue of this report : November 2010

Start date of project : **01/04/2008** Duration : **48 Months**

Project co-funded by the European Commission under the Seventh Framework Programme (2007 to 2011) of the European Atomic Energy Community (EURATOM) for nuclear research and training activities		
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Work package: 6 **Task: :** 6.1	**CARBOWASTE document no:** CARBOWASTE-1007-D-WP6.Task.1	**Document type: T** D=Deliverable / M=Minutes / P=Progress report / T=Technical Report
Issued by: CEA **Internal no.:** Technical report CEA G2 leaching WP6		**Document status:** Final

Document title

Behaviour of ^{36}Cl in irradiated graphite samples from UNGG G2 reactor – First results

Executive summary

This report gives the first results of the behaviour of ^{36}Cl in irradiated graphite samples from the UNGG (*gas-cooled graphite-moderated reactor fuelled with natural uranium*) G2 reactor:

- general characteristics of the G2 reactor and graphite properties,
- characterisation of the porosity and microstructure of non-irradiated and irradiated graphite samples,
- measurement of water impregnation kinetics in graphites and analysis of the effect of irradiation,
- progress of experimental leaching tests of ^{36}Cl and chlorine in irradiated graphites.

The results show that the leaching rate of ^{36}Cl depends on the position of the sample studied in the reactor and particularly the temperature of the graphite during reactor operation. The release kinetics of the labile fraction of ^{36}Cl in solution can be described by a diffusion process through the graphite porosity. Two chemical forms of chlorine can be found in solution: chlorides for the most part and chlorites.

Revisions

Rev.	Date	Short description	Author	Internal Review	Task Leader	WP Leader
		Issue	Name, Organisation	Name, Organisation Signature	Name, Organisation Signature	Name, Organisation Signature
00	7/12/2010	First issue	J. COMTE CEA	C. GUY CEA		B. Grambow SUBATECH

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INTRODUCTION

UNGG reactors (gas-cooled graphite-moderated reactors fuelled with natural uranium) represented the first French nuclear power technology in the 1950s thanks to the use of non-enriched fuel. Graphite was largely used in these reactors, including “stacks” used as neutron moderators, “reflectors” which provided biological shielding, and “sleeves” which housed the clad fuel while promoting the flow of gas.

All the UNGG reactors have been shut down and the fuel elements unloaded. Today, the stacks and reflectors are still in the reactors; the sleeves are stored by the various operators (EDF, CEA and AREVA NC). The “graphite” waste thus includes the various elements derived from decommissioning of the UNGG reactors, employed by the CEA and EDF from the 1950s to the 1990s.

French law No. 2006-739 dated 28 June 2006 concerning the programme on the sustainable management of radioactive materials and waste accelerated researches into the management of graphite waste. This act, *inter alia*, sets the objective for developing disposal solutions for the graphite waste.

Among the radionuclides (RN) contained in UNGG graphite, a distinction is made between activation products and fission products. The relevant isotopes for disposal are chlorine-36 and carbon-14 because of their long radioactive half-life and high mobility in the natural environment. Consequently, and according to the impact studies, graphite waste cannot be stored in large quantities in surface disposal facilities, and the possibility of a dedicated disposal facility is currently the subject of studies conducted jointly by ANDRA, EDF and the CEA.

A research program has been proposed to investigate and quantify the release mechanisms of these radionuclides in water. The release of the radionuclides in solution depends on various physicochemical processes :

- Intake or impregnation of water through the porosity of the material,
- Solubilisation of radionuclides,
- Transport of radionuclides in solution through the graphite pores towards the solution.

All of these parameters have been investigated, and this note provides a progress report on the studies focusing on the behaviour of ^{36}Cl in G2 reactor graphites. It comprises:

- A state-of-the-art report with a general overview of the properties of graphite (manufacture, structure, etc.) and its use in a reactor, as well as its behaviour in an aqueous environment[1],

- The preliminary results of the porosity and microstructural characterisations (porosity, pore size distribution, Raman spectrometry, XRD). These studies were carried out jointly with the ENS (*Ecole Normale Supérieure*, team headed by Jean Noël Rouzaud), both on

non-irradiated and irradiated materials, in order to quantify the structural modifications during irradiation[2],

- Water impregnation studies in the porous environment of the graphite, which constitutes one of the essential parameters that may control the physicochemical processes leading to the release of radionuclides in solution. For this purpose, the impregnation of samples from the G2 reactor was investigated on non-irradiated and irradiated graphites[3],

- Release kinetics and fractions of labile activity in ^{36}Cl were measured in a series of experiments, making it possible to propose a preliminary release model.

In addition to this summary, we have to mention the first measurements taken by SIMS[4] with the aim of investigating the chlorine distribution and particularly that of ^{36}Cl in irradiated graphites, measurements by absorption spectrometry (EXAFS) on the SOLEIL synchrotron to determine the speciation of stable chlorine in samples of non-irradiated graphite[5] and the studies conducted by IPNL (*Institut de Physique Nucléaire de Lyon*) to understand the behaviour of chlorine during the operation of UNGG reactors under the effect of temperature and irradiation[6].

STATE-OF-THE-ART REPORT

1. GENERAL INFORMATION ON THE UNGG REACTOR TECHNOLOGY AND NUCLEAR-GRADE GRAPHITES

1.1. The UNGG reactor

The French Natural Uranium-Graphite-Gas technology was developed jointly by the CEA and EDF after the Second World War, until it was abandoned in 1969 in favour of pressurised water reactors (PWR). In the 1950s and 1960s, nine nuclear reactors (3 CEA, 6 EDF) were built [7, 8].

Reactor	Divergence	Shutdown	Thermal power (MW)	Layout	Fuel stack mass (tonnes)	Pressure CO_2 (bar)	T CO_2 (°C) inlet-outlet	GAS (FLOW DIRECTION)
G1	1956	1968	40	Horizontal	1000	Air, P_{atm}	30-200	→
G2	1958	1980	260		1500	15	140-380	
G3	1959	1984	260		1500	15	/	
CHA1	1962	1973	300	Vertical	1400	25	145-345	↑
CHA2	1964	1985	850		1730	26,5	200-370	
CHA3	1966	1990	1560		2000	26,5	/	
SLA1	1969	1990	1650		2200	26,5	225-400	↓
SLA2	1971	1992	1700		2200	28,5	235-410	
Bugey 1	1972	1994	1920		2550	40	220-400	

TABLE 1: MAIN CHARACTERISTICS OF UNGG REACTORS (CHA: CHINON, SLA: ST LAURENT)

At the outset, after the air-cooled G1 reactor prototype, construction began on the G2 and G3 reactors in Marcoule. The French electricity generating programme was composed of six EDF reactors (Table 1) whose developments helped to increase the specific power. A reactor exists in Spain (Vandellos) of the same design as St Laurent (SLA), commissioned in 1972 and shut down in 1989 after a fire on a generator.

1.2. Structure and properties of graphite

Graphite is a particular crystalline form of carbon[1]. It exists naturally and can also be formed from petroleum coke and coal tar pitch. The monocrystal structure (Figure 1) is formed of non-compact hexagonal sheets, called graphenes, separated by about 0.336 nm all along the direction of their normal line. In each sheet, the carbon atoms are strongly bound by covalent bonds of the sp^2 type in a regular paving of hexagons, while the bonds between the flakes are weak, of the Van der Waals type. This explains the cleaving and poor hardness of the material.

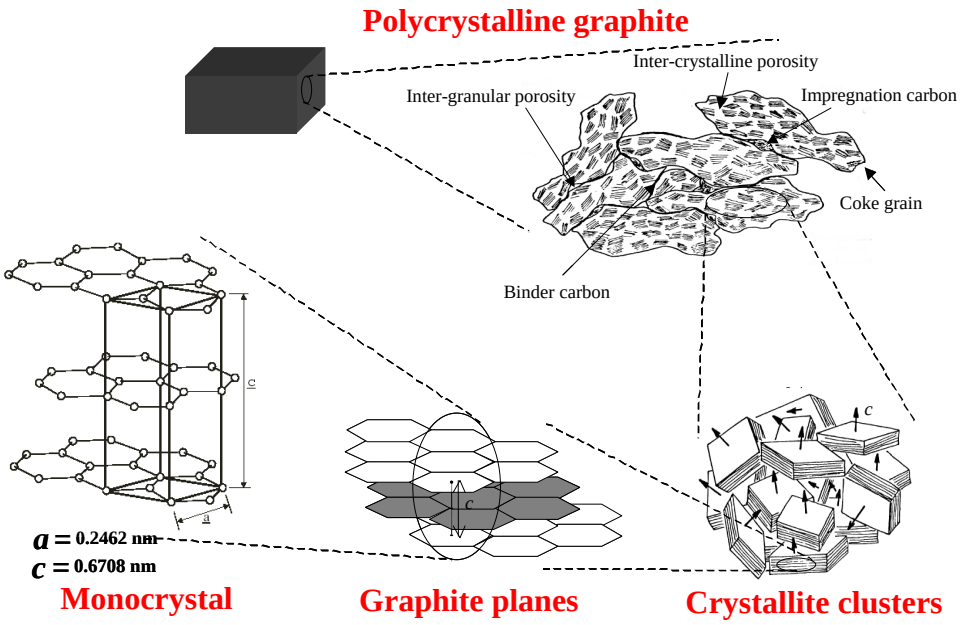


FIGURE 1: STRUCTURE OF GRAPHITE

Polycrystalline graphite is used as structural material in gas-cooled reactors. It is manufactured (Figure 2) from petroleum coke or coal tar pitch and a binder. The calcinated coke is ground, sifted, and the grains obtained are then mixed with the binder in appropriate proportions to obtain a good density and allow the release of the volatile materials from the binder. The coke blend is generally mixed at 165°C with coal tar pitch, shaped by extrusion, or by compression, either unidirectional or isostatic[1], and then heated between 800°C and 1200°C to coke the binder[8]. This firing, which lasts about 1 month, induces a mass loss and gas release.

The product can then undergo one or more impregnations, generally with petroleum pitch, to increase its density and its mechanical properties. It is finally graphited between 2500°C and 3000°C for about 1 week to obtain the hexagonal crystalline structure.

This graphitisation can also be done in the presence of chemical stripping agents (NaF, MgF_2, etc.), making it possible to obtain a nuclear-grade graphite with low impurity content.

[1] Isostatic compression results from isotropic pressure, i.e. which has the same value in all directions.

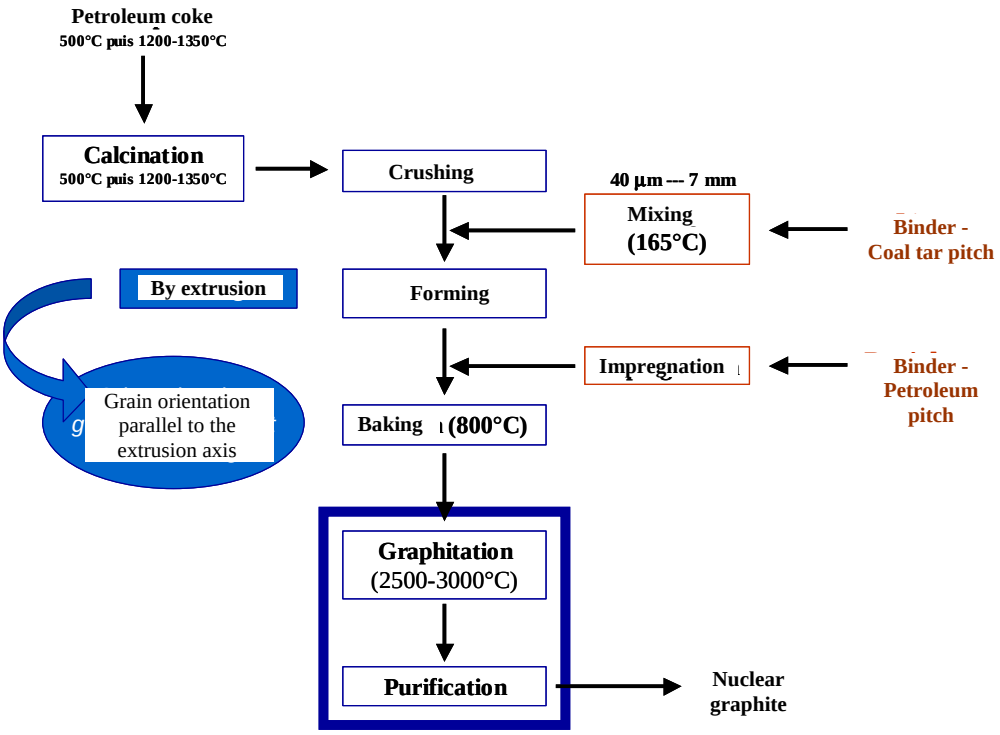


FIGURE 2: FABRICATION OF GRAPHITE

Over time, several types of "coke" have been used to manufacture nuclear graphite. As a furnace can contain about 20 tonnes of graphite, a hundred of batches is needed to manufacture the quantity of graphite required for the construction of a reactor. The bibliographic summary of Brie (C53.02) [9] deals with the principles of graphite manufacture and also the main properties of graphite (fuel stacks and sleeves).

All the graphite elements of the fuel stacks and reflectors were manufactured by *Compagnie Péchiney-Société des Electrodes et Réfractaires Savoie* (SERS). The sleeves surrounding the fuel elements were manufactured by Péchiney-SERS and Savoie-Acheson (Union Carbide France UCF).

The use of graphite in a UNGG reactor is justified by the low neutron capture section of carbon (3.7 to 4.2 mbarns depending on the ash content), its refractory nature and its corrosion resistance. Moreover, the manufacture of graphite was well known, readily available and relatively cheap. However, since the coolant in the reactors is carbon dioxide, the operating temperatures must be limited and are imposed in the range of 400 to 450°C.

Good nuclear-grade graphite must contain very small amounts of capturing impurities (such as boron, lithium and rare earths). In nuclear graphites, the chlorine content varies between 5 and about 20 ppm. Boron is one of the elements with the strongest influence on the capture cross section of industrial graphite, because 1 ppm of boron increases the capture section of graphite by 0.838 mbarn. The ash content roughly represents the impurities contained in the graphite and passed into the oxide state. Nuclear industrial graphites have ash contents between 50 and 500 ppm.

Irradiation causes atomic shifts within the structure and radiolytic corrosion increases the porosity. This is why good mechanical properties, particularly with high density, are necessary in order to minimise these effects.

1.3. Behaviour of graphite in the reactor

During nuclear reactor operation, the effects of neutrons, temperature and coolant induces damage in graphite structure.

Coolant effects

The exposure of carbon dioxide in UNGG reactors to high ionising radiation tends to divide the CO_2 molecule into a CO molecule and a O^{2-} ion. The interaction between oxygen ion and graphite leads to the formation of CO_2 gas. This mechanism is associated with radiolytic corrosion in the graphite.

The main parameters affecting radiolytic corrosion are:

- Temperature of the graphite,
- Radiation flux adsorbed,
- Pore texture of the graphites,
- Content of corrosion inhibitor in the coolant gas (CO, methane).

The main consequence is wear which may be substantial, in the range of a few % to about 10 per cent (weight loss), with especially pronounced corrosion for medium to high pore sizes[10].

Radiation effects

The graphites used as moderator are aimed to slow down the neutrons produced by fission by absorbing part of their energy. At the start, the fast neutrons (~ 2 MeV), having a low probability of interaction with the carbon nucleus, are slowed down and give up their energy by ionising the molecules of graphene. Once they are sufficiently slow (thermal neutrons), they can again fission a uranium nucleus and also cause a shift of the carbon atoms from their equilibrium position, thereby creating defects (interstitial and vacancies) which are materialised by an increase in the parameter c and a slight contraction of the parameter a of the graphite crystal lattice (Figure 1). After a certain period of irradiation, this mechanism also causes variations:

- in thermal conductivity, which decreases due to the defects created,
- in the mechanical properties (higher mechanical strength),
- in the volumetric contractions.

If, during irradiation, the temperature is not sufficient to make the atoms mobile and to correct the defects (200°C), the graphite will continue to store internal energy. This mechanism is also called Wigner energy [11, 12, 13].

In conclusion, the porosity in graphite depends on the manufacturing process (initial porosity) and is modified during its use in UNGG reactors. Under the combined effect of radiolytic corrosion and irradiation, this property is modified both in the total fraction and in the distribution between open and closed porosity and pore size.

1.4. Source of radionuclides in graphites

Among the radionuclides contained in the graphite after operation in the reactor, a distinction is made between activation products and fission products:

- fission products are produced either from the uranium present in the initial graphite, or by contamination following a rupture of the cladding,
- activation products result from neutronic activation of impurities in the graphite, the coolant gas or the air introduced during reactor shutdown periods of the reactor, etc.

The main ways of formation of the activation products ^{3}H, ^{14}C, ^{36}Cl of interest in the context of this work are the following:

^{3}H ($T_{1/2}$ = 12.34 years)	^{6}Li (n, α) ^{3}H σ = 942 barns
^{14}C ($T_{1/2}$ = 5730 years)	^{13}C (n, γ) ^{14}C σ = 0.0009 barns
	and ^{14}N (n, p) ^{14}C σ = 1.8 barns
^{36}Cl ($T_{1/2}$ = 3.10^{5} years)	^{35}Cl (n, γ) ^{36}Cl σ = 43.7 barns

For ^{36}Cl, knowledge of the chlorine impurity content and its chemical form is necessary to understand its behaviour during and after reactor operation. The documents [9,14] provide a summary of the influence of the chemical purity on the nuclear properties of graphite and lists the analytical methods for graphite used during production control.

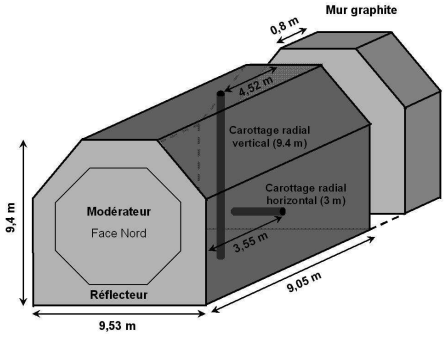
2. G2 REACTOR AND THE PHYSICOCHEMICAL PROPERTIES OF GRAPHITE

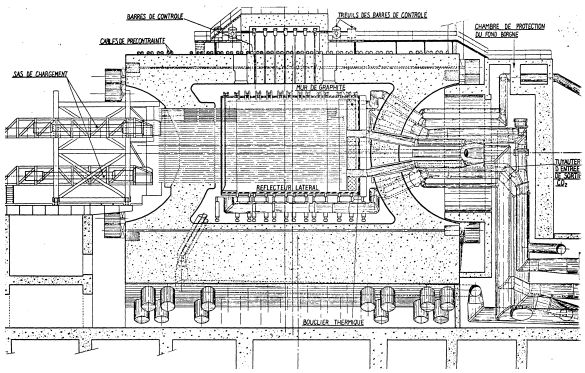
G2 reactor built on the Marcoule site (Gard), its first divergence was on 21 July 1958 and it was shut down on 1 February 1980. Its rated thermal power was 250-260 MW. Cooling was provided via pressurised CO_2.

FIGURE 3: VIEW OF G2, G3 REACTORS

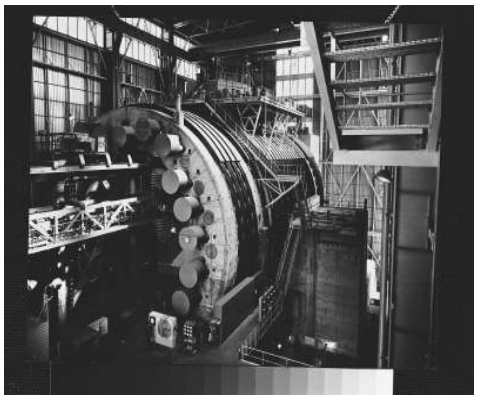
Graphite	G2 moderator	G2 Reflector
Coke	*Special A*	*Lockport L*
Section capture (mbarn)	*3.95*	*4.02*
Density (g/cm^3)	*1.71*	*1.68*
CTE (// dir.) (25-525°C) - (10^{-6} K^{-1})	*1.25*	*2.68*
$\alpha(\perp)$ / $\alpha(//)$	*2.3*	*1.3*
Compression (//) (MPa)	*27*	*33.9*

TABLE 2: PROPERTIES OF G2 GRAPHITE



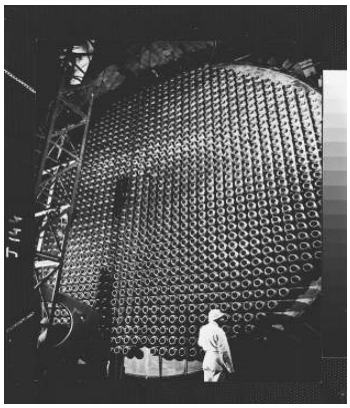


Schematic diagram of G2 reactor



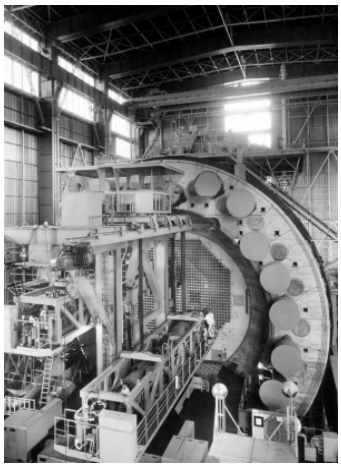
Title: G2: View of reactor block

Picture date: 01/04/1959



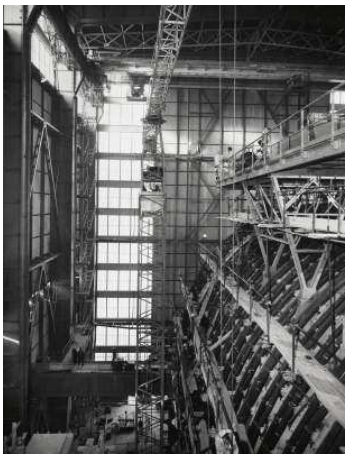
Title: G2 vessel: Internal view of loading face
Picture date: 01/12/1957

Title: G2 vessel: The 4 heat exchangers on the back of G2
Picture date: 01/12/1957



Title: G2 vessel: View of loading face with loading machine

Unit: CEA Site: MAR-MARCOULE
Author: JAHAN P. /Written by: LAMARE F



Title: G2 vessel: With west side hoops

Picture date: 01/12/1957

Title: G2 vessel: Metal frame of vessel block and CO_2 duct; at ceiling, passage of control rods
Picture date: 01/12/1957

FIGURE 4: VIEW OF G2 REACTOR

The graphite stack of G2 (Table 2), based mainly on “special” Grade A coke and Lockport L coke, consists of 14,092 parallelepiped shaped bricks with a square section of 200 mm sides and a maximum length of 1,500 mm. These bricks are laid out horizontally to form a horizontal prism 9.05 m long, 9.40 m high and 9.53 m wide perforated with 1200 channels[15].

The reactor consists of three types of graphite distributed in four distinct zones (Figure 5):

- Zone A: The active cylinder of G2 consists of Special A coke (similar to English Grade A coke) impregnated once and purified, having a specific gravity generally stated as 1.71[16].
- Zone B: Internal reflector: graphite based on special “A” coke (similar to English Grade A graphite) that had undergone both impregnation and purification.
- Zone C: External reflector: graphite based on Lockport L coke that had undergone both impregnation and purification.
- Zone D: The 80 cm thick graphite wall plays the role of a reflector on the back of the graphite block (side opposite the loading face) to avoid the exposure of the back end concrete to fast neutrons. It consists of purified graphite based on non-impregnated Lockport L coke.

Cooling is provided by circulating carbon dioxide under a pressure of 15 bar. The gas inlet temperature was set at 140°C and the outlet temperature ranges from 300 to 390°C according to the zone (centre or periphery). The temperature of the graphite ranges in the same range of values [15]. The fuel consists of natural uranium surrounded by a magnesium-zirconium (0.7% Zr) alloy clad.

During operation in the G2 reactor, many cores were taken of small samples, particularly to monitor the evolution of graphite under the combined effect of CO_2, irradiation and temperature. The technical report [17] gives information on the sampling dates and the number of samples taken during operation (some of these samples are still stored in the cellars of G2).

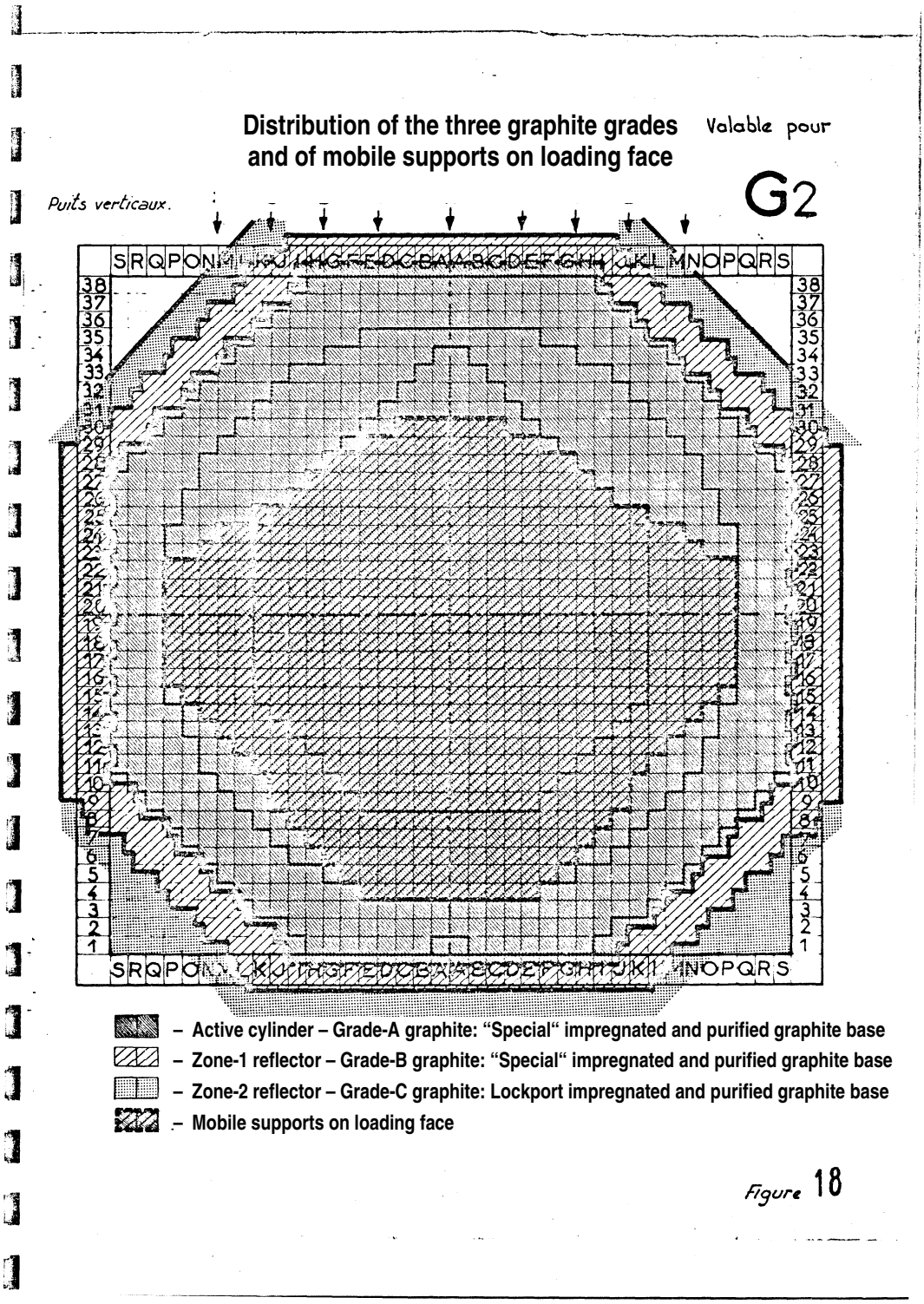


FIGURE 5: DISTRIBUTION OF THE DIFFERENT GRAPHITES IN G2

Since its shutdown in 1980, the G2 reactor has been the subject of three coring campaigns:

- axial coring along two fuel channels performed in 1980 (central channel W17A and peripheral channel W14P),
- horizontal radial coring in 1988 on 15 cores with diameter 80 mm and total length 3 m. A summary of the coring operations is presented in document [18],
- vertical radial coring of the median plane of the reactor on the entire graphite stack (47 cores) performed in 1989. This coring is located in a zone where the neutron flux corresponds to about 85% of the maximum flux of the reactor.

From these three campaigns, no more samples remain from the first two corings. Only the vertical coring is available for the selection of samples for new measurements.

During previous corings, the samples taken were mainly used for radiological inventory, for leaching and impregnation tests[18] (axial coring). However, some of the structural data were measured (density, more seldom porosity).

2.1. Microstructural characterisations of G2 graphite

The report by J Rappeneau[19] of 1959 provides a review of the density measurements taken during the G2/G3 graphite production campaign. The bulk density of G2 graphites consisting of "Special" Grade-A ("batch") is 1.703 with a dispersion of 0.01 (n=41, K=1), but with a value range between 1.65 and 1.73. The results obtained on sub-samples, call "barreaux balançoire" are very close with an average value of 1.698, whereas the density of virgin bars before rework is 1.72 on average (789 values, some of which probably result from mixed batches) [20, 21].

Graphite based on special coke					Graphite based on Lockport coke				
Type	Density (sp. gr.)	Difference (σ)	Interval	No. of values	Type	Density (sp. gr.)	Difference (σ)	Interval	No. of values
Barreaux balançoires	1.698	0.024	1.60-1.78	235	Swing bars	1.672	0.025	1.59-1.72	78
Batches	1.703,	0.01	1.65-1.73	41	Batches	1.670	0.013	1.65-1.69	11
Rough rods	1.725	-	-	789	Rough rods	1.680			247
33% of the values lower than 1.70 17% equal to 1.70 50% of the values are higher than 1.70					36% of the values lower than 1.67 15% equal to 1.67 49% of the values are higher than 1.67				

TABLE 3: DENSITY OF NON-IRRADIATED G2 GRAPHITE

Studies on the porous texture of virgin graphites were also conducted on simply impregnated Lockport-coke-based graphite [22] identical to the graphite of the G2 reflector and on Grade-A coke-based graphite close to "Special" Grade-A coke (English) of the G2 moderator. The authors present notably porosity ranges by mercury intrusion (Figures 3 and 4). The main parameters indicated in this study are summarised in Table 4.

Graphite	Bulk density	Total porosity P_t	Open porosity accessible to	Closed porosity	Porosity peaks

			Hg (P_{Hg})	($Pt-P_{Hg}$)	
Lockport L	1.691	25.38%	21.42%	3.96%	2 µm 0.02 µm
Grade A	1.788	21.09%	17.17%	3.92%	3 µm 0.015µm

TABLE 4: SUMMARY OF HG POROSITY MEASUREMENTS ON INACTIVE SAMPLES TAKEN FROM [ERREUR ! SIGNET NON DEFINI.]

2.2. Chemical compositions

Document [23] gives an average of the results of analyses performed by *Société des Electrodes et Réfractaires Savoie* during the G2 graphite production campaign.

- TABLEAU I - CAMPAGNE G2 -

MOYENNE DES RESULTATS ANALYTIQUES DE L'OPERATION 385 à l'OPERATION 537

Caractéristiques étudiées	Unité	Moyennes générales		Coke Spécial "A"		Coke Lockport		Fours à échantillonnage mixte	
azote déduit	mb	3,78	76	3,75	46	3,82	14	3,80	16
B chimie	ppm	0,23	76	0,23	46	0,20	14	0,25	16
B Spectro CEA **	"	0,12	22	0,12	12	0,12	5	0,10	5
B Spectro Chedde	"	0,16	76	0,16	46	0,16	14	0,16	16
Cendres E P P	"	181-25=156	76	145-20=125	46	291-40=251	14	187-25=162	16
Cendres R P	"	156-20=136	76	126-20=106	46	239-35=204	14	169-20=149	16
Hydrogène I	"	3,2	76	4	46	1,7	14	2,7	16
Hydrogène II+III	"	16,0	76	16	46	14	14	16,2	16
Cl Chimie	"	4,5	76	4,3	46	4,6	14	5,1	16
Dy	"	0,010	50	0,008	20	0,011	3	0,012	27
Gd *	"	0,025	(*)	0,020	(*)	0,027	(*)	0,030	(*)
Eu	"	0,0006	50	0,0006	20	0,0010	3	0,0006	27
Sm	"	0,024	50	0,020	20	0,020	3	0,028	27
Mo	"	14	59	13	21	18	4	14	34
Ti	"	8	75	7	30	9	8	8	37
V	"	23	75	18	30	41	8	23	37
Na	"	27	75	33	30	14	8	25	37
Ca	"	45	75	41	30	38	8	51	37

** dosage abandonné en cours de Campagne.
* on a admis que Gd = 2,5 Dy

TABLE 5: CHEMICAL COMPOSITION OF G2 GRAPHITES

This document gives the chlorine content without mentioning the measurement technique used at that time, nor the range of variations in concentration, which are approximately 5 ppm regardless of the initial coke.

2.3. Summary of existing data

Several measurements were taken on non-irradiated graphites from the G1/G2/G3 reactors, chiefly measurements of density, capture cross section, during the fabrication of the graphites. Many active samples from G2 were used, but few of them were fully characterised from the point of view of the physical properties of the solid. As a rule, the densities provided are based on dimensional measurements mentioned with a descriptive objective and not for an accurate determination of their density. Based on these data, the density of the irradiated samples is often lower than that of the non-irradiated graphite. However, these variations appear to be small and difficult to interpret in view of the measurement methodology and the variability of the densities of the non-irradiated graphite.

The lack of data needed the performance of new measurements on both non-irradiated and irradiated samples.

3. SUMMARY OF KNOWLEDGE ON WATER IMPREGNATION IN GRAPHITES

Few data are available in the open literature on the study of the kinetics of water impregnation in nuclear grade graphites. The data are taken from previous studies conducted in France, particularly CEA, on graphites from the sample of moderator and sleeves of the UNGG reactors or the Hanford reactor, with the exception of another study conducted on irradiated graphite from a Magnox reactor[18, 24, 25, 26, 27, 28, 29].

A summary of these data was compiled in the note "Determination of water impregnation kinetics in nuclear graphites of UNGG reactors" LARC 2009-13[3].

These preliminary data acquired both on nuclear graphites of sleeves and stacks and on non-irradiated and irradiated samples show that:

- on non-irradiated graphite, the impregnation of water in the porous medium is relatively slow and remains incomplete for time intervals up to 90 days. The kinetics is a linear law of the V/S ratio (volume / area of sample) and could possibly be connected with a diffusion process (linearity of kinetics in square root scale of time),
- irradiation causes an increase in the kinetics and the impregnation rate.

Studies by J.R. Costes *et al.*[18, 26] concern measurements of water impregnation kinetics in two stack graphites including that of the G2 reactor. The influence of the grade of graphite, the size of the samples and the rate of oxidation by radiolytic corrosion, was investigated. The results show that the impregnation kinetics is relatively slow for non-irradiated samples of G2 graphite, with a maximum saturation rate of 10% to 17% of the open porosity, which is reached after about 400 hours (#15 days). The maximum porosity percentage reached by the water for samples of graphite B is very different, ranging from 41 to 57% for durations of 400 to 1000 hours, as shown in Figure 6, whereas the two grades of graphite have substantially similar open porosity volumes and pore size distribution spectra.
The effect of radiolytic conversion is identified on the graphite B samples with a substantial increase in the kinetics and the maximum saturation rate (Figure 7). The most corroded sample, which displays a rate of wear of 16.4%, reaches in 600 h (25 days) a saturation rate of 90%, to be compared with the saturation of 35 to 50% after the same interval for non-irradiated graphites. The authors explain this result by the fact that radiolytic corrosion increases the pore diameter, inducing a better impregnation of water.

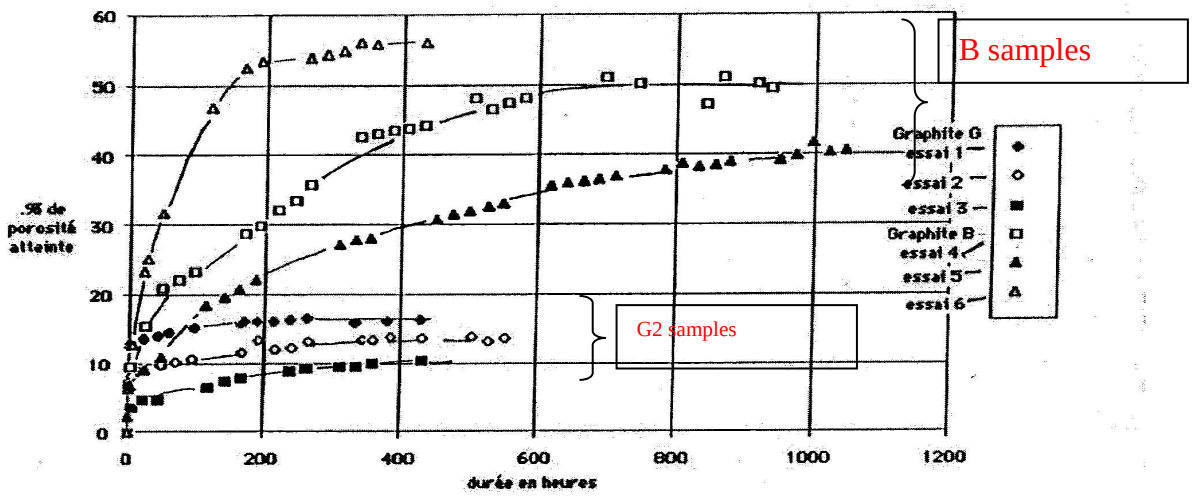


FIGURE 6: SATURATION RATE OF NON-IRRADIATED SAMPLES FROM G2 AND B REACTORS

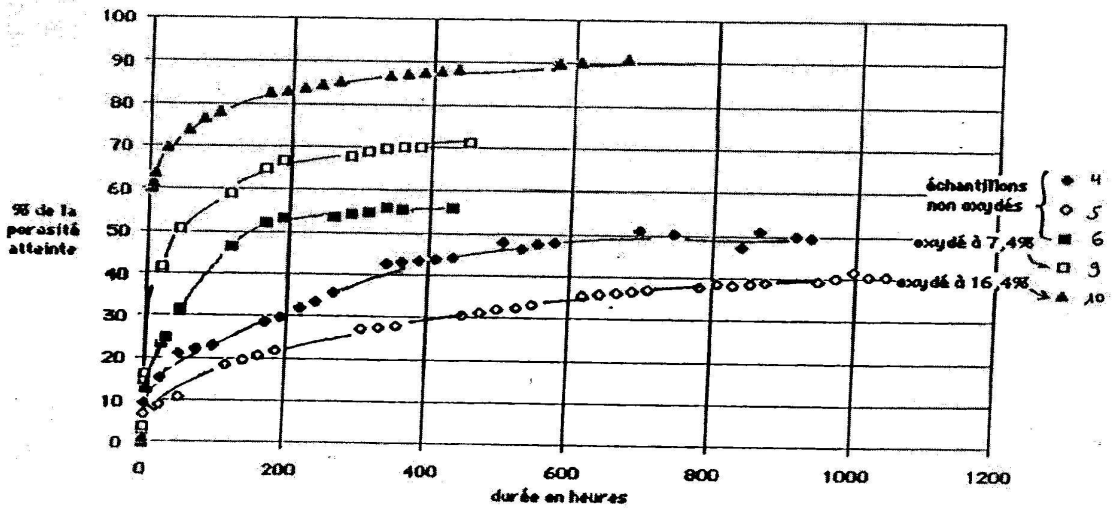


FIGURE 7: EFFECT OF RADIOLYTIC CORROSION ON THE SATURATION RATE

Nevertheless, there is little information available and data on the G2 samples need to be completed.

4. SUMMARY OF DATA ON THE BEHAVIOUR OF RADIONUCLIDES DURING LEACHING

Most leaching investigations were carried out by the CEA laboratories[27, 28, 30, 31] on graphites of the EDF (Bugey et Saint-Laurent A) and CEA (G2) reactors, except those carried out by the PNL (Pacific Northwest Laboratory) in the USA on stack graphites from CEA (G2)[32] and American (Hanford) reactors[27], and those carried out by CIEMAT on fuel sleeve graphites from the UNGG Vandellos reactor[33].

Other studies, with very partial results, are available in particular on graphite samples from RMBK reactors, whose results were presented at the IAEA conference in Manchester[34] and on graphites from Magnox[29].

These studies were concerned with samples of variable size (from a few grams to 600 g) in different conditions (pure water, water saturated with $Ca(OH)_2$, from ambient temperature to 90°C, duration of the tests, inert atmosphere or air) and obviously on samples of different types (starting coke, neutron and heat transfer history, stack – sleeves). Appendix 1 gives the various parameters for all these experimental investigations.

4.1. G2 reactor

A first study conducted in parallel by the CEA and PNL on samples from radial cores took place in the years 1988-1989[27]. A second study was carried out in 2004-2006 on samples from a vertical core.

First studies of 1988-1989

The two PNL and CEA laboratories performed radiochemical analyses on samples from G2. Table 6 shows the good agreement of the analyses concerning gamma emitters. However, significant differences exist for measurements of ^{14}C and ^{36}Cl. A review of the characterisation methods does not help to identify any analytical problem. The methods employed for determination in solution are similar to those still used today for ^{14}C and ^{36}Cl.

Sample	No. 2 (KBq/g)		No. 13 (KBq/g)		No. 14 (KBq/g)	
	CEA	PNL	CEA	PNL	CEA	PNL
^{3}H	382±60		367±21		345±16	
^{14}C	6.1±1.2	16.3	18.6±6	53.9	23.3±3.5	65.3
^{36}Cl	0.4±0.1	0.94	1.3±0.3	4.46	0.53±0.15	4.48
^{60}Co	2.19±0.15	2.12	12.0±1.6	11.1	13.4±0.9	11.4
^{63}Ni	1.6±0.2	n.a.	5.8±0.5		7.3±1.2	
^{133}Ba	0.07±0.06	0.1	0.065±0.05	0.093	0.17±0.04	0.179
^{134}Cs	<0.05	0.015	<0.1	0.034	0.07±0.04	0.025
^{137}Cs	<0.06	0.011	0.075±0.06	0.097	0.095±0.06	0.075
^{154}Eu	0.48±0.1	0.503	0.4±0.08	0.525	0.75±0.07	0.758
^{155}Eu	0.16±0.08	0.21	0.15±0.1	0.277	0.33±0.09	0.374

TABLE 6: RADIOCHEMICAL ANALYSES PERFORMED BY THE CEA AND PNL

The leaching rates obtained by the two laboratories display wide differences (Table 7 and Figure 8)

Date	Sample ref	Coke		Test lab	Mass	Ao 36Cl	F (%)	Duration
					(g)	Bq/g		
1988	H-2	Lockport	Reflector	CEA	641.5	400	0.34	90
1988	H-13	Special A	Moderator	CEA	628	1275	1.74	90
1988	H-14	Special A	Moderator	CEA	643.6	530	1.05	90
1989	H2-BA	Lockport	Reflector	PNL	37.27	4480	0.96	91
1989	H13-North Sub	Special A	Moderator	PNL	37.01	4460	39.1 (29%)	91
1989	H14-Sup North	Special A	Moderator	PNL	36.2	940	3.7	91
1991	H12	Special A	Moderator	CEA	47	654	20.2	90
1991	H15	Special A	Moderator	CEA	47	920	53	90

TABLE 7: LEACHING RATES OF ^{36}CL OBTAINED BY CEA AND PNL

PNL obtains ^{36}Cl leaching rates ranging from 1 to 40%. The leaching rates obtained by the CEA are lower and virtually identical between the tests, between 0.3 and 1.7%. Apart from the measurement and testing conditions (washing to remove cutting powders, reactor sealed for the tests), the main difference indentified is the mass of the sample. Thus to check the influence of the mass of graphite, additional experiments were performed on cores 12 and 15 of G2. According to the horizontal radial coring plan of G2 in 1988, these cores are positioned on either side of cores 13 and 14 and should therefore, according to the authors, display a ^{36}Cl release similar to those obtained by PNL. The results contradict this assumption. The authors at the time did not conclude on the differences.

It should be noted however that the determination of the initial activities of the samples was performed on samplings (cutting scrap) of the samples during their shaping for the leaching tests. The leaching rate was therefore not determined from the residual activity of the samples after leaching, implying that the ^{36}Cl concentration is uniform throughout the sample. The experience gained since then by LARC clearly shows that the chlorine distribution is not uniform in a sample.
Only PNL measured the residual activity of sample No. 13. In this case, the leaching rate obtained from the analysis of the cutting scrap and the residual activity of the sample after leaching is 38% and 29% respectively.

A comparison of the tests shows that chlorine release is fast until about 20 days (Figure 8). After this, the ^{36}Cl analyses are under the measurement detection limit. These results confirm the importance of considering the measurement performance as well as the volumes of test samples devoted to the quantification of chlorine 36, in order to avoid exclusively obtaining values at the detection limit.

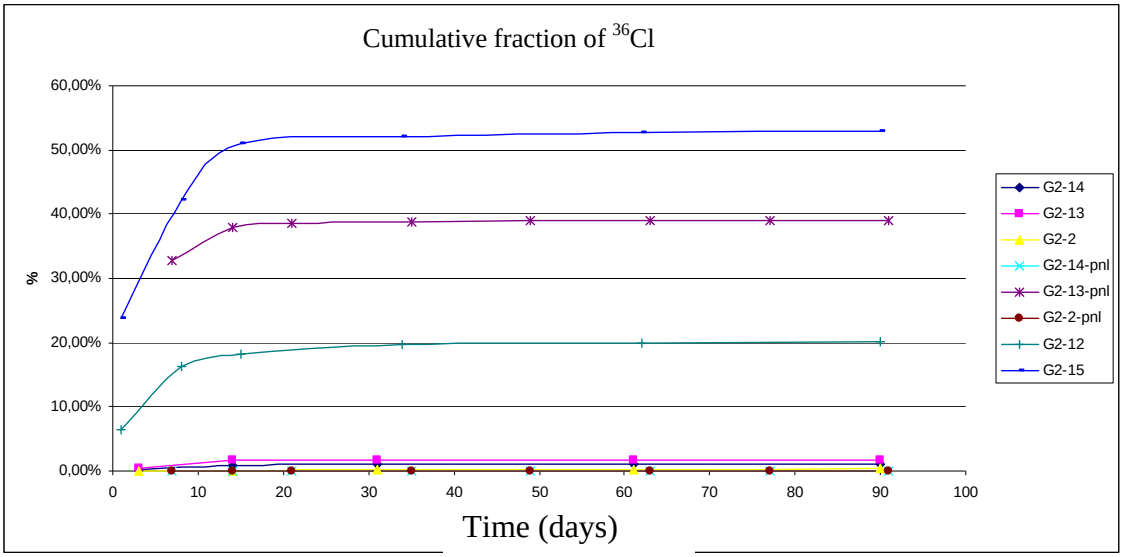


FIGURE 8: CUMULATIVE FRACTION OF ^{36}CL ACTIVITY RELEASED IN CEA-PNL TESTS OF G2 GRAPHITES G2

The differences observed in these tests also contain results on the leaching of the radionuclides ^{14}C, ^{3}H, certain gamma emitters, as well as the results on samples coated in conditioning matrices.

Summary of tests conducted in 2004-2006

The second series of leaching test was undertaken in 2004 on a reference sample No. 36 taken from a vertical core [35]. This sample was subdivided into several lamellae. Each sample weighing between 72 to 90 g approximately is introduced into a sealed reactor under inert atmosphere (Ar). The volume of leachate is 150 ml, with complete renewal at each sequence. The total activity of the sample is determined at the end of the tests by summating the leached activity and the residual activity. Table 8 shows the sample references and gives the mass and percentage of activity leached.

Date	Sample ref	Coke			Test lab	Mass	Ao 36Cl (±20%)	F (%)	Duration
						(g)	Bq/g	%	(j)
2004	V36-2	Special A	Moderator	UP water	CEA	87.2746	216	82%	455
2004	V36-6	Special A	Moderator	UP water	CEA	74.8385	254	82%	455
2004	V36-9	Special A	Moderator	UP water	CEA	90.0182	394	89%	455
2004	V36-5	Special A	Moderator	Lime water	CEA	72.8569	283	83%	455
2004	V36-8	Special A	Moderator	Lime water	CEA	90.7171	353	83%	455
2004	V36-10	Special A	Moderator	Lime water	CEA	90.656	307	89%	455

TABLE 8: LEACHING RATE OF ^{36}CL ON G2 CORE 36

The activity fractions of ^{36}Cl released are all between 82 and 89% regardless of the leaching medium investigated (water saturated with $Ca(OH)_2$, or ultrapure water). The leached fractions in ^{36}Cl are high and the mechanism of release in solution is relatively fast, because more than 80% of the chlorine is leached during the first month, as shown in Figure 9.

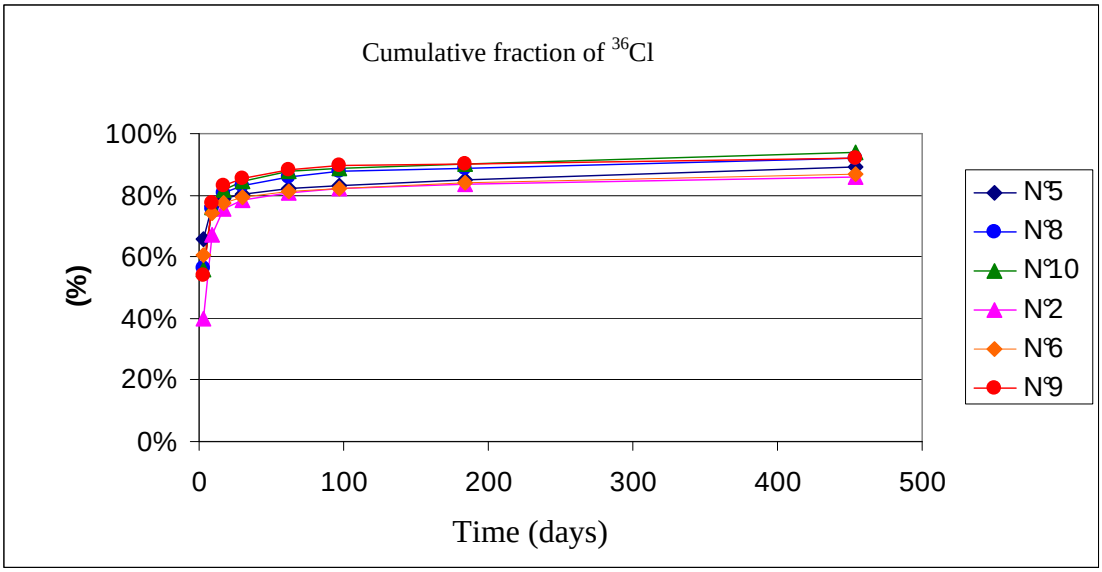


FIGURE 9: LEACHED KINETICS OF ^{36}CL

Measurement of diffusion coefficient

Diffusion tests of ^{36}Cl across a thin lamella of non-irradiated G2 graphite (1.8 cm thick) were also performed in order to determine the diffusion coefficients of ^{36}Cl in the graphite. For this purpose, a lamella of graphite is placed in a sealed manner between two reservoirs between which a constant concentration gradient is imposed. Thus the measurement of the amount of ^{36}Cl crossing the lamella over time serves to calculate the effective diffusion coefficient. In steady state conditions, the equation is given by:

$$Q = \frac{D_e C_0}{L} t - \frac{\alpha L C_0}{6}$$

where Q: quantity of ^{36}Cl having passed through the lamella per unit area (Bq/m^2), De: effective diffusion coefficient (m^2/s), C_0: initial concentration (Bq/m^3), L: thickness of lamella (m), $\alpha = \theta + (1 - \theta)\rho.K_d$, where θ: porosity of material, ρ: graphite density and K_d: retention coefficient of element in the material.

By plotting QL/C_0 as a function of time, the slope corresponds to the effective diffusion coefficient. The figure below shows the results obtained for chlorine.

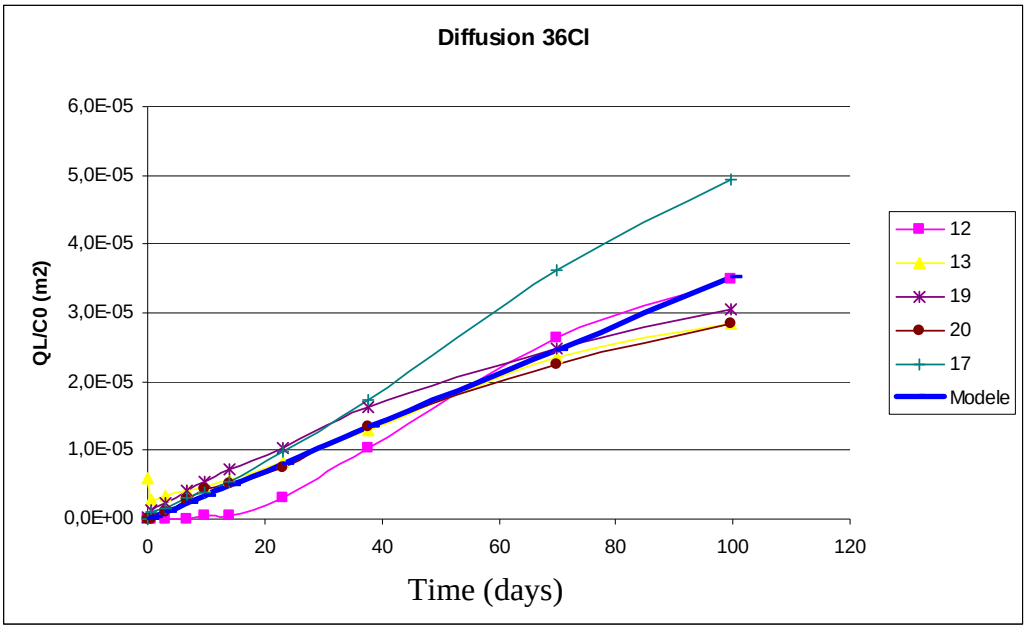


FIGURE 10: DIFFUSION OF ^{36}CL ACROSS A LAMELLA OF NON-IRRADIATED G2 GRAPHITE

The mean effective diffusion coefficient calculated is $D_e = 4.1 \pm 1.2 \times 10^{-12} m^2/s$ with a range of values between 3.2 and 6.0×10^{-12} m^2/s.

In view of the results obtained and as a first approximation, the assumption of the control of leaching by diffusion of chlorine through the pores of the graphite was considered. Thus the diffusion calculations were carried out by adjusting the value of the diffusion coefficients to reproduce the experimental data of the leached tests according to the equation:

$$F = 2 \times \frac{S}{V} \times \sqrt{\frac{D_a \times t}{\pi}}$$

where F: leached fraction, S: geometric area subject to leaching, V: geometric volume of sample, t: time, D_a: apparent diffusion coefficient.

To correctly adjust the experimental points, two forms of chlorine were considered:

- a fraction of labile ^{36}Cl (80%), called site 1,
- a fraction of ^{36}Cl diffusing slower (20%) called site 2, located in the smallest pores of the graphite (heads less accessible to water).

The adjustment of the experimental points according to the above equation serves to calculate two diffusion coefficients corresponding to sites 1 and 2, and which the values are respectively calculated as D_a site 1 = 2.5×10^{-11} m^2/s and D_a site 2 = 1.5×10^{-13} m^2/s, which corresponds to an effective diffusion coefficient $D_e = 5 \times 10^{-12}$ m^2/s in the case of site 1 ($D_e = \theta . D_a$ with $\theta = 0.2$ porosity of graphite). This value is identical to the figure obtained with the diffusion tests across the non-irradiated graphite lamellae.

Summary of tests on G2 reactor

The tests review the following main points:

- The release kinetics of chlorine 36 appear to be fast regardless of the final release rate.
- The tests conducted in parallel on sub-samples of the same core reveal good experimental reproducibility.
- An absence of any effect of the chemistry of the leachate water (UP water or water saturated with $Ca(OH)_2$) for the release of chlorine 36.
- A difference in the release rate between the various cores, not explained by the operating conditions of the tests.
- Consistency between the diffusion coefficient measured with the leaching tests and those of the diffusion tests.

It appears that this results need to be supplemented to determine the release rate of chlorine 36 by taking account of the position of the samples in the reactor.

4.2. Bugey reactor

Leaching

Two series of experiments were performed on graphite samples from the Bugey stacks:

- one series on cores[36] in order to determine the leaching kinetics of the dimensioning radionuclides for disposal studies.
- a series of powders[37] connected with underwater decommissioning studies of reactors with the aim of estimating the release rate in solution of the radionuclides contained in graphite fines possibly present in the reactor.

The two slightly different objectives led the experimental workers to perform tests in different conditions. Table 9 summarises the test parameters and the chlorine 36 release rates. The kinetics are shown in Figure 11 and Figure 12.

Date	Sample ref	Channel + level	Form	leachate	Temp	Atm	R	Mass	36Cl A_0	F	Duration
					°C			(g)	(Bq/g)	%	(days)
2006	N87-test1	B8J0-17,3	Powder	UP water	20	E	C	1.4857	10	51	181
2006	N67/68-test2	B3I9-20.4	Powder	UP water	20	E	C	1.48	340	1.5	181
2006	N88-test3	B8J0-20,4	Powder	UP water	20	E	C	1.54	18	14.5	181
2002	N55	D6J4-12	Block	UP water	20	A.I.	P	11.347	22	83.5	455
2002	N58	D6J4-20.4	Block	UP water	20	A.I.	P	9.56	3.6	38.2	455
2002	N75	D1J1-12	Block	UP water	20	A.I.	P	11.61	65	87.5	455
2002	N76	D1J1-13.7	Block	UP water	40	A.I.	P	9.383	161	83.5	144
2002	N85	B8J0-12	Block	UP water	40	A.I.	P	11.935	82	73.5	144
2002	N86	B8J0-13.7	Block	UP water	40	A.I.	P	6.457	104	36.1	144
2002	N57	D6J4-17,3	Block	Lime water	20	A.I.	P	8.191	16	18.4	455
2002	N59	D6J4-21.4	Block	Lime water	20	A.I.	P	9.508	18	<3.8	455
2002	N98	C6J0-20.4	Block	Lime water	20	A.I.	P	10.94	3.6	<18	455

TABLE 9: ^{36}CL LEACHING RATES OBTAINED ON BUGEY SAMPLES

E: Tests performed in sealed reactor to limit evaporation of leaching solution or A.I.: Tests performed in sealed reactor and with inert atmosphere (Ar, N2)
R: Renewal of leachate (C: Complete at each sequence, P partial at each sequence)

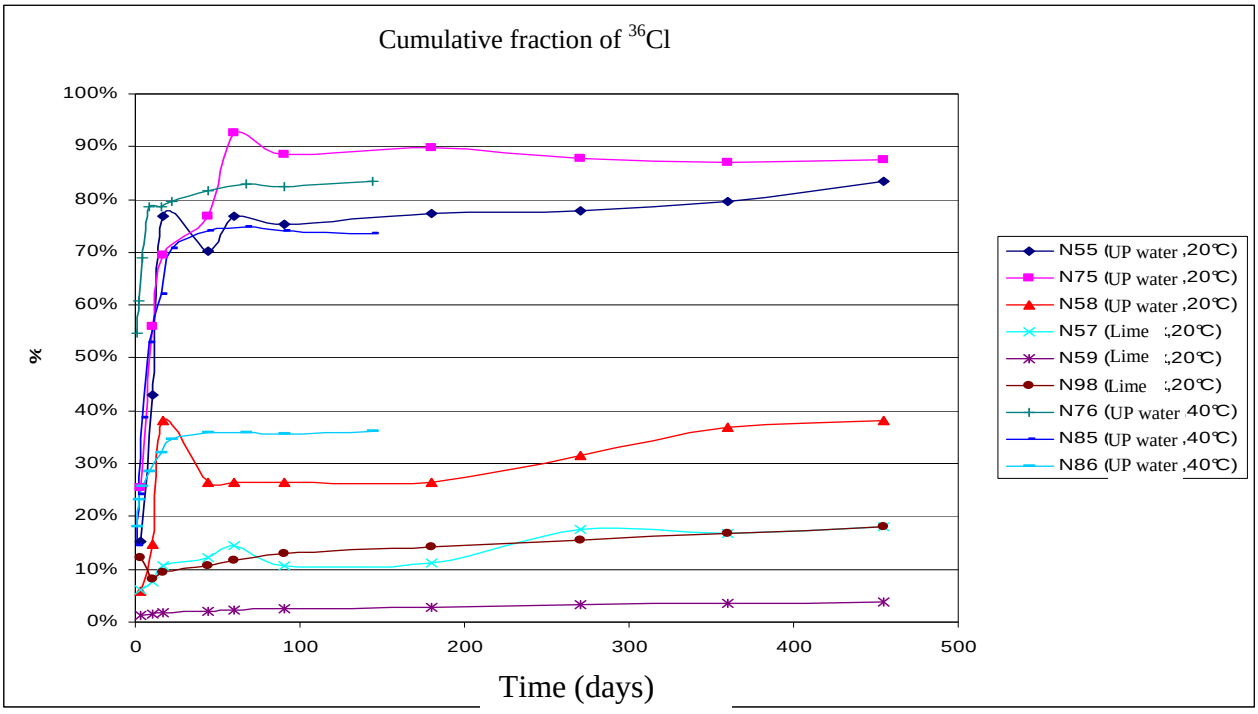


FIGURE 11: ^{36}CL RELEASE KINETICS ON BUGEY GRAPHITE BLOCKS

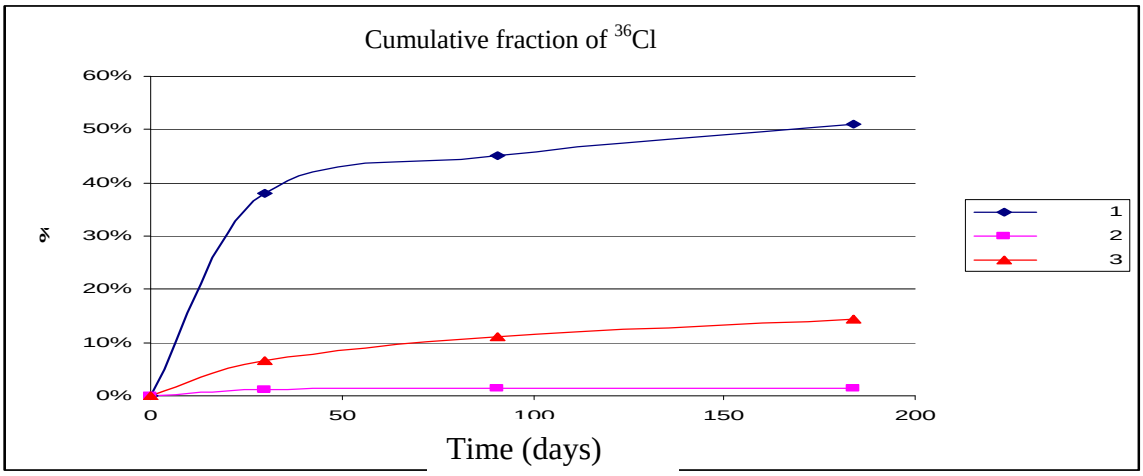


FIGURE 12: ^{36}CL RELEASE KINETICS ON BUGEY GRAPHITE POWDERS

It may be observed that the release kinetics of chlorine 36, as in the case of G2, is fast both on powder and on block. However, the leaching rates reached are different in the tests. The results obtained on the cores show that:

- the temperature has a very slight effect on the release kinetics in the 20 to 40°C range.
- the ^{36}Cl leaching rates in water saturated with $Ca(OH)_2$ are lower than those obtained in ultrapure water.

The authors[36] emphasise that the lack of identical test specimens led to a dispersion of the results making interpretation difficult.

However, after a re-examination of these results by EDF/CIDEN in order to confirm the correlation between the leaching rates and the position of the samples in the Bugey stack, dependence was observed between the sampling height and the leaching rate (Figure 13). The temperature of the Bugey graphite varied between 230 and 580°C according to its position in the stack. The temperature to which the graphite was subjected during operation in the reactor could therefore have an effect on the release of chlorine in leached conditions.

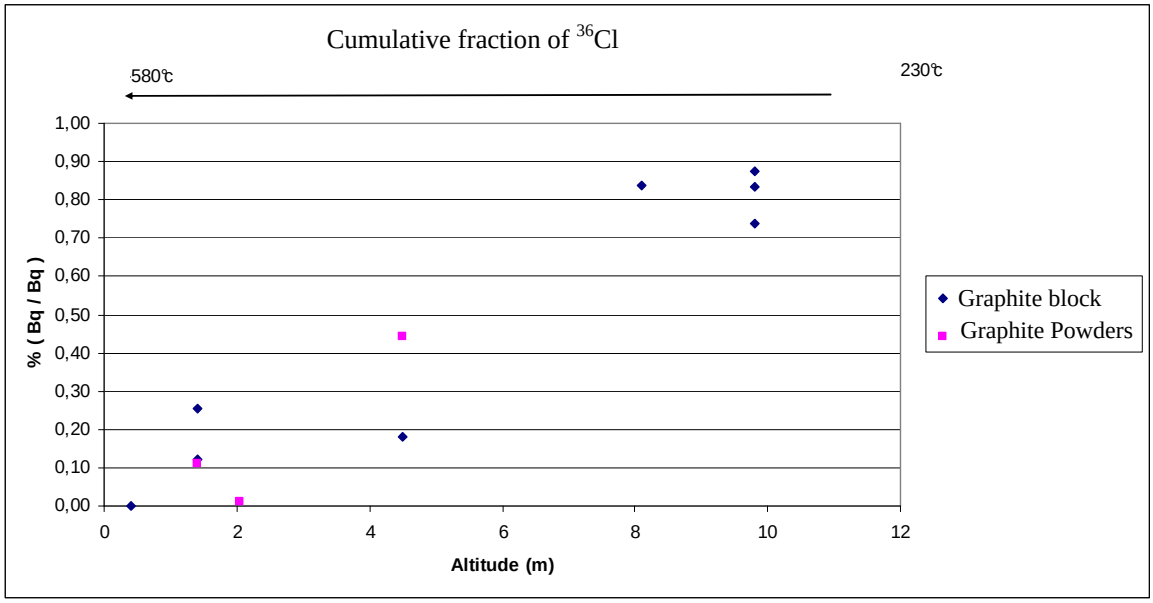


FIGURE 13: RELEASED FRACTION OF ^{36}CL AS A FUNCTION OF POSITION OF GRAPHITE IN STACK

These results are important because, for the first time, they serve to explain the differences in chlorine 36 release rates and to presume the existence of different chemical forms of chlorine.

Measurement of diffusion coefficient

Measurements were performed in diffusion cells on an inactive sample (piece of a brick similar to that of the Bugey 1 stack). The experimental conditions were as follows:

- graphite lamellae: 5.5 mm thick, diameter 75 mm
- diffusion cell: volume 350 ml, effective area 33 cm^2
- 0.1 M NaCl solution doped with a standard solution containing 3.7 GBq/m^3 ^{36}Cl.

No delay in diffusion was observed in the tests. The effective diffusion coefficient of chlorine 36 across graphite is about 5×10^{-12} m^2/s, an identical value to the one obtained for G2.

STUDY PROGRAM AND PRESENTATION OF PRELIMINARY RESULTS

1. STUDY PROGRAM

Considering all the available data, an R&D program has been proposed to investigate and quantify the mechanisms of radionuclide release in water.

The release of chlorine in solution depends on physicochemical processes such as:

- Water impregnation in graphite. Given the hydrophobic nature of graphite, the water saturation of the material may be a limiting process,
- Solubilisation of chlorine in solution. The types of bond between the chlorine and the graphite will control this process,
- Transport of chlorine in solution through the pores of the graphite from the chlorine site to the solution.

The release kinetics will be controlled by the slowest mechanism. For this purpose, each process will be investigated by:

- Determination of the pore distribution of the graphite,
- Measurement of the water saturation kinetics of graphite specimens,
- Determination of the location and chemical form of chlorine. Measurements of ^{36}Cl will be taken by SIMS on irradiated graphite samples. Preliminary determinations of chemical speciation of stable chlorine were also performed in EXAFS on the SOLEIL synchrotron. A program is also carried to investigate the behaviour of ^{36}Cl at temperature. These measurements consists in studying chlorine vaporization (^{36}Cl for irradiated graphite, ^{35}Cl for non-irradiated graphite) as a function of time and temperatures, in order to distinguish different forms of chlorine according to their vaporisation temperature (gaseous forms adsorbed in graphite, metal chlorides and organic forms),
- Release kinetics of chlorine in solution on samples taken at various positions in the reactor.

Characterisation studies of the porous medium were conducted. The parameters were measured both on irradiated materials and on non-irradiated samples in order to quantify the structural changes:

- density, porosity, pore size distribution, or providing information on the pore structure of the graphite and on the volume accessible to water.
- Raman spectrometry and X-ray diffraction (XRD), which serve to understand the change in the crystal structure under the combined effect of temperature, coolant gas and irradiation.

In addition, water impregnation studies in the porous medium of the graphite were initiated. This process is one of the essential parameters conditioning the release of radionuclides in solution. For this purpose, the impregnation of samples from the G2 reactor was investigated on non-irradiated and irradiated graphites, taking into account the literature data.

The release kinetics and fractions of ^{36}Cl labile activity were measured on a series of experiments, allowing the proposal of a first release model. This release model is based on the assumptions of a labile fraction of chlorine 36 for which leaching process is controlled by a diffusion law. The percentage of labile fraction, based on the Bugey tests, appears to be correlated with the position of the samples in the stack, and it can be assumed that one of the influential factors is the irradiation temperature.

To confirm these assumptions, series of experiments were conducted on four G2 samples selected among those available from the vertical radial coring and distributed at various sampling heights, hence at different temperatures. The sampling sequences were calculated on the basis of the diffusion coefficients to have closer time intervals in the first part of the leaching tests; this serves to obtain more significant points for calculating the diffusion coefficient.

The programme also covers the study of the St Laurent A2 reactor according to the same approach, and will be the subject of a forthcoming summary. The choice of the G2 and St Laurent A2 (SLA2) reactors is justified by the different characteristics of the stack graphite and the operating conditions of the reactors, in particular:

- type of coke and initial impurities,
- neutron and thermal powers, CO_2 pressure, thermal history of graphite during reactor operation, presence of carboxyhydrogenatred deposits.

Table 10 recalls the main differences between the G2 and SLA2 reactors. Note that this choice is also justified by the sufficient amount of samples of non-irradiated and irradiated graphite available, whose thermal and neutron history are perfectly known.

Reactor	G2	SLA2
Divergence date	July 1958	June 1971
Shutdown date	February 1980	May 1992
Thermal power (MW)	260	1700
CO_2 pressure (Mpa)	1.5	28.5
Mass of graphite stack (tonnes)	1500	2200
Graphite temperature during operation	140-380℃	240-470℃
Type of graphite (core)	"Special" Grade A coke	Lima coke stripped of MgF_2
Carbonaceous deposits	"Low"	"High"
Graphite density (g/cm^3)	1.71	1.68

TABLE 10: CHARACTERISTICS OF G2 AND SLA2 REACTORS

2. SAMPLE PREPARATION

2.1. Inactive G2 samples

The brick used as a reference for the non-irradiated samples was taken from a stock of bricks located under G2 reactor. This brick, with a square section of 200 mm sides, has two half-channels 70 mm in diameter. It corresponds to the shape of the bricks of the G2 moderator which is manufactured on the basis of special coke. Based on this brick, successive slices of about 3 cm were cut using a wire saw of the *Laboratoire d'Expertise et de Caractérisation Destructive* (DSN/SEEC/LECD) and transferred to the various laboratories participating in the programme: *Laboratoire de Caractérisations Physico-Chimiques des Matériaux Irradiés* (DMN/SEMI/LPCMI), IPNL (*Institut de Physique Nucléaire de Lyon*) and *Ecole de Mines of Nantes* (Subatech). For the LARC, the initial slice was cut again, still using a wire saw, to obtain various samples for the test (see drawing). The samples were characterised by measurements of geometric density, He pycnometry, Hg porosimetry, X-ray diffraction and Raman spectroscopy[2].

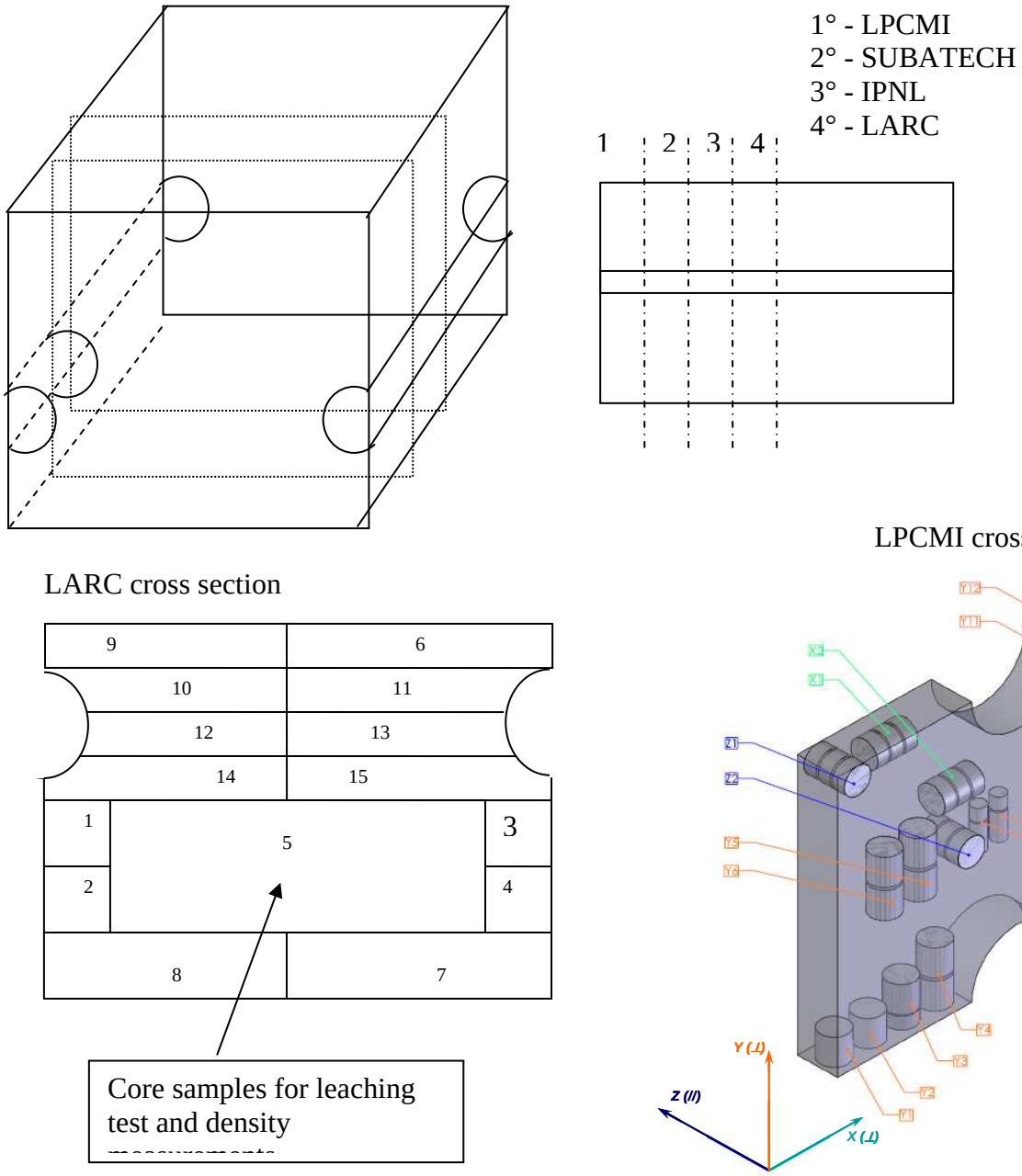


Figure 14: Cross sections of the G2 inactive graphite brick

2.2. G2 irradiated samples

We chose four core samples from the lower half of the reactor: three in the moderator (Nos 27, 32 & 42) and one in the reflector (n°46). It was therefore possible to add the leaching results of core sample No. 36 from a previous study[35] to those obtained with the core samples chosen here. The five core samples were more or less equidistant from each other, as shown in Figure 15.

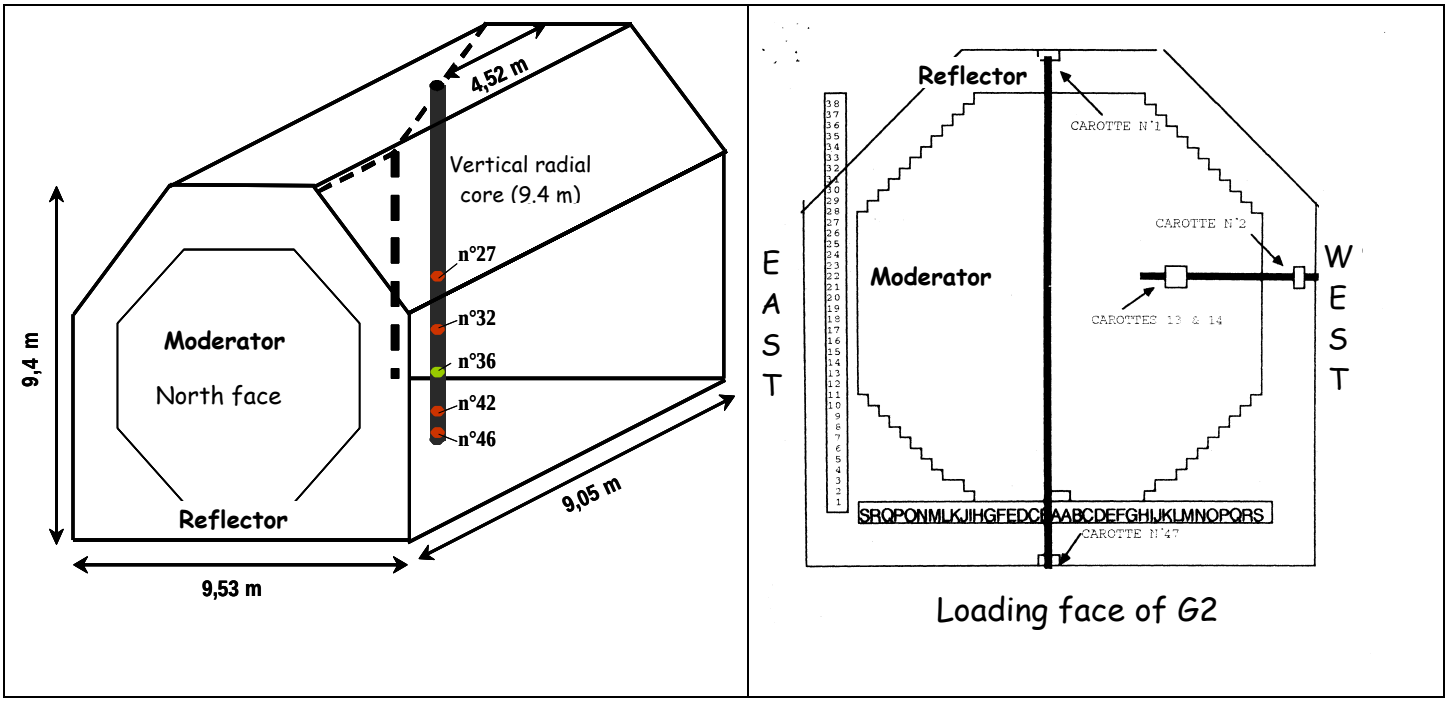


FIGURE 15: REPRESENTATION OF G2 REACTOR WITH VERTICAL CORING AND CHOSEN CORE SAMPLES

Table 11 lists all the sampling heights and the reactor operating temperatures in terms of the samples chosen for the impregnation and leaching tests.

Sample No.	Position	Presumed original coke	Sampling height (m)	Temperature (°C)[38]
G2-27	Moderator	special A coke	13.60-13.80	327
G2-32	Moderator	special A coke	14.60-14.80	320
G2-36	Moderator	special A coke	15.40-15.60	314
G2-42	Moderator	special A coke	16.60-16.80	309
G2-46	Reflector	Lockport coke	17.40-17.60	285

TABLE 11: G2 SAMPLES CHOSEN FOR LEACHING TESTS

The temperatures are estimated in a technical report [38] giving the graphite temperature in relation to the radial position of the channels (see Figure 16) and the depth.

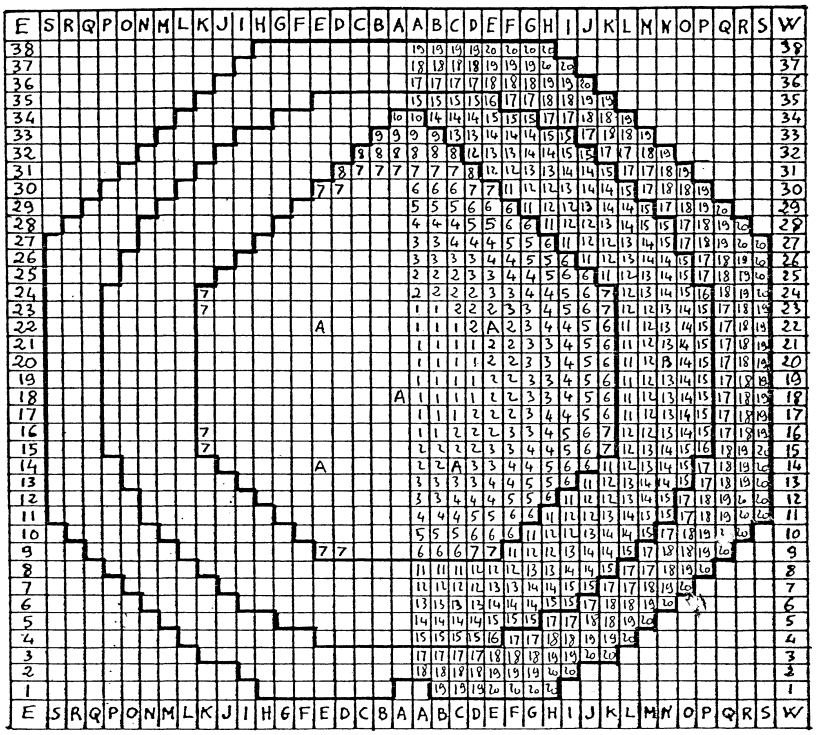


FIGURE 16: RADIAL CROSS SECTION OF THE CORE SHOWING TEMPERATUES

It can be seen that the moderator samples all have a rather similar operating temperature. The reflector sample shows different characteristics (lower temperature and different fabrication).

The core samples taken from the G2 reactor measured 20 cm long and 6.3 cm in diameter. This meant it was necessary to cut them up for the leaching tests and characterisations. The diagrams in Figures 17 and 18 show the cuts made on the moderator and reflector core samples of G2 graphite.

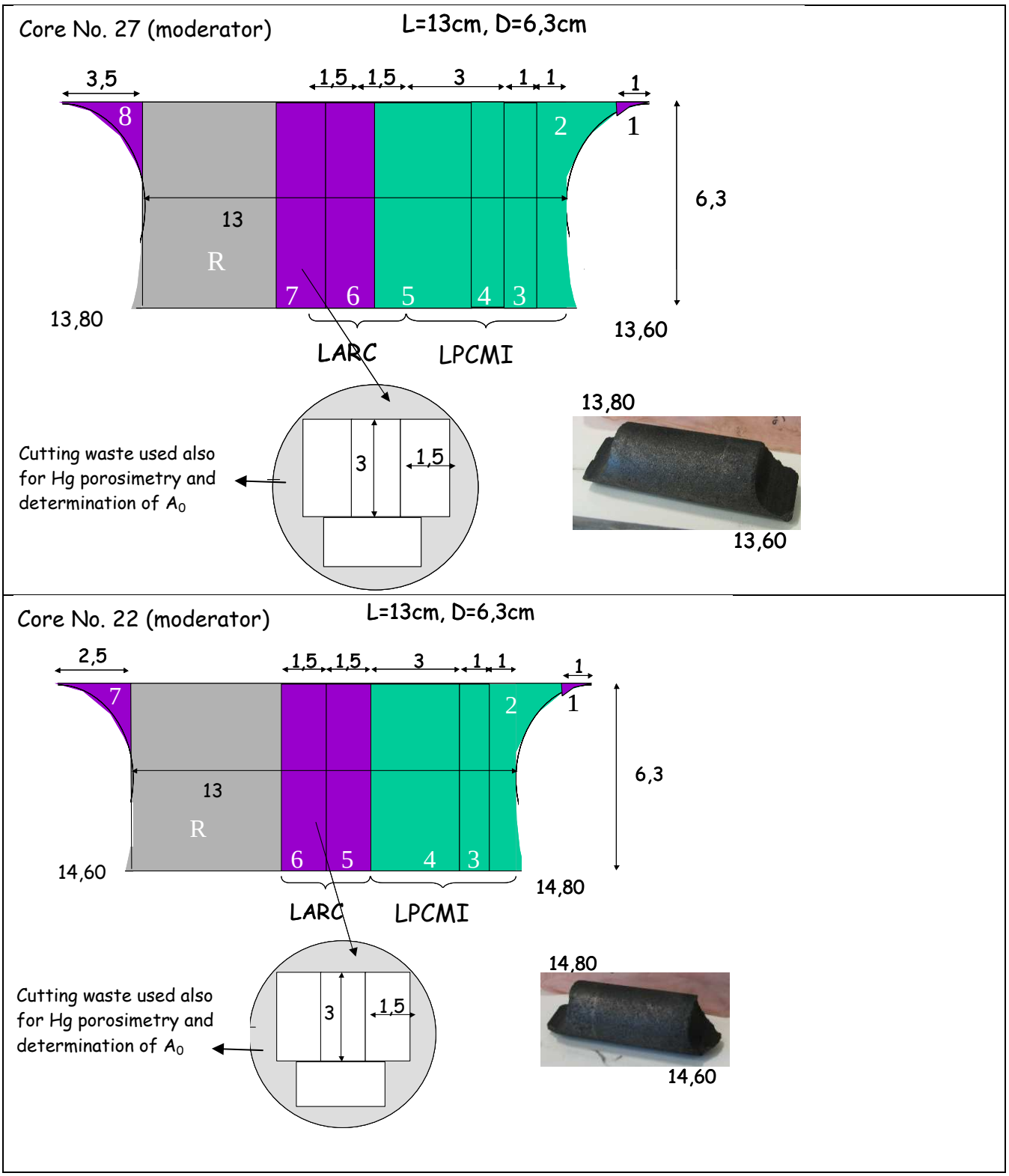


FIGURE 17: CUTS MADE ON CORE SAMPLES 27 & 32 OF G2 MODERATOR GRAPHITE

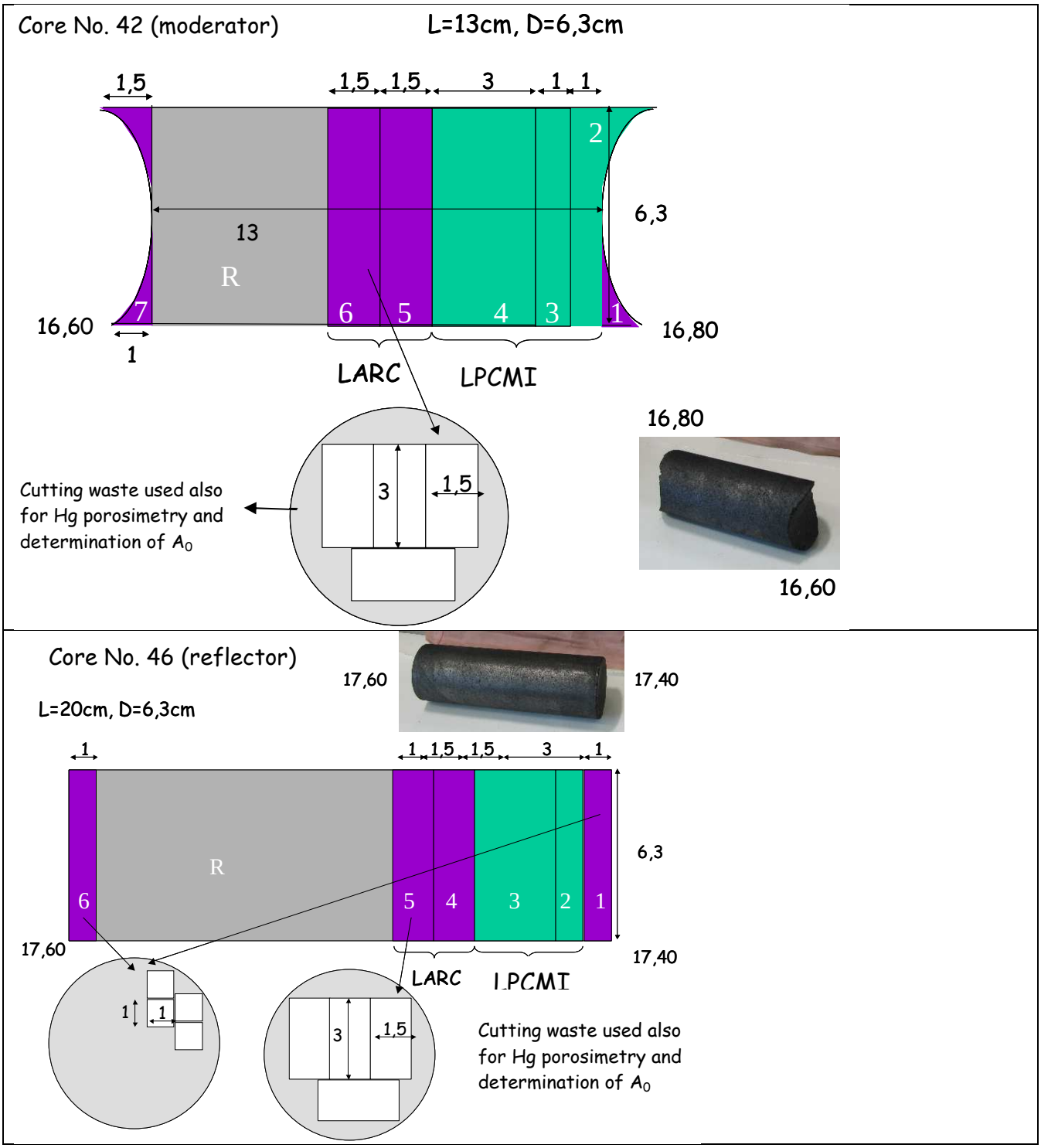


FIGURE 18: CUTS MADE ON CORE SAMPLES 42 & 46 OF G2 MODERATOR AND REFLECTOR GRAPHITE

The two central lamellae were used for the leaching and impregnation tests with density measurements. The cutting scrap of the central lamella and the pieces taken at the ends are used for the characterisations: density, mercury porosimetry, helium pycnometry and determination of initial ^{36}Cl activity. The intermediate lamellae were cut out of the LPCMI (geometric and hydrostatic densities, XRD and Raman spectroscopy).

The overall programme is shown in the table below.

Sample	lamella	Lab	Geo. density	Hg poro.	He pycno.	Bromo benzene	XRD	Leach	^{36}Cl	SIMS
G2-27 13,60-13,80	1	LARC/LECD		X	X				x	
	2	LPCMI								
	3	LPCMI	X			x#1	x#1			
	4	LPCMI	X							
	5	LPCMI	X							
	6	LARC	X					X		
	7	LARC/LECD	X#1	x#1	x#1			x#1	x#1	x#1
	8	LARC/LECD		x	x				x	
	Reserve	LARC								
G2-32 14,60-14,80	1	LARC/LECD		x	x				x	
	2	LPCMI	x							
	3	LPCMI	x			x#1	x#1			
	4	LPCMI	x							
	5	LARC/LECD	x					x		
	6	LARC/LECD	x#1	x#1	x#1			x#1	x#1	x#1
	7	LARC/LECD		x	x				x	
	Reserve	LARC								
G2-42 16,60-16,80	1	LARC/LECD		x	x				x	
	2	LPCMI								
	3	LPCMI	x			X	x#1			
	4	LPCMI	x							
	5	LARC	x					x		
	6	LARC/LECD		x#1	x#1			x	x	x#1
	7	LARC/LECD		x#1	x#1				x	
	Reserve	LARC								
G2-46 17,40-17,60	1	LARC/LECD		x	X				x	
	2	LPCMI	x			x	x#1			
	3	LPCMI	x							
	4	LARC	x						x	
	5	LARC/LECD	x#1	x#1	x#1			x	x	x#1
	6	LARC/LECD		x#1	x#1				x	
	Reserve	LARC								

TABLE 12: SUMMARY TABLE OF THE USES FOR SAMPLES

#1 Measurement taken on a sub-sample of the initial lamella

3. CHARACTERISATION OF G2 GRAPHITE

The sections below provide a summary of the structural characterisation studies[2] conducted on non-irradiated and irradiated samples with a focus on the properties that may be associated with leaching mechanisms as well as the effects of residence in the reactor.
On the non-irradiated samples, the results reveal:

- a wide heterogeneity in density of the material at the scale of centimetre sized samples,
- the existence of a density gradient between the core and the edge of the brick caused during the less complete impregnation of the graphite in the core of the material,
- that the porosity is essentially open (22 to 30%) whereas the closed porosity remains low, about 3 to 4%,
- that the distribution displays a high fraction of pore sizes between 1 and 30 µm (about 75%) with a maximum at 3.5 µm.

	Measurement Slice 4	Measurement Slice 4	Measurement Slice 4	Measurement Block
Sampling	**Core**	**Core**	**Periphery**	**Block**
Mean	1.66±0.07	1.67±0.03	1.72±0.05	1.717±0.009
Min	1.61±0.04	1.65±0.03	1.71±0.02	-
Max	1.73±0.06	1.68±0.02	1.76±0.02	-
Number	11	6	8	1
Mean total porosity %	26.9±1.2	26.5±0.5	23.9±0.7	24.2±0.1

TABLE 13: DENSITY OF G2 GRAPHITE SAMPLES

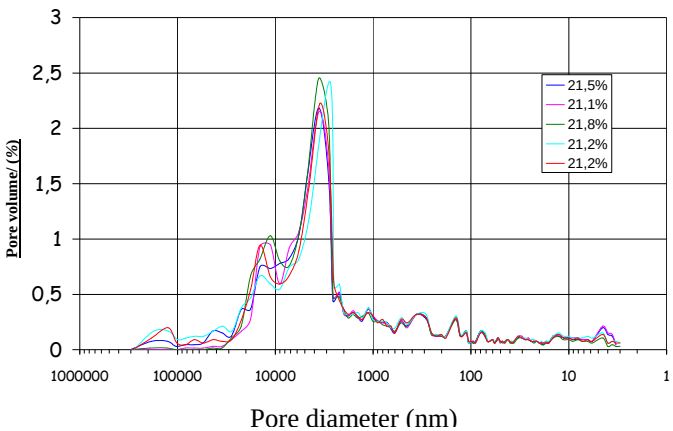


FIGURE 19: PORE SIZE DISTRIBUTION OF NON-IRRADIATED G2 SAMPLES

Irradiated samples from the radial-vertical coring in 1989 of the G2 reactor were also characterised. The results show that irradiation cause a slight change in the properties of the graphite in view of the power developed (260 MW over 22 years) and the moderate operating temperatures (285 to 327°C for

the samples characterised). The maximum wear rate is only 5% locally at the periphery of the most irradiated samples.

The following results were obtained:

- a decrease in the density associated with an increase in the open porosity and a decrease in closed porosity in relation with the irradiation rate of the sample,
- a greater decrease in density at the periphery of the brick, logically associated with radiolytic corrosion,
- an increase in open porosity essentially affecting the macroporosity,
- an increase in the mesh parameter *c* and an increase in the width of the XR diffraction lines which illustrates the greater disorder of the structure caused by irradiation, particularly pronounced if the neutron fluence received is higher.

G2	***Parameter c (Å)***	***Δc/c (%) (ref. Y3-2)***	***Parameter a (Å)***	***Δa/a (%) (ref. Y3-2)***
Theoretical parameters	6.707	NA	2.461 ± 0.002	NA
Non-irradiated reference Y3-2 (⊥)	6.725 ± 0.002	NA	2.460 ± 0.002	NA
G2-27-3	6.805 ± 0.002	1.19 ± 0.06	2.454 ± 0.002	-0.24 ± 0.16
G2-32-3	6.777 ± 0.002	0.77 ± 0.06	2.454 ± 0.002	-0.24 ± 0.16
G2-42-3	6.775 ± 0.002	0.74 ± 0.06	2.454 ± 0.002	-0.24 ± 0.16
G2-46-2	6.745 ± 0.002	0.29 ± 0.07	2.463 ± 0.002	0.12 ± 0.16

TABLE 14: MESH PARAMETERS OF IRRADIATED G2 SAMPLES

The overall properties of the non-irradiated and irradiated samples provided basic data on the material and particularly on the pore network and the crystal structure, data which are indispensable for studies on the behaviour of the radionuclides in disposal conditions.

4. EXPERIMENTAL MEASUREMENTS OF IMPREGNATION

The impregnation of water in irradiated graphites is the first process leading to the release of the radionuclides present in the graphite. This step, while slow and partial, can control both the kinetics and the release rate of the radionuclides in solution.

Impregnation tests were therefore conducted on non-irradiated and irradiated samples of G2 graphite [3].

The results show that the water impregnation of the non-irradiated graphites from G2 is slow and partial (Figure 20). The maximum saturation rates only reach 30 to 40% of the open porosity of the samples after 500 days. The addition of ethanol, by changing the dielectric constant of the fluid, substantially increases the saturation rate (60%).

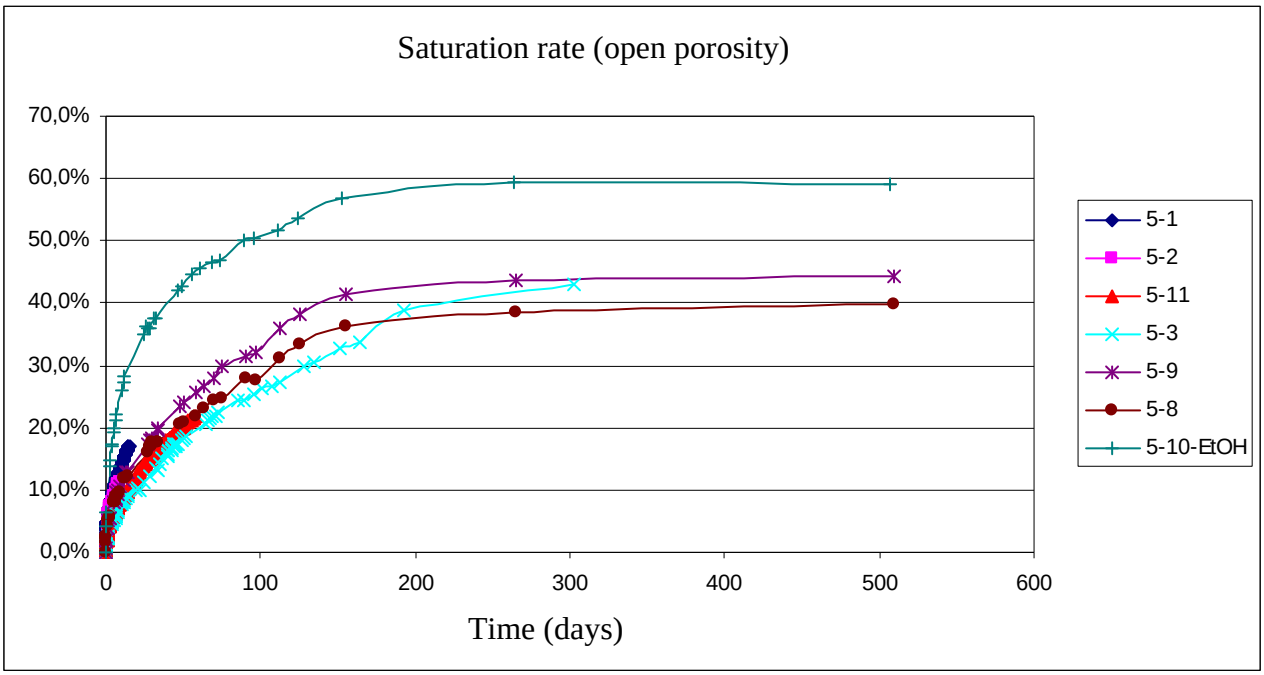


FIGURE 20: SATURATION RATE OF NON-IRRADIATED G2 SAMPLES

The impregnation results on active samples show that irradiation significantly increases the kinetics and the saturation rate on G2 graphites. The impregnation kinetics is faster and the saturation rate with regard to open porosity is close to 100% (Figure 21).

Several processes can explain the effect of irradiation on the water impregnation of graphite:

- Radiolytic corrosion causes an increase in the open porosity. However, this increase is relatively slight (a few per cent), whereas the quantity of water impregnated is doubled in the irradiated samples. On the other hand, it also changes the macroporosity in particular, especially by enlarging the mean pore diameter, as shown by the mercury intrusion porosity spectra, which may facilitate the impregnation of the water.

- Irradiation and radiolytic corrosion cause a failure of C-C bonds in the crystallites and/or the grain boundaries of the graphite to form more hydrophilic C-H or C-O bonds. This causes faster and more complete impregnation.

- Irradiation, coupled with temperature, altered the crystal structure. These changes may induce variations in electrostatic repulsion of the graphite and made it more hydrophilic.

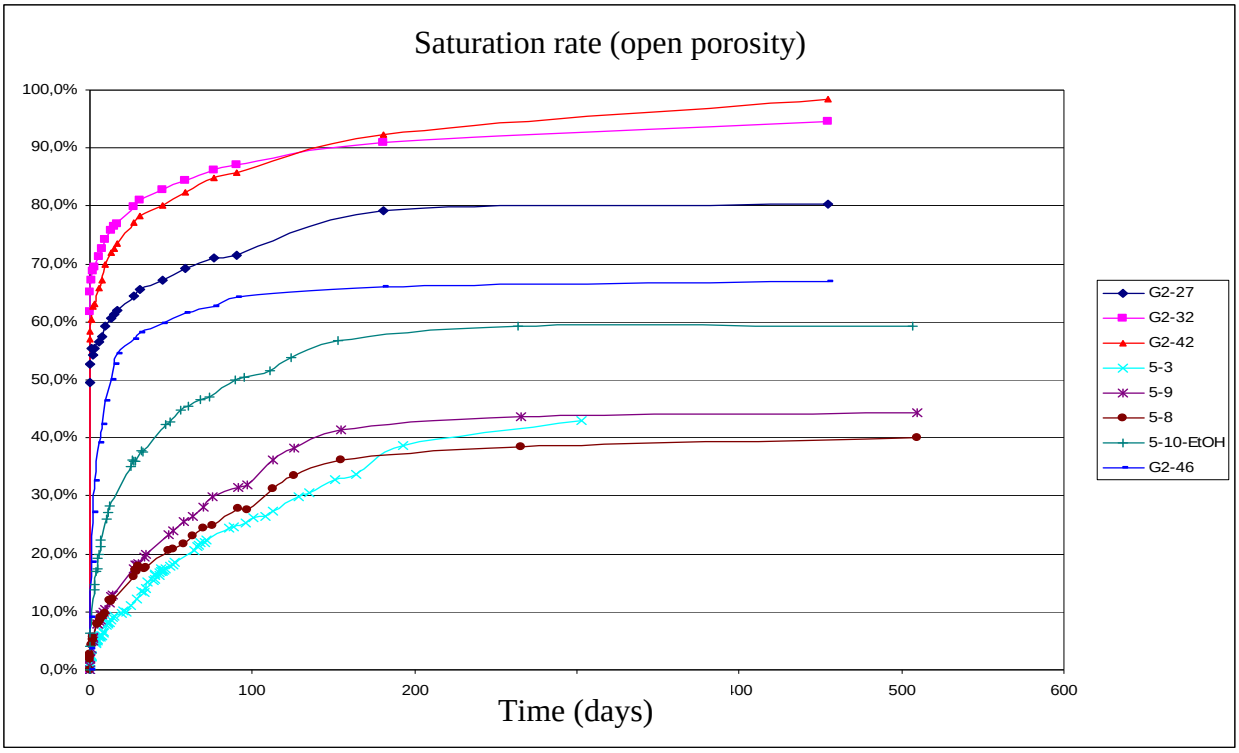


FIGURE 21: COMPARISON OF SATURATION RATES OF NON-IRRADIATED AND IRRADIATED G2 GRAPHITES BASED ON SPECIAL A COKE

5. MEASUREMENT OF INITIAL ACTIVITIES OF SAMPLES

For the needs of the leaching test and in order to have several specimens, cores G2-27, G2-32, G2-42, G2-46 were cut into several samples:

- two samples for the leaching tests,
- three samples taken at the edges and middle of the core,
- the powder produced by the cutting operations represent an average sampling of the core.

Analyses of ^{36}Cl were carried out on each of these samples.

The results are given in the table below.

	G2-27	G2-32	G2-42	G2-46
Isotope	Bq/g	Bq/g	Bq/g	Bq/g
^{3}H	$3.5\pm0.2\times10^{4}$	$4.2\pm0.4\times10^{4}$	$4.2\pm0.3\times10^{4}$	$1.4\pm0.1\times10^{4}$
^{14}C	$2.57\pm0.16\times10^{4}$	$2.24\pm0.15\times10^{4}$	$1.23\pm0.08\times10^{4}$	$4.6\pm0.3\times10^{3}$
^{36}Cl	180±24	149±22	225±50	108±19
^{51}Cr	<25	<18	<11	<8
^{54}Mn	<5	<4	<2	<1,2
^{60}Co	880±50	1200±70	480±28	130±8
^{133}Ba	30±4	25±3	45±3	27±2
^{134}Cs	<3	<2,7	<1,5	<1,0
^{137}Cs	87±8	124±9	24±3	10±2
^{152}Eu	<9	<6	<4	<3
^{154}Eu	94±8	59±5	49±4	136±8
^{155}Eu	18±4	11±2	6±1	17±3

TABLE 15: RADIOCHEMICAL CHARACTERISATION OF G2 SAMPLES – POWDERS

The results are given dated 14 November 2009 – 1 test sample per sample except ^{36}Cl 2 test samples – results provided with an uncertainty enlarged to k=2 dated 27 November 2008.

It may be observed that, on the whole, the reflector is much less active than the moderator, and that the ^{36}Cl activities are about one hundred Bq/g, which is fairly consistent with the values obtained for core G2-36[35].

^{36}Cl measurements were also made on small samples of each edge and middle of the cores (Table 16 and Figure 22). The analysis obtained from the leached samples ("balance tests", see section 6) are also reported (sum of activity after leaching and leached activities).

	Ref.	36Cl (Bq/g)	Ref.	36Cl (Bq/g)	Ref.	36Cl (Bq/g)	Ref.	36Cl (Bq/g)
Edge 1	27-1	230±27	32-1	190±25	42-1	698±80	46-1	7±1
Middle	27-7	180±24	32-6	123±14	42-6	135±17	46-5	115±17
Edge 2	27-8	256±30	32-7	211±24	42-7	1316±150	46-6	15±2
Powder	Powder	180±24	Powder	149±22	Powder	225±50	Powder	108±19
Leaching results	27-7A	132±16	32-6A	126±16	42-6A	154±20	46-5A	162±20

TABLE 16: MEASUREMENT OF ^{36}CL IN SAMPLES OF G2 CORES (2 TEST SAMPLES – RESULTS PROVIDED WITH UNCERTAINTY ENLARGED TO K=2 DATED 1 DECEMBER 2008)

The measurements on the samples used for the leaching tests are closer to those obtained on the central core (middle), produced by the same slice (see cutting drawing) and on the cutting powder. However, the activities measured on samples taken at the edges display wide difference.

These values show the more or less pronounced heterogeneity of the ^{36}Cl activities in the samples. The graphs below show the results as a function of the position of the samples compared to the mean value obtained on the cutting powders.

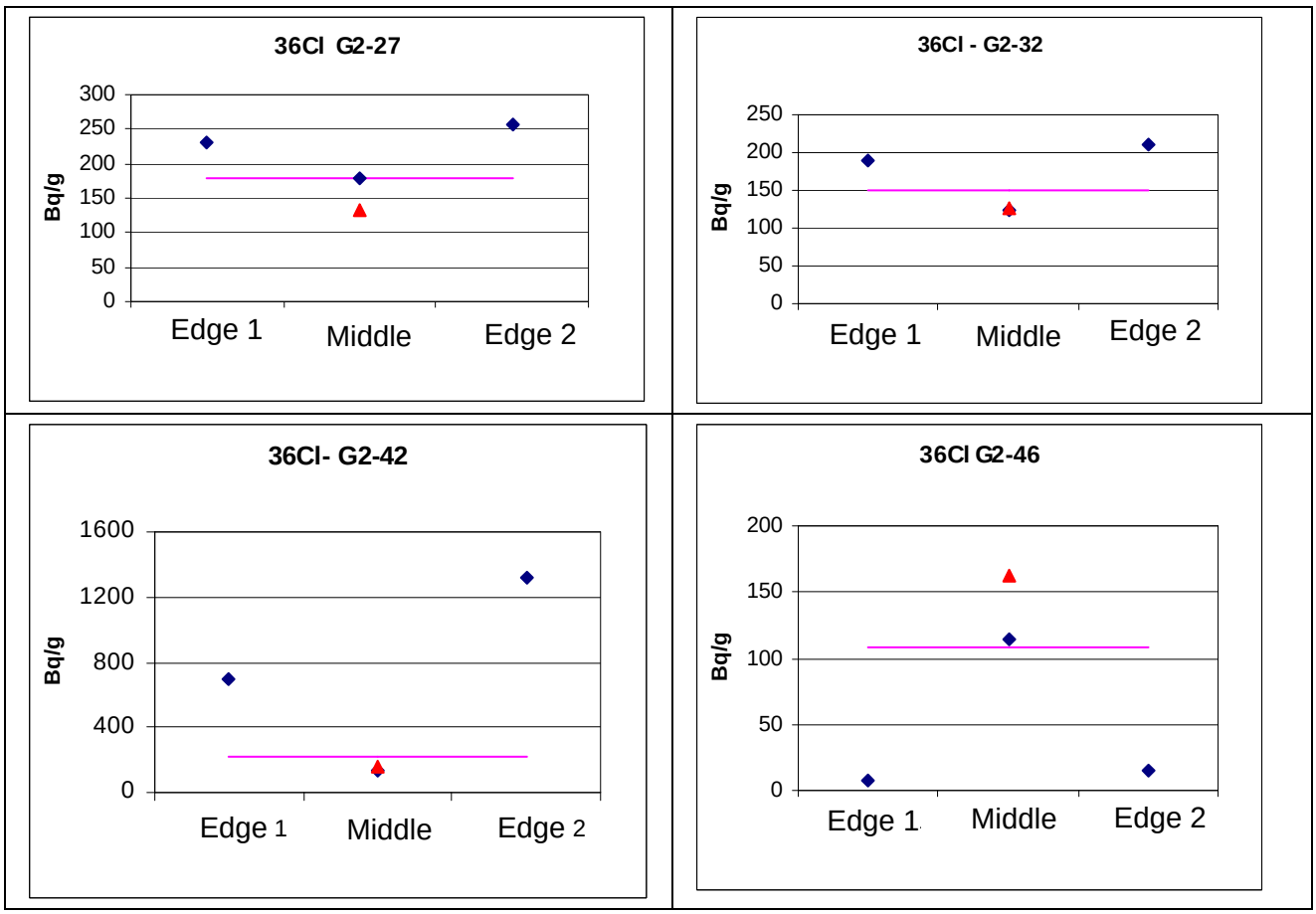


FIGURE 22: CHLORINE-36 DISTRIBUTION IN SAMPLES

Key:
Red: Activity of samples used for leaching tests
Blue: Activity determined on other samples
Purple line: Activity determined on cutting powder

6. LEACHING BEHAVIOUR OF CHLORINE-36

This section deals with the first results obtained on the leaching tests, some of which have not yet been completed. A preliminary summary on the release model is also discussed and presented.

Two series of tests were initiated on the G2 samples:

- one series (called "**balance tests**" below) aimed to continuously measure the water impregnation in the sample and the release of ^{36}Cl in solution in order to establish a correlation between the water saturation rate and the leaching rate. The sample is suspended on the arm of a Sartorius balance and completely immersed in a container filled with ultrapure water (non-sealed reactor). This configuration serves to continuously measure the change in apparent mass of the sample in the water. The measurements were taken during periods of about 10 to 40 days depending on the samples. To determine the longer term kinetics, the samples were then placed in reactors filled with ultrapure water, by preserving the area/volume ratio.
- a series (called "**reactor tests**" below) carried out in a sealed reactor under inert atmosphere on a larger amount of graphite.

FIGURE 23: EXPERIMENTAL DEVICE

The series of "balance test" has been completed. The ^{36}Cl leaching results are presented here. Other data on ^{14}C and the other radionuclides will be addressed later.

The series of "reactor tests" is still under way. The leaching results of ^{36}Cl will not be discussed because of the need to determine the residual activity at the end of the tests to compile ^{36}Cl behaviour.

The measurements are nevertheless reported in Appendix 3. However, new data on stable chlorine and its chemical forms are discussed.

The overall physicochemical conditions are given in Table 17 and the characteristics of the samples are in Appendix 5.

Conditions	"Balance" tests	"Reactor" tests
Leachate	Deionised water	Deionised water
Leachate volume	150 ml	150 ml
Temperature	Ambient	21°C
Reactor	Unrinsed glass	Prewashed glass
Reactor internal volume	250 ml	430 ml
Atmosphere	Non-sealed air	Sealed and flushed by inert gas (N2) after each renewal
Sample type	Cube Mass # 12g (L*l*h =15*15*30 in mm)	Cylindrical lamella Mass # 80g (diam = 63 mm * 15 mm)
Sample A/V	#3.3	# 2
Leachate A/V	#0.15	#0.6
Duration	211 days	610 days
Renewal	Partial on first sequences (16 days) more complete (16 days to 211 days)	Complete at each sequence
Number of sequences	20	20
Samplings	30 min, 1h, 4h, 7h, 24h, 30h, 48h, 54h, 3d, 4d, 7d, 10d, 16d, 21d, 35d, 50d, 63d, 154d, 211d	1h, 6h, 1d, 2d, 3d, 6d, 7d, 9d, 13d, 15d, 17d ,27d, 31d, 45d, 59d, 76d, 90d, 181d, 455d, 610d
Analyses	^{3}H, ^{14}C, ^{36}Cl, gamma spectrometry, ion chromatography	^{3}H, ^{14}C, ^{36}Cl, gamma spectrometry, ion chromatography, TOC, pH

TABLE 17: PHYSICOCHEMICAL CONDITIONS OF LEACHING TESTS

6.1. Results

The tables of results given in Appendix 3 show the activities measured in Bq in each sampling of each test and the residual activity in Bq measured on the samples at the end of leaching. For each analysis on solution (sampling sequence), the results are given with a large uncertainty of k=2 dating from the start of the leaching test. The principle of the analytical methods is given in Appendix 2.

The leached fractions and cumulative activities were calculated when the measured activities were significant or when the detection limits, particularly in the leachate solutions, are sufficiently low in comparison with the final activity to be ignored in calculating the cumulative activities and leached fractions.

As stated in the section "measurement of initial activities of samples", the heterogeneity of the samples, especially for ^{36}Cl, needs compiling a complete inventory of the sample. After the final sampling, the sample is drained and dried with absorbent paper. The graphite samples are then completely ground under a press in a cell in the nuclear facility Chicade. Grinding was carried out with all the usual precautions. The "press" station is systematically cleaned between each sampling (top end bottom plates, vinyl protection, etc.). The sample grinding conditions are the same as those used for the characterisation analysis. The analytical methods applied are given in Appendix 2.

6.2. Results of ^{36}Cl leaching tests

The final analyses were performed on four samples of the "balance tests". After 210 days of leaching, the residual ^{36}Cl activity of the samples is found to be higher, ranging from 16 to 50 Bq/g.

	G2-27-7	**G2-32-6**	**G2-42-6**	**G2-46-5**
	Bq/g	**Bq/g**	**Bq/g**	**Bq/g**
^{36}Cl	50±6	42±6	16±2	42±5

TABLE 18: FINAL ANALYSIS OF SAMPLES AFTER LEACHING

The analyses are provided with uncertainty k=2. Two subsamples were analysed.

The ^{36}Cl release profiles are shown for the four samples in the figures below in time and in the square root of time.

For the samples from the moderator, the release of chlorine 36 is fast over a period of a few days, and then decreases sharply with a very slow change after 30 days. For the reflector sample, the chlorine 36 release kinetics is slower. The graph as a square root of time shows in particular for the moderator samples that the release appears to be a linear law in the first leaching sequences. This behaviour can be treated as a diffusion process.

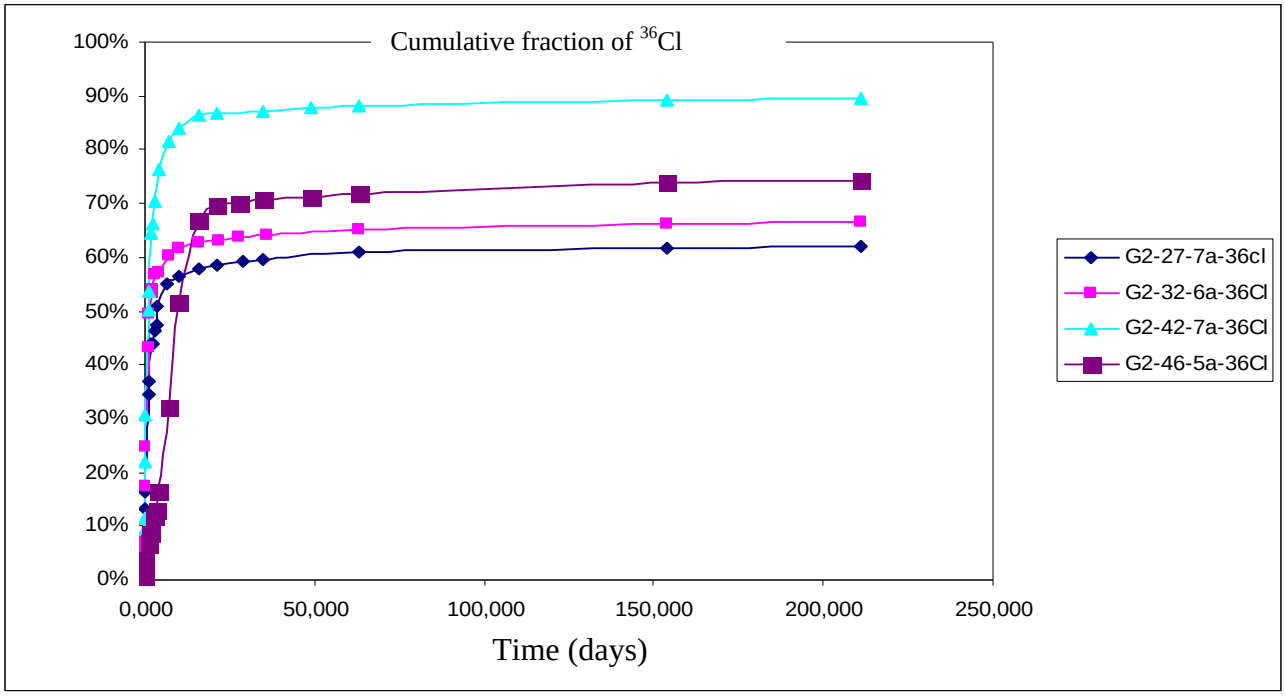


FIGURE 24: LEACHING KINETICS OF ^{36}CL FOR "BALANCE TESTS"

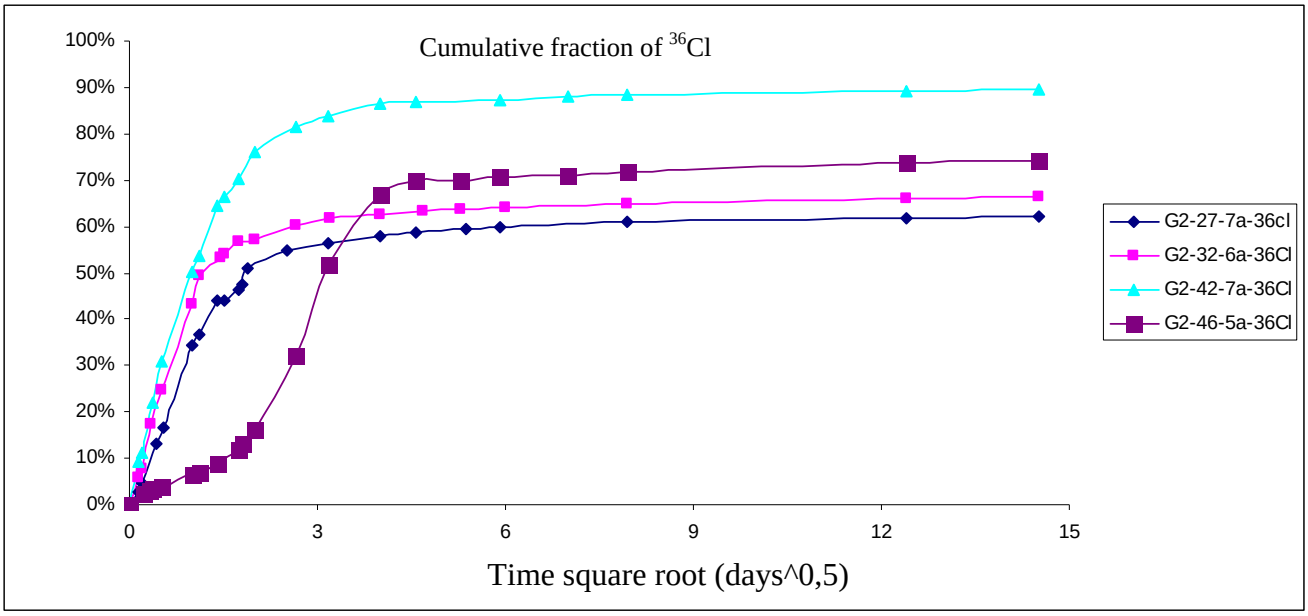


FIGURE 25: LEACHING KINETICS OF ^{36}CL FOR THE "BALANCE TEST" EXPRESSED AS A SQUARE ROOT OF TIME

The leaching rates obtained at the end of the tests vary according to the samples and are lower than those obtained for core No. 36 of the study conducted in 2004-2006 (Table 19).

Sample No.	Position	initial coke	Sampling level (m)	Temperature (°C)[38]	Leaching rate (Tf)
G2-27	Moderator	Special A coke	13.60-13.80	327	62±5%
G2-32	Moderator	Special A coke	14.60-14.80	320	67±6%
G2-36	Moderator	Special A coke	15.40-15.60	314	90±3%
G2-42	Moderator	Special A coke	16.60-16.80	309	90±8%
G2-46	Reflector	Lockport coke	17.40-17.60	284.7	74±6%

TABLE 19: LEACHING RATES OF G2 TESTS

6.3. Results of stable chlorine leaching

In each leaching sequence, the various forms of chlorine in solution were determined by ion chromatography: chloride Cl^- (-I), chlorite ClO_2^- (+III), chlorate ClO_3^- (+V) and perchlorate ions ClO_4^- (+VII).

The tables of results are given for each test in Appendix 4. For the “balance tests” the measured values are extremely low, close to the quantification limit of the determination method. This means that the results are associated with a high uncertainty. For the “reactor tests”, the measured concentrations are higher and display a lower uncertainty.

The results (Figures 26 & 27) show that the chloride and chlorite forms were detected with values higher than the quantification limit of the method (about 10 µg/L).

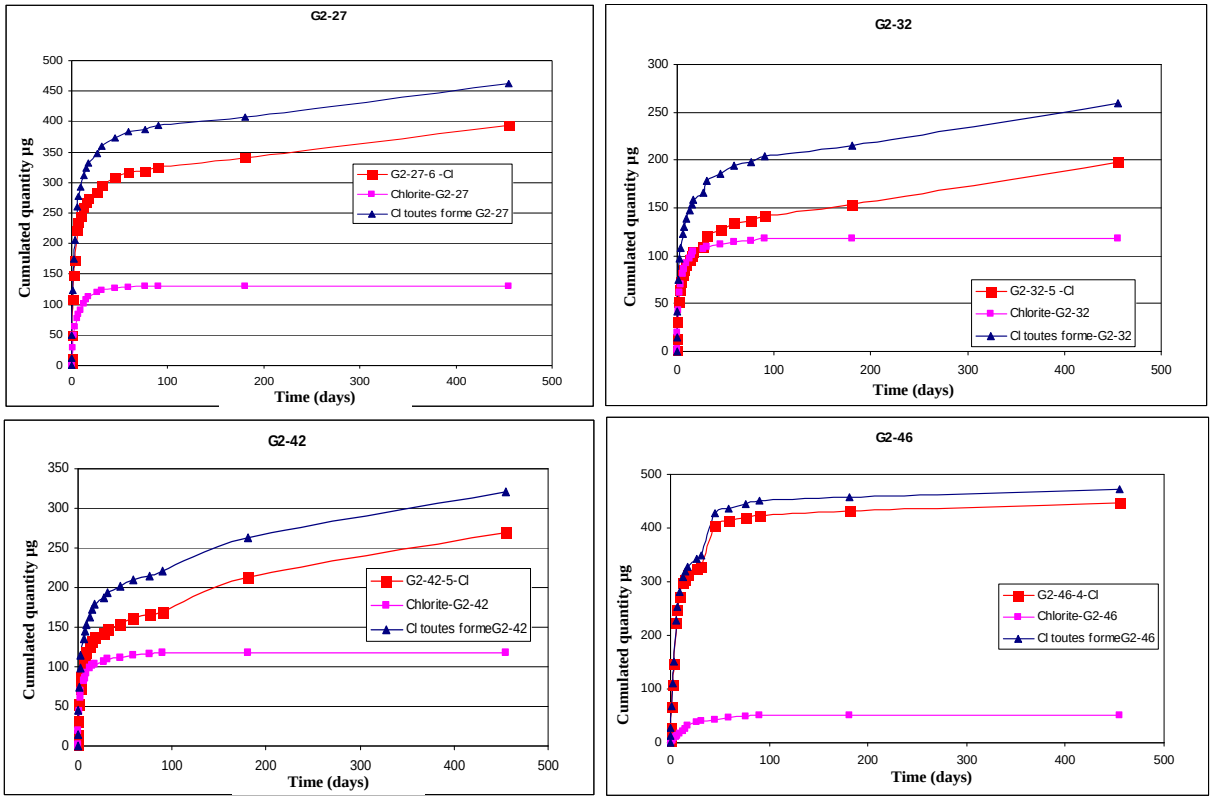


FIGURE 26: CHLORINE RELEASE AND MEASUREMENT OF ITS SPECIATION (“REACTOR TESTS”)

For the “reactor tests”, the ratio between the two species varies with the samplings. In particular, it is observed that in the final sampling sequences, the chlorites are no longer detected. However, this must be seen with caution because a degradation of the chlorites to chloride cannot be excluded. Conversely, the chloride release continues to increase over time.

This behaviour is less pronounced than for the “balance tests”, but the quantities measured are smaller because a lower mass of graphite was used.

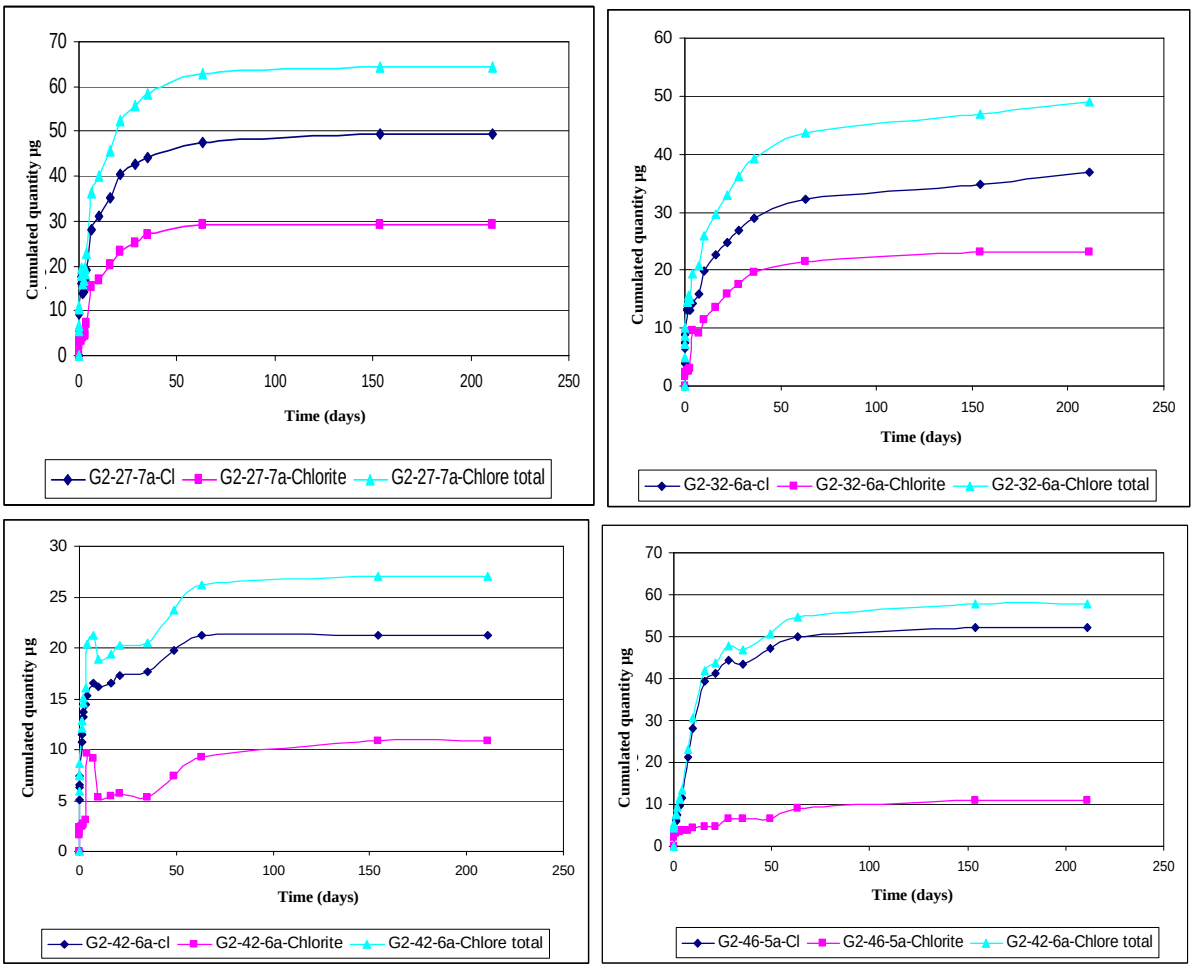


FIGURE 27: CHLORINE RELEASE AND MEASUREMENT OF SPECIATION "BALANCE TESTS")

The two series of tests are nevertheless fairly consistent because the quantities of total chlorine released in solution calculated per gram of graphite are fairly similar (2 to 5 ppm, Table 20). The chloride/chlorite distribution expressed in moles is about 75 to 90%.

	G2-27			G2-32		
	Cl-	ClO2-	Cl tot	Cl-	ClO2-	Cl tot
Reactor tests Quantity leached (µg)	395±46	130±23	463±58	197±32	118±27	260±46
Quantity leached (g/g graphite)	$4.9\pm0.6\times10^{-6}$	$1.6\pm0.3\times10^{-6}$	$5.8\pm0.7\times10^{-6}$	$2.7\pm0.4\times10^{-6}$	$1.6\pm0.4\times10^{-6}$	$3.6\pm0.6\times10^{-6}$
Distribution %	#85	#15		#75	#25	
Balance test Quantity leached (µg)	49±15	29±15	65±23	37±15	23±15	49±24
Quantity leached (g/g graphite)	$4.1\pm1.2\times10^{-6}$	$2.4\pm1.2\times10^{-6}$	$5.3\pm1.9\times10^{-6}$	$3.5\pm1.4\times10^{-6}$	$2.2\pm1.6\times10^{-6}$	$4.6\pm2.3\times10^{-6}$
Distribution %	#76	#24		#75	#25	

	G2-42			G2-46		
	Cl-	ClO2-	Cl tot	Cl-	ClO2-	Cl tot
Reactor test Quantity leached (µg)	270±37	96±27	321±51	346±42	51±23	396±57
Quantity leached (g/g graphite)	$3.3\pm0.5\times10^{-6}$	$1.2\pm0.3\times10^{-6}$	$3.9\pm0.6\times10^{-6}$	$4.3\pm0.5\times10^{-6}$	$6\pm3\times10^{-7}$	$4.9\pm0.7\times10^{-6}$
Distribution %	#84	#16		#93	#7	
Balance test Quantity leached (µg)	21±12	10.9±8.1	27±16	52±15	11±6	58±18
Quantity leached (g/g graphite)	$1.6\pm0.9\times10^{-6}$	$8\pm6\times10^{-7}$	$2\pm1\times10^{-6}$	$4.4\pm1.3\times10^{-6}$	$9\pm5\times10^{-7}$	$5\pm2\times10^{-6}$
Distribution %	#79	#21		#90	#10	

TABLE 20: QUANTITY OF STABLE CHLORINE LEACHED AND DISTRIBUTION BETWEEN CHLORIDE AND CHLORITE

Using the Cl and ^{36}Cl analyses, the isotopic ratios were calculated for each sampling (Figure 28). The variation over time shows that ^{36}Cl is preferentially leached at the start of the test with a net enrichment. The isotopic ratio then decreases. This result shows that Cl and ^{36}Cl do not have the same behaviour, which suggests that they are not in the same chemical form or that they are not located on the same sites in the graphite.

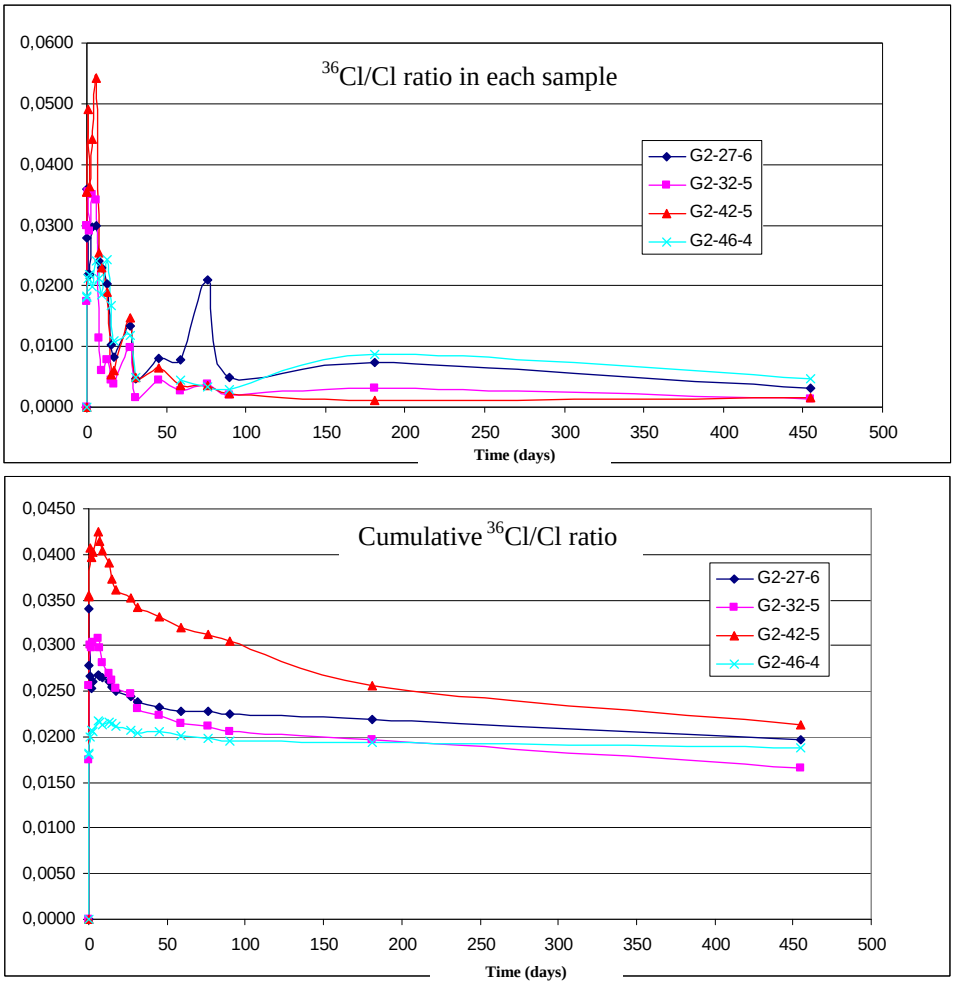


FIGURE 28: ^{36}CL/CL RATIO. VARIATION OVER TIME

6.4. Discussion

The chlorine release kinetics can be controlled by several processes, and particularly:

- the water impregnation kinetics in the pores of the graphite. Considering the hydrophobic nature of graphite, the arrival of water on the chlorine sites may be a limiting factor. However, we showed that irradiation substantially accelerates the impregnation kinetics,
- the diffusion of solubilised chlorine through the pores of the graphite. In previous studies, we demonstrated a consistency of the data between the diffusion coefficients obtained from the leaching tests and those measured by the diffusion tests,
- the existence of several chemical forms of chlorine in the graphite. The measurements taken by XPS and EXAFS on non-irradiated graphite samples reveal the existence of a majority organic form of chlorine and the possible existence of an inorganic form.
- a chlorine distribution in the graphite that is both in the pores accessible to water and also in the nanoporosity and the microstructure of the graphite (in the grains, graphene plane), inaccessible to water. Previous studies on G2 and Bugey showed different leaching behaviour with a “labile” form which displays a very fast release kinetics controlled by diffusion of the solubilised chlorine through the pores of the graphite, and a form that displays a much slower release kinetics.

These overall assumptions are discussed below.

Control of ^{36}Cl release by water impregnation kinetics in graphite

A comparison of the water impregnation kinetics with those of the ^{36}Cl release is shown in the figure 24, for which the leached ^{36}Cl release rate is plotted as a function of the water saturation rate of the sample.

The shape of the curves for the samples of the moderator show:

- A first period for which the water impregnation is very fast compared to chlorine leaching. This can be explain by an impregnation of water in the largest pores. Since this period is very short (a few hours), a few amount of ^{36}Cl is solubilised,
- A second period during which most of the chlorine is leached, whereas the water impregnation of the graphite changes very slightly (about 10% for the moderator samples). This period represents about 30 days for which the “labile” chlorine is completely leached,
- A final period is marked by a slow water impregnation in the smallest pores of the graphite, associated with a very low leaching rate of ^{36}Cl.

This less pronounced tendency is also observed for the moderator sample.

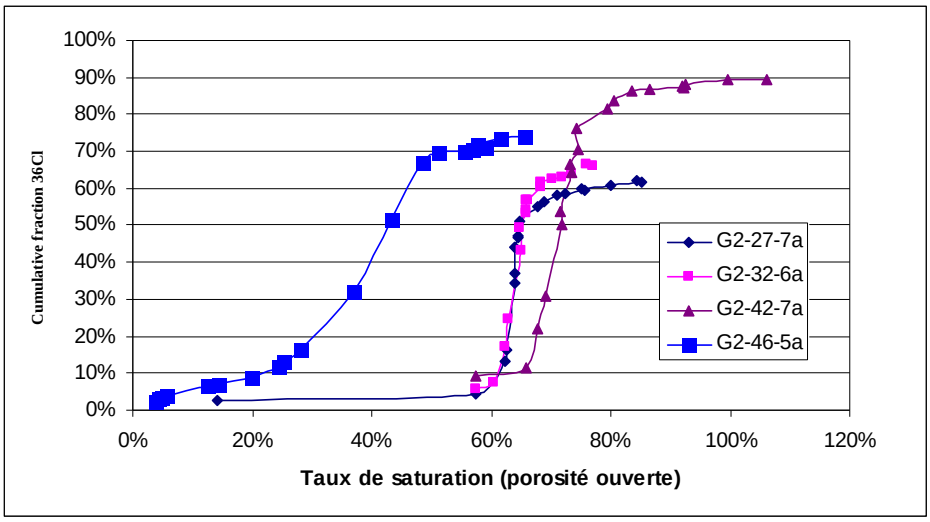


FIGURE 29: CORRELATION BETWEEN ^{36}CL RELEASE RATE AND SATURATION RATE

An absence of a linear correlation shows that the process of water impregnation in the irradiated graphite samples does not alone control the release of ^{36}Cl in solution.

Control of ^{36}Cl release by diffusion through the pores

In previous studies, we examined the eventuality of the control of chlorine leaching by diffusion through the pores of the graphite. The apparent coefficient determined from these tests is about 2.5×10^{-11} m^2/s.

Identical calculations were performed on the new leaching tests by adjusting the value of the diffusion coefficients to resume the experimental data according to the equation:

$$F = 2.\frac{S}{V}.\sqrt{\frac{D_a.t}{\pi}}$$

F: Leached fraction
S: Geometric area subject to leaching
V: Geometric volume of sample
t: Time
D_a: Apparent diffusion coefficient

The calculations were carried out exclusively considering the fraction of labile chlorine (normalisation of release to 100% of labile chlorine). The values of the apparent diffusion coefficient for the moderator samples determined on the two series of tests are very similar and vary from 1.3×10^{-11} m^2/s to 4.6×10^{-11} m^2/s with a mean of 3×10^{-11} m^2/s (Table 21). These values agree with the values determined in previous studies for G2 from leaching tests, and also from diffusion tests (2.5×10^{-11}

m^2/s). These new data are more accurate and more reliable than those obtained in the studies of 2004-2006, because the sampling times were adjusted in order to have a larger number of samples at the start of leaching during the period of labile chlorine release.

Sample No.	Type	$D_{a\ reactor}$ m^2/s	$D_{a\ balance}$ m^2/s
G2-27	Moderator	2.4×10^{-11}	1.3×10^{-11}
G2-32	Moderator	4.6×10^{-11}	3.4×10^{-11}
G2-42	Moderator	3.3×10^{-11}	2.2×10^{-11}
G2-46	Reflector	1.7×10^{-11}	1.0×10^{-12}

TABLE 21: APPARENT DIFFUSION COEFFICIENT DETERMINED FROM LEACHING TESTS OF "REACTOR AND BALANCE" TESTS

For the moderator, graphite based on Lockport coke, the values of the diffusion coefficients determined appear to be lower and about 9×10^{-12} m^2/s.

The experimental curves are compared with the simulated curves in Figure 30.

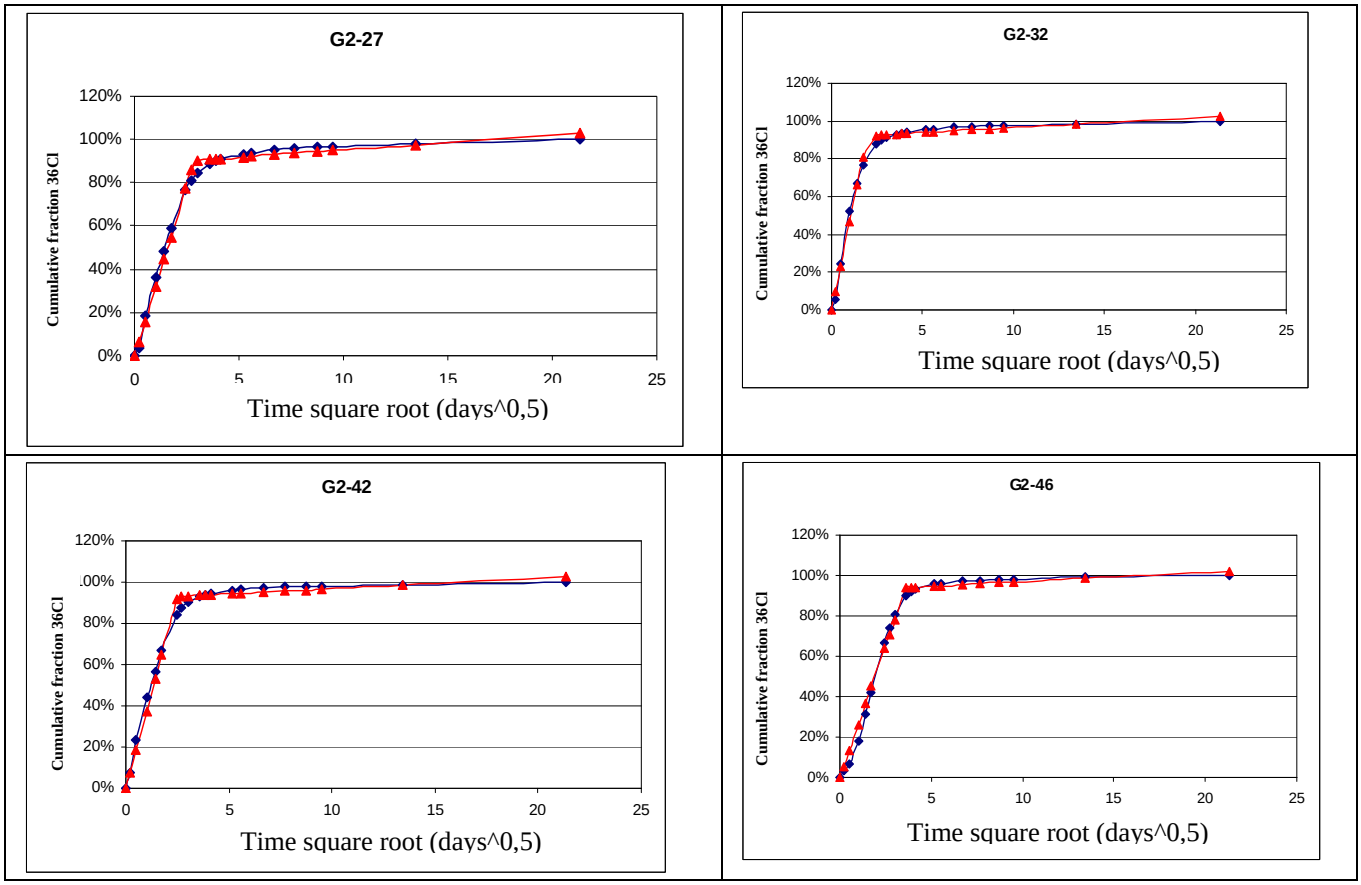


FIGURE 30: COMPARISON OF LEACHED ^{36}CL RATES WITH DIFFUSION MODEL

Experimental points in blue – model points in red, case of reactor tests

These results confirm the assumption of the control of labile ^{36}Cl release by diffusion through the pores of the graphite.

The various chemical forms and/or location of the chlorine

The leaching tests appear to reveal two different types of behaviour for ^{36}Cl:

- a "labile" fraction which displays a very fast release in solution controlled by diffusion through the pores of the graphite,
- a second fraction whose leaching kinetics is much lower. The results obtained on Bugey had shown that a correlation existed between the quantity of "labile" chlorine and position of the sample in the reactor.

To confirm this assumption, all the tests in the literature and those performed in connection with this study were considered (Table 22 and Figure 31). With the exception of one sample, the data reveal a correlation between the fraction of "labile" ^{36}Cl and the temperature of the sample, despite the many differences in the protocols employed.

Date	Sample reference	Irradiation °C [38]	Fraction of activity released ^{36}Cl	Test lab
1988	H-13	347	2%	CEA
1988	H-14	334,7	1%	CEA
1989	H13-North South	347	4%	PNL
1989	H14-Sup Nord	334,7	39%	PNL
1991	H12	347	20%	CEA
1991	H15	337,1	53%	CEA
2004	G2-36	314	90%	CEA
2009	G2-27	327	62%	CEA
2009	G2-32	320	67%	CEA
2009	G2-42	309	90%	CEA

TABLE 22: CORRELATION BETWEEN FRACTION OF LABILE ^{36}CL AND SAMPLE TEMPERATURE DURING OPERATION IN REACTOR

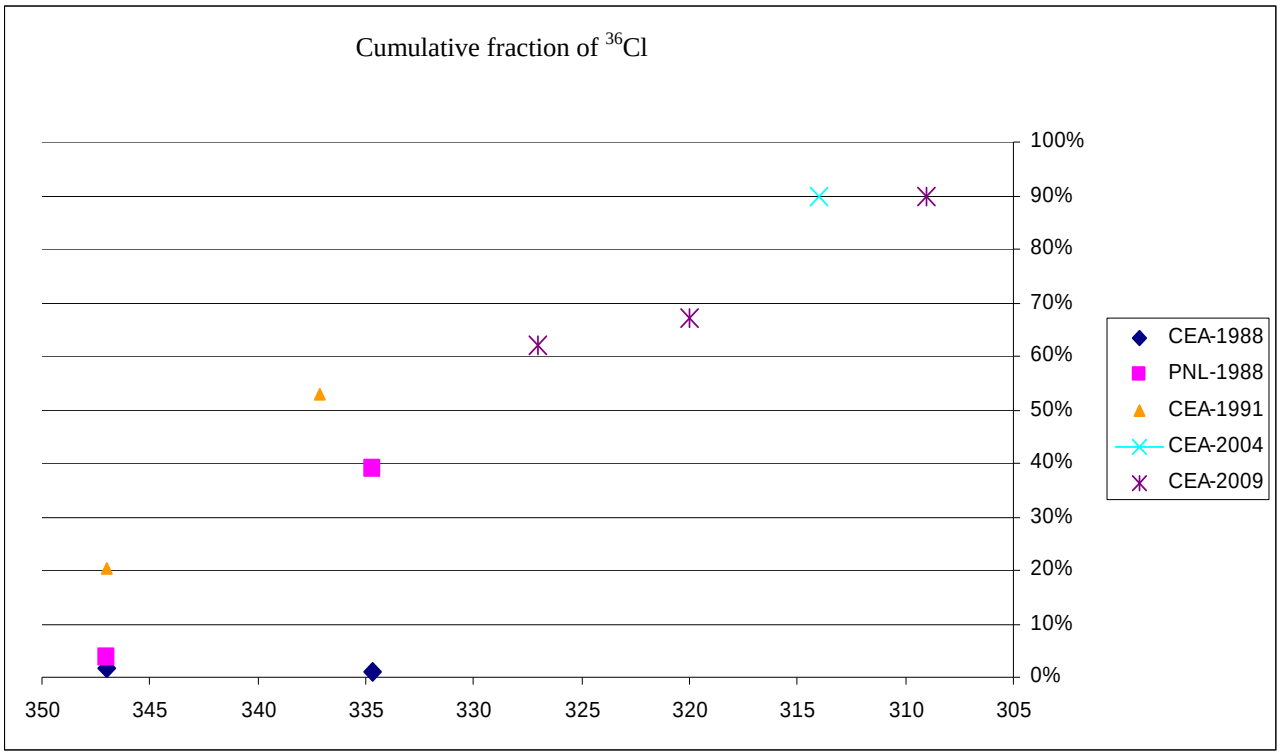


FIGURE 31: FRACTION OF ^{36}CL RELEASED AS A FUNCTION OF GRAPHITE TEMPERATURE IN THE STACK

Several assumptions can be discussed to explain these two different behaviour patterns:

- with identical chemical form, ^{36}Cl is distributed differently in the samples; the "labile" form represents the quantity accessible to water distributed at the pores of the material, whereas the "non-labile" form is located in the microstructure of the graphite which is inaccessible to water. This distribution varies according to the thermal/neutron history of the sample.
- ^{36}Cl exists in several chemical forms with a rapidly leachable chemical form and a more stable form which dissolves more slowly in solution.

The current data do not allow any conclusion and new studies are required to discuss/confirm one of these assumptions.

SUMMARY AND CONCLUSIONS

The new data collected during this study made it possible to :

- characterise the graphite and its porosity,
- measure the water impregnation kinetics in graphite,
- study the behaviour of ^{36}Cl in relation to the position of the sample in the reactor.

The main conclusions that can therefore be drawn are :

- Water impregnation in accessible porosity occurs rather fast and does not control the release of ^{36}Cl in solution,
- There is a correlation between the sample temperature during reactor operation and the quantity of labile ^{36}Cl,
- The release kinetics of labile ^{36}Cl can be described by a diffusion model of chlorine dissolved through the graphite porosity,
- Stable chlorine and ^{36}Cl have not the same behaviour. This result suggest that they are not in the same chemical form in graphite or that their distribution/ location is different,
- Two chemical forms of stable chlorine were identified in solution during leaching tests: a chloride form (the must abundant) and a chlorite form.

The reactor tests will soon be finished and will complete the preliminary data.

Future prospects for this research consist in focusing on analysing the "non labile" fraction with the aim of understand if it is a different chemical form or if this fraction is located in the structure (in the grains, the graphene plane, etc.) not accessible to water. The experimental tests will involve studying the behaviour of ^{36}Cl with different water chemistry, particularly in water with a high pH which is more representative of waste storage in cement environments. These tests will also help study ^{36}Cl by de-structuring the graphite (e.g. under ultrasounds) so that water can access other chlorine sites.

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APPENDIX 1

Leaching test conditions recorded in the literature for tests on stack graphite

Ref: sample reference (for G2: H = horizontal coring, V = vertical coring)
UP water: ultra pure water (for French tests – de-ionised water with a resistivity of 18.2 MΩ at the purification device outlet
E: tests performed in leaktight reactors to limit the evaporation of the leaching solution or A.I: tests performed in leaktight reactor with inert atmosphere (Ar, N2)
R: leaching solution renewed (C: completely renewed for each sequence, P: partially renewed for each sequence)
V/Se: sample volume/surface ratio - V/Sl : ratio between the leaching solution volume and the sample surface

G2 reactor graphite – stack (reference: 27, 28, 30, 31, 35)

Date	Sample ref.	Coke	Test lab	Lixiviant	Temp. °C	Atm	R	Weight (g)	Diam (mm)	H (mm)	ρ (g/cm3)	V (cm^3)	S (cm^2)	Vol mL	V/Se cm	V/Sl cm	Duration (days)
1988	H-2	Lockport	CEA	UP water	20	E	C	641,5	78	80	1,68	382	301,00	3000	1,27	9,97	90
1988	H-13	Special A	CEA	UP water	20	E	C	628	78	80	1,64	382	301,00	3000	1,27	9,97	90
1988	H-14	Special A	CEA	UP water	20	E	C	643,6	78	80	1,68	382	301,00	3000	1,27	9,97	90
1989	H13-Nord Sub	Special A	PNL	UP water	20	E	C	36,2			1,63	21,21	43,80	406	0,48	9,27	91
1989	H14-Sup Nord	Special A	PNL	UP water	20	E	C	37,01			1,66	21,21	43,80	406	0,48	9,27	91
1989	2-BA	Lockport	PNL	UP water	20	E	C	37,27			1,66	21,21	43,80	406	0,48	9,27	91
1991	H12	Special A	CEA	UP water alkaline	20	E	C	47	33	33	1,67	28,22	51,32	500	0,55	9,74	90
1991	H15	Special A	CEA	UP water alkaline	20	E	C	47	33	33	1,67	28,22	51,32	500	0,55	9,74	90
2004	V36-2	Special A	CEA	UP water	20	A.I.	C	87,2746	63,15	16,75	1,66	52,46	95,87	150	0,55	1,56	455
2004	V36-6	Special A	CEA	UP water	20	A.I.	C	74,8385	63,2	15,2	1,57	47,68	92,92	150	0,51	1,61	455
2004	V36-9	Special A	CEA	UP water	20	A.I.	C	90,0182	63,25	17,45	1,64	54,83	97,51	150	0,56	1,54	455
2004	V36-5	Special A	CEA	lime water	20	A.I.	C	72,8569	63,3	14,15	1,64	44,53	91,08	150	0,49	1,65	455
2004	V36-8	Special A	CEA	lime water	20	A.I.	C	90,7171	63,15	17,55	1,65	54,97	97,46	150	0,56	1,54	455
2004	V36-10	Special A	CEA	lime water	20	A.I.	C	90,656	63,25	17,6	1,64	55,30	97,81	150	0,57	1,53	455

Handford Reactor B graphite (reference: 27, 28)

Date	Sample ref.	Coke	Test lab	Lixiviant	Temp. °C	Atm	R	Weight (g)	Diam (mm)	H (mm)	ρ (g/cm3)	V (cm^3)	S (cm^2)	Vol mL	V/Se cm	V/Sl cm	Duration (days)
1988	HGW-25-N°2		PNL	ground water – pH 8.3	25	E	C	36,013	30,51	30,099	1,64	22,00	43,46	406	0,51	9,34	56
1988	HGW-90-N°1		PNL	ground water – pH 8.3	90	E	C	36,6767	30,47	30,607	1,64	22,31	43,88	406	0,51	9,25	56
1988	DIW-25-N07		PNL	UP water	25	E	C	35,7013	30,52	30,5562	1,64	22,35	43,93	406	0,51	9,24	56
1988	DIW-50N°5		PNL	UP water	50	E	C	36,503	30,48	30,5054	1,64	22,26	43,80	406	0,51	9,27	56
1988	DIW-90N°3		PNL	UP water	90	E	C	36,5645	30,35	30,5562	1,65	22,11	43,61	406	0,51	9,31	56
1989	D1		CEA	UP water	23	E	C	631,39	79,4	79,1	1,61	391,66	296,34	3000	1,32	10,12	91
1989	E2		CEA	UP water	23	E	C	636,24	79,6	79,4	1,61	395,13	298,08	3000	1,33	10,06	91
1989	G3		CEA	UP water	23	E	C	642,62	79,5	79,2	1,63	393,14	297,09	3000	1,32	10,10	91

Date	Sample ref.	Coke	Test lab	Lixiviant	Temp. °C	Atm	R	Weight (g)	Diam (mm)	H (mm)	ρ (g/cm3)	V (cm^3)	S (cm^2)	Vol mL	V/Se cm	V/Sl cm	Duration (days)
?	Magnox	?	?	simulated ground water	25	1 bar				48		18690	4251,36	250,	0,66	1,90	100
?	Magnox	?	?	demineralised water	20	1 bar				48		14805	5436,41	300,	0,66	2,30	100
?	Magnox	?	?	sea water	2,5	450 Bar				48		14812	5411,72	278,	0,66	2,10	100
?	Magnox	?	?	sea water	20 23	1 bar				26		18698	4246,82	125,	0,66	1,40	100

Bugey reactor (reference: 36, 37)

Date	Sample ref.	Coke	Test lab	Lixiviant	Temp. °C	Atm	R	Weight (g)	Diam (mm)	H (mm)	ρ (g/cm3)	V (cm^3)	S (cm^2)	Vol mL	V/Se cm	V/Sl cm	Duration (days)
2006	N87	Lima	CEA	UP water	20	E	C	1,4857	powder < 200 µm					10			93
2006	N67/68	Lima	CEA	UP water	20	E	C	1,48	powder < 200 µm					10			93
2006	N 88	Lima	CEA	UP water	20	E	C	1,54	powder < 200 µm					10			93
2002	N55	Lima	CEA	UP water	20	A.I.	P	11,347	16,37	33,4	1,61	7,03	21,37	20	0,33	0,94	455
2002	N58	Lima	CEA	UP water	20	A.I.	P	9,56	16,45	30	1,50	6,37	19,74	20	0,32	1,01	455
2002	N75	Lima	CEA	UP water	20	A.I.	P	11,61	16,3	33,4	1,67	6,97	21,27	20	0,33	0,94	455
2002	N76	Lima	CEA	UP water	40	A.I.	P	9,383	16,45	32,8	1,35	6,97	21,19	20	0,33	0,94	144
2002	N85	Lima	CEA	UP water	40	A.I.	P	11,935	16,59	33,4	1,65	7,22	21,72	20	0,33	0,92	144
2002	N86	Lima	CEA	UP water	40	A.I.	P	6,457	16,53	21,5	1,40	4,62	15,44	20	0,30	1,30	144
2002	N57	Lima	CEA	lime water	20	A.I.	P	8,191	16,48	28,7	1,34	6,12	19,11	20	0,32	1,05	455
2002	N59	Lima	CEA	lime water	20	A.I.	P	9,508	16,1	32,6	1,43	6,63	20,55	20	0,32	0,97	455
2002	N98	Lima	CEA	lime water	20	A.I.	P	10,94	16,8	30,4	1,61	6,80	20,59	20	0,33	0,97	455

APPENDIX 2

Analytical methods

Dissolution of graphites: LARC MO 038 Index 0

A sample of about 1 g is dissolved in hot acid medium with recovery of volatiles (^{3}H and ^{14}C) in a series of traps. Due to the difficulty of dissolving this type of matrix, the attack time is long, about 48 hours. At least two dissolution sets are performed per sample. A systematic blank is provided in the same conditions. All the reactants used are of "analytical grade".

Determination of gamma activity by gamma spectrometry: Analytical method LARC MA 014 Index B

On 50 ml of attack solution, a gamma spectrometry is performed in normalised 50 ml geometry. The results are given by date of activity on 1 July 2006.
Apparatus: 100% gamma spectrometry circuit

Determination of gamma activity by gamma spectrometry on solid

On the entire core, a solid gamma spectrometry is performed in a normalised flask. The results are expressed in Bq/g but are given for information. The results are given on the date of activity at the start of the leaching tests.

Determination of ^{3}H: Analytical method LARC MA 030 Index 0

On an aliquot of the attack solution, the tritium is separated by distillation before counting by liquid scintillation.
Reference of standard solution of ^{3}H: H3-ELSB-50-5021/17, DAMRI
Apparatus: Quantulus liquid scintillator, Wallac

Determination of ^{14}C: Analytical method LARC MA 001 Index B

On an aliquot of basic traps, CO_2 is separated. The CO_2 is released and trapped in a specific ^{14}C scintillating liquid before measurement by liquid scintillation.
Reference of standard solution of ^{14}C: C14 - ELSB 30 7037/7, DAMRI
Apparatus: Quantulus liquid scintillator, Wallac

Determination of ^{36}Cl: Analytical method LARC MA 040 Index 0

On each ground sample, at least two test samples weighing about 0.6 g of graphite were prepared. On each test sample, mineralisation is carried out by combustion in a bomb under oxygen pressure. The chlorine contained in the solution is then separated by precipitation and ion chromatography. The final fraction is measured by liquid scintillation.
Reference of standard solution of ^{36}Cl: Cl36-ELSB-30 No. 4806, DAMRI
Apparatus: Quantulus liquid scintillator, Wallac

APPENDIX 3

^{36}Cl leaching results

The following notations are adopted for the tables of results:

(a)$_i$: *Values of activities measured in Bq in leaching sequence No. i.*

A$_{residual}$: *Residual activity after leaching sequences in Bq.*

(A)$_i$: *Cumulative values of activities measured in leaching sequence No. i.*

FL: *Percentage of cumulative leached activities in leaching sequence No. i (sum of leached activities over sum of activities measured in the leaching sequences and after leaching expressed in %).*

A total: *Sum of activities (in Bq) determined in leachates and residual activity in graphite after leaching.*

Ao: *Sum (expressed in Bq/g) of activities determined in the leachates and residual activity in graphite after leaching*

The results are provided with a large uncertainty of k=1 dated at the start of the leaching tests.

Leached activities measured on each sequence, cumulative leached activities and fractions of activities released for ^{36}Cl from samples 27 and 32 ("balance tests").

G2-27-7					G2-32-7				
date	days	Bq seq.	Bq cumul.	%	date	days	Bq seq.	Bq cumul.	%
08/09/2008	0	0	0	0%	15/09/2008	0	0	0	0%
08/09/2008	0,021	43±3	43,5±3	2,7±0,3%	15/09/2008	0,021	76±5	76±5	5,8±0,5%
08/09/2008	0,042	31±2	74,2±4	4,6±0,4%	15/09/2008	0,042	25±2	101±6	7,7±0,7%
08/09/2008	0,17	139±8	213±13	13,2±1,1%	15/09/2008	0,125	128±8	229±14	17,3±1,5%
08/09/2008	0,29	51±3	264±16	16,4±1,4%	15/09/2008	0,25	100±6	329±20	25±2%
09/09/2008	1	290±17	554±33	34,5±3%	16/09/2008	1	242±15	572±34	43±4%
09/09/2008	1,25	37±2	591±35	37±3%	16/09/2008	1,25	83±5	655±39	49±4%
10/09/2008	2	113±7	705±42	44±4%	17/09/2008	2,10	51±3	705±42	53±5%
10/09/2008	2,27	3,2±0,2	708±42	44±4%	17/09/2008	2,25	11,5±0,7	717±43	54±5%
11/09/2008	3,	39±3	747±45	46±4%	18/09/2008	3	34±2	751±45	57±5%
11/09/2008	3,25	13±1	761±46	47±4%	19/09/2008	4	3,6±0,2	754±45	57±5%
11/09/2008	3,5	59±4	820±49	51±4%	22/09/2008	7,	42±3	796±48	60±5%
14/09/2008	6,25	64±4	884±53	55±5%	25/09/2008	10,	18,9±2,5	815±49	62±6%
18/09/2008	10,	24±1	908±54	56±5%	01/10/2008	16	12,4±0,7	828±50	63±6%
24/09/2008	16,	24±1	932±56	58±5%	07/10/2008	22	8,4±0,5	836±50	63±6%
29/09/2008	21	11±1	943±57	59±5%	13/10/2008	28	6,5±0,4	843vv±51	64±6%
07/10/2008	29	11±1	954±57	59±5%	21/10/2008	36	6,4±0,4	849v±51	64±6%
13/10/2008	35	7,1±0,4	961±58	60±5%	17/11/2008	63	10,8±0,6	860±52	65±6%
10/11/2008	63	18±1	979±59	61±5%	16/02/2009	154	14,8±0,9	875±52	66±6%
09/02/2009	154	15±1	994±60	62±5%	14/04/2009	211	6,4±0,4	881±53	67±6%
07/04/2009	211	5,3±0,3	1000±60	62±5%					
Afinal Bq/g			50±3					42±3	
Atot final Bq/ech			608±73	**38**±6%				442±63	33±7%
Bq tot			1608±96					1312±84	
Bq/g Aini eq			132±8					126±8	

Leached activity measured for each sequence, cumulated leached activity and fraction of leached activity released for ^{36}Cl in samples 42 & 46 (balance tests)

G2-42-7					G2-46-5				
date	days	Bq seq.	Bq cumul.	%	date	days	Bq seq.	Bq cumul.	%
01/12/2008	0	0	0	0%	13/10/2008	0	0	0	0%
01/12/2008	0,021	189±11	189±11	9,2±0,8%	13/10/2008	0,05	43,8±2,6	43,8±2,6	2,3±0,2%
01/12/2008	0,043	44±3	232±14	11,4±1,0%	13/10/2008	0,10	14,0±0,8	57,8±3,5	3,0±0,3%
01/12/2008	0,14	215±13	447±27	22±2%	13/10/2008	0,14	7,7±0,5	65,5±3,9	3,4±0,3%
01/12/2008	0,25	182±11	629±38	31±3%	13/10/2008	0,25	7,5±0,4	73±4	3,8±0,3%
02/12/2008	1	394±24	1023±61	50±4%	14/10/2008	1	56,4±3,4	129±8	6,7±0,6%
02/12/2008	1,25	77±5	1100±66	54±5%	14/10/2008	1,25	5,6±0,3	135±8	7,0±0,6%
03/12/2008	2	216±13	1317±79	64±5%	15/10/2008	2	34,5±2,1	169±10	8,7±0,7%
03/12/2008	2,25	40±2	1356±81	66±6%	16/10/2008	3	61,0±3,7	230±14	12±1%
04/12/2008	3	81±5	1437±86	70±6%	16/10/2008	3,25	22,0±1,3	252±15	13±1%
05/12/2008	4	122±7	1558±94	76±6%	17/10/2008	4	63±4	315±19	16±1%
08/12/2008	7	110±7	1668±100	82±7%	20/10/2008	7	308±19	623±37	32±3%
11/12/2008	10	45±3	1713±103	84±7%	23/10/2008	10	379±23	1002±60	52±4%
17/12/2008	16	53±3	1766±106	86±7%	29/10/2008	16	292±18	1293±78	67±6%
22/12/2008	21	9,7±0,6	1776±107	87±7%	03/11/2008	21	58±4	1351±81	70±6%
05/01/2009	35	4,4±0,3	1780±107	87±7%	10/11/2008	28	2,5±0,2	1354±81	70±6%
19/01/2009	49	16±1	1796±108	88±7%	17/11/2008	35	13,2±0,8	1367±82	71±6%
02/02/2009	63	8,7±0,5	1805±108	88±8%	01/12/2008	49	8,2±0,5	1375±83	71±6%
04/05/2009	154	19±1	1824±109	89±8%	15/12/2008	63	18,4±1,1	1394±84	72±6%
30/06/2009	211	8,0±0,5	1832±110	90±8%	16/03/2009	154	34,4±2,1	1428±86	74±6%
					12/05/2009	**211**	8,5±0,5	143786	74±6%
Af : Bq/g			16±1					42±3	
Atot : Bq/ech			212±13	**10±1%**				500±30	33±7%
Bq tot			2044±123					1938±116	
Bq/g Aini eq			154±10					164±10	

Leached activity measured for each sequence, cumulated leached activity and fraction of leached activity released for ^{36}Cl in “reactor test” samples

		G2-27-6		G2-27-5		G2-42-5		G2-46-4	
date	days	Bq seq.	Bq cumul	Bq seq.	Bq cumul	Bq seq.	Bq cumul	Bq seq.	Bq cumul
22/07/2008	0	0	0	0	0	0	0	0	0
22/07/2008	0,042 (1H)	383±23	383±23	309±19	309±19	608±36	608±36	302±18	302±18
22/07/2008	0,25 (6H)	1684±100	2067±124	986±59	1295±78	1351±81	1959±118	312±19	613±37
23/07/2008	1	1969±120	4036±242	1438±86	2733±164	1742±105	3701±222	1036±62	1649±99
24/07/2008	2	1334±80	5370±322	776±47	3509±211	1044±63	4744±285	1171±70	2821±169
25/07/2008	3	1163±70	6533±392	522±31	4031±242	871±52	5615±337	982±59	3803±228
28/07/2008	6	1983±119	8516±511	576±35	4607±276	1405±84	7021±421	2254±135	6057±363
29/07/2008	7,3	513±31	9029±542	102±6	4709±283	300±18	7321±439	635±38	6692±402
31/07/2008	9	420±25	9450±567	70±4	4779±287	217±13	7538±452	639±38	7332±440
04/08/2008	13	446±27	9896±594	76±5	4855±291	233±14	7771±466	806±48	8138±488
06/08/2008	15	149±9	10045±603	33±2	4888±293	62±4	7833±470	197±12	8335±500
08/08/2008	17	103±6	10148±609	27±2	4916±295	46±3	7879±473	133±8	8468±508
18/08/2008	27	245±15	10392±624	82±5	4998±300	137±8	8016±481	204±12	8672±520
22/08/2008	31	64±4	10456±627	22±1	5020±301	39±2	8055±483	38±2	8709±523
05/09/2008	45	143±9	10599±636	39±2	5059±304	64±4	8120±487	74±4	8784±527
19/09/2008	59	93±6	10692±642	28±2	5087±305	37±2	8156±489	48±3	8831±530
06/10/2008	76	70±4	10762±646	19±1	5106±306	25±2	8182±491	35±2	8866±532
20/10/2008	90	42±3	10804±648	14±1	5121±307	15±1	8197±492	20±1	8886±533
19/01/2009	181	133±8	10937±656	44±3	5164±310	53±3	8250±495	77±5	8964±538
20/10/2009	455	214±13	11150±669	71±4	5235±314	1016	8351±501	88±5	9052±543
24/03/2010	610	63±4	11213±673	29±2	5264±316	31±2	8383±503	36±2	9087±545

APPENDIX 4

Results of stable Cl leaching

Concentration in µg/l determined for each sequence, cumulated quantity released in µg taking into account the partial renewal of solutions and in terms of the percentage of the form of chlorine released over the total leached quantity.

Reactor test G2-27

G2-27-6	Chloride			Chlorite			Total chlorine	
Time (d)	(µg/l)	µg cumulated	% leached	(µg/l)	µg cumulated	% leached	µg cumulated	% leached
0	0	0	0%	0	0	0%	0	0%
0,042	75±10	11±2	2,9±0,4%	< 10	<1.5	<1%	11±2	2±1%
0,25	257±25	50±5	13±1%	< 10	<1.5	<1%	50±5	11±4%
1	391±39	108±11	27±3%	196±20	29±3	23±2%	124±13	27±10%
2	261±26	148±15	37±4%	137±15	50±5	38±4%	174±18	38±14%
3	165±17	172±18	44±4%	93±10	64±6	49±5%	206±21	45±16%
6	320±32	220±22	56±6%	83±10	76±8	59±6%	261±27	56±21%
7,3	91±10	234±24	59±6%	49±10	84±9	65±7%	278±29	60±22%
9	76±10	245±25	62±6%	46±10	91±11	70±8%	293±31	63±24%
13	86±10	258±27	65±7%	64±10	100±12	77±10%	311±33	67±26 %
15	55±10	267±28	68±7%	46±10	107±14	83±11%	323±36	70±28 %
17	49±10	274±30	69±8%	35±10	112±15	87±12%	333±38	72±29 %
27	72±10	285±31	72±8%	52±10	120±17	93±13%	348±40	75±31 %
31	65±10	294±33	75±8%	20±10	123±18	95±14%	359±43	78±33 %
45	87±10	308±34	78±9%	19±10	126±20	97±15%	374±45	81±35 %
59	58±10	316±36	80±9%	13±10	128±21	99±17%	383±47	83±36 %
76	12±10	318±37	81±9%	12±10	130±23	100±18%	386±50	83±3 8%
90	47±10	325±39	82±10%	< 10	130±23	100±18%	393±51	85±3 9%
181	100±10	340±40	86±10%	< 10	130±23	100±18%	408±53	88± 40%
455	363±36	395±46	100±12%	< 10	130±23	100±118%	463±58	100±45%

Reactor test G2-32

G2-32-5	Chloride			Chlorite			Total chlorine	
(µg/l)	µg cumulated	% leached	(µg/l)	µg cumulated	% leached	µg cumulated	% leached	(µg/l)
0	0	0		0	0	0%	0	0%
0,04	88±10	13±2	7±1%	16±10	2±2	2±1%	14±2	6±1%
0,25	119±12	31±3	16±2%	116±12	20±3	17±3%	41±5	16±2%
1	138±14	52±5	26±3%	158±16	44±6	37±5%	75±8	29±3%
2	85±10	65±7	33±3%	116±11	61±7	51±6%	97±11	37±4%
3	50±10	72±8	36±4%	60±10	70±9	59±7%	109±13	42±5%
6	51±10	80±10	40±5%	78±10	82±10	69±9%	123±15	47±6%
7,3	33±10	85±11	43±6%	31±10	86±12	73±10%	130±18	50±7%
9	43±10	91±13	46±7%	37±10	92±13	78±11%	139±20	54±8%
13	33±10	96±14	49±7%	39±10	98±15	83±13%	147±22	57±9%
15	28±10	100±16	51±8%	22±10	101±16	85±14%	153±24	59±9%
17	29±10	105±17	53±9%	20±10	104±18	88±15%	159±27	61±10%
27	35±10	110±19	56±10%	21±10	107±19	90±16%	166±29	64±11%
31	71±10	120±20	61±10%	15±10	109±21	92±18%	178±31	69±12%
45	39±10	126±22	64±11%	16±10	112±22	94±19%	185±34	71±13%
59	51±10	134±23	68±12%	14±10	114±24	96±20%	194±36	75±14%
76	20±10	137±25	69±13%	15±10	116±25	98±21%	198±38	76±15%
90	33±10	142±26	72±13%	15±10	118±27	100±23%	204±40	79±16%
181	75±10	153±28	78±14%	< 10	118±27	100±23%	215±42	83±16%
455	295±30	197±32	100±16%	< 10	118±27	100±23%	260±46	100±18%

Reactor test G2-42

G2-42-5	Chloride			Chlorite			Total chlorine	
(µg/l)	µg cumulated	% leached	(µg/l)	µg cumulated	% leached	µg cumulated	% leached	(µg/l)
0	0	0	0%	0	0	0%	0	0%
0,04	87±10	13±2	5±1%	13±10	2±2	2±2%	14±2	4±1%
0,25	120±12	31±3	12±1%	167±17	27±4	28±4%	45±5	14±2%
1	146±15	53±5	20±2%	92±10	41±6	42±6%	74±8	23±3%
2	132±13	73±7	27±3%	48±10	48±7	50±7%	98±11	31±3%
3	94±10	87±9	32±3%	26±10	52±9	54±9%	114±13	36±4%
6	120±12	105±11	39±4%	41±10	58±10	60±10%	135±16	42±5%
7,3	49±10	112±12	42±5%	29±10	62±12	65±12%	145±18	45±6%
9	37±10	118±14	44±5%	28±10	67±13	69±14%	153±21	48±6%
13	49±10	125±15	46±6%	34±10	72±15	74±15%	163±23	51±7%
15	51±10	133±17	49±6%	24±10	75±16	78±17%	172±25	54±8%
17	27±10	137±18	51±7%	30±10	80±18	83±18%	179±27	56±9%
27	35±10	142±20	53±7%	30±10	84±19	88±20%	186±30	58±9%
31	32±10	147±21	54±8%	22±10	88±21	91±21%	193±32	60±10%
45	45±10	154±23	57±8%	18±10	90±22	94±23%	201±34	63±11%
59	49±10	161±24	60±9%	13±10	92±24	96±24%	209±37	65±11%
76	32±10	166±26	61±10%	12±10	94±25	98±26%	215±39	67±12%
90	29±10	170±28	63±10%	15±10	96±27	100±28%	221±41	69±13%
181	286±29	213±32	79±12%	< 10	96±27	100±28%	264±45	82±14%
455	380±38	270±37	100±14%	< 10	96±27	100±28%	321±51	100±16%

Reactor test G2-46

G2-46-4	Chloride			Chlorite			Total chlorine	
(µg/l)	µg cumulated	% leached	(µg/l)	µg cumulated	% leached	µg cumulated	% leached	(µg/l)
0	0	0	0%	0	0	0%	0	0±%
0,04	91±10	14±2	4±0,4%	< 10	<2	<4%	14±2	3±0,4%
0,25	93±10	28±3	8±1%	< 10	<2	<4%	28±3	7±1%
1	259±26	66±7	19±2%	14±10	2±2	4±3%	68±8	17±2%
2	284±28	109±11	31±3%	16±10	5±3	9±6%	111±13	28±3%
3	258±26	148±15	43±4%	21±10	8±5	15±9%	152±17	38±4%
6	503±50	223±23	64±7%	18±10	10±6	20±12%	229±26	58±7%
7,3	154±15	246±25	71±7%	20±10	13±8	26±15%	253±29	64±7%
9	174±17	272±27	79±8%	28±10	18±9	35±18%	282±32	71±8%
13	165±10	297±30	86±9%	31±10	22±11	44±21%	309±35	78±9%
15	50±10	305±31	88±9%	28±10	26±12	52±24%	319±38	81±10%
17	51±10	312±33	90±10%	30±10	31±14	61±27%	329±40	83±10%
27	71±10	323±34	93±10%	43±10	37±15	74±30%	343±42	87±11%
31	32±10	328±36	95±10%	20±10	40±17	80±33%	349±45	88±11%
45	PB	328±37	95±11%	10±10	42±18	83±36%	350±47	88±12%
59	45±10	335±39	97±11%	27±10	46±20	91±38%	359±49	91±12%
76	48±10	342±40	99±12%	17±10	48±21	96±41%	367±51	93±13%
90	30±10	346±42	100±12%	15±10	51±23	100±44%	373±54	94±14%
181	40±10	346±42	100±12%	< 10	51±23	100±44%	380±55	96±14%
455	102±10	346±42	100±12%	< 10	51±23	100±44%	396±57	100±14%

Balance test G2-27

G2-27-7a		Chloride			Chlorite			Total chlorine	
date	days	[Cl-]mes (µg/l)	Cl- µg	% leached	Chlorite (µg/l)	Chlorite (µg)	% leached	(µg)	% leached
08/09/2008	0	0	0	0%	0	0	0%		0%
08/09/2008	0,021	37±10	5,6±1,5	11±3%	15±10	2,3±1,5	8±5%	6,7±2,3	10±4%
08/09/2008	0,042	29±10	4,4±1,8	9±4%	14±10	2,3±1,7	8±6%	5,6±2,7	9±4%
08/09/2008	0,17	55±10	9,2±2,0	19±4%	15±10	2,7±1,8	9±6%	11±3	17±4%
08/09/2008	0,29	50±10	9,3±2,1	19±4%	15±10	3±2	10±7%	11±3	17±5%
09/09/2008	1	100±10	18±2	36±5%	16±10	3±2	11±7%	19±3	30±5%
09/09/2008	1,25	81±10	16±2	33±5%	17±10	4±2	13±8%	18±4	28±5%
10/09/2008	2	58±10	14±2	28±5%	19±10	4±2	15±8%	16±4	25±5%
10/09/2008	2,27	54±10	14±3	29±5%	19±10	5±3	16±9%	17±4	26±6%
11/09/2008	3,	60±10	16±3	32±6%	18±10	5±3	16±9%	18±4	29±7%
11/09/2008	3,25	60±10	17±3	34±6%	17±10	5±3	16±10%	19±4	30±7%
11/09/2008	3,5	68±10	19±3	39±6%	31±10	7±4	25±15%	23±5	35±8%
14/09/2008	6,25	61±10	28±5	57±9%	55±10	15±6	53±20%	36±8	56±12%
18/09/2008	10,	20±10	31±6	63±12%	11±10	17±7	59±25%	40±10	62±16%
24/09/2008	16,	26±10	35±8	71±16%	21±10	20±9	70±30%	46±12	71±19%
29/09/2008	21	35±10	40±9	82±19%	20±10	23±10	80±36%	52±15	81±23%
07/10/2008	29	15±10	43±11	86±22%	13±10	25±12	87±41%	56±17	86±26%
13/10/2008	35	12±10	44±12	90±25%	13±10	27±13	93±46%	59±19	91±30%
10/11/2008	63	21±10	47±14	96±28%	13±10	29±15	100±51%	63±21	97±33%
09/02/2009	154	12±10	49±15	100±31%	< 10	29±15	100±51%	65±23	100±36%
07/04/2009	211	<10	49±15	100±31%	< 10	29±15	100±51%	65±23	100±26%

Balance test G2-32

G2-32-6a		Chloride			Chlorite			Total chlorine	
date	days	[Cl-]mes (µg/l)	Cl- µg	% leached	Chlorite (µg/l)	Chlorite (µg)	% leached	(µg)	% leached
15/09/2008	0	0	0	0%	0	0	0%		0%
15/09/2008	0,021	43±10	6,5±1,5	18±4%	11±10	1,7±1,5	7±7%	7,3±2,3	15±5%
15/09/2008	0,042	26±10	3,9±1,8	11±5%	11±10	1,8±1,7	8±7%	4,9±2,7	10±5%
15/09/2008	0,125	43±10	7,5±2,0	20±5%	12±10	2,1±1,8	9±8%	9±3	18±6%
15/09/2008	0,25	48±10	8,9±2,1	24±6%	12±10	2,3±2,0	10±8%	10±3	21±6%
16/09/2008	1	71±10	13±2	35±6%	12±10	2,5±2,1	11±9%	14±3	29±7%
16/09/2008	1,25	65±10	13±2	36±7%	11±10	2,5±2,3	11±10%	15±4	30±7%
17/09/2008	2,10	65±10	14±3	39±7%	10±10	2,5±2,4	11±10%	16±4	32±8%
17/09/2008	2,25	58±10	14±3	38±7%	10±10	2,7±2,6	12±11%	16±4	32±8%
18/09/2008	3	46±10	13±3	36±8%	12±10	3,1±2,7	14±12%	15±4	30±9%
19/09/2008	4	49±10	14±3	39±8%	54±10	9,6±2,9	42±12%	**19**±4	40±9%
22/09/2008	7,	55±10	16±3	43±9%	45±10	9,1±4,4	39±19%	21±5	42±11%
25/09/2008	10,	26±10	20±5	54±13%	15±10	11±6	49±25%	26±8	53±16%
01/10/2008	16	18±10	23±6	61±17%	15±10	14±7	59±32%	30±10	61±20%
07/10/2008	22	14±10	25±8	67±21%	15±10	16±9	69±38%	33±12	67±25%
13/10/2008	28	15±10	27±9	73±125	11±10	17±10	76±45%	36±15	74±30%
21/10/2008	36	14±10	29±11	79±29%	14±10	20±12	85±51%	39±17	80±35%
17/11/2008	63	22±10	32±12	88±33%	12±10	21±13	93±58%	44±19	89±39%
16/02/2009	154	16±10	35±14	94±37%	11±10	23±15	100±64%	47±21	96±44%
14/04/2009	211	14±10	37±15	100±41%	< 10	23±15	100±71%	49±24	100±49%

Balance test G2-42

G2-42-6a		Chloride			Chlorite			Total chlorine	
date	days	[Cl-]mes (µg/l)	Cl- µg	% leached	Chlorite (µg/l)	Chlorite (µg)	% leached	(µg)	% leached
01/12/2008	0	0		0%	0	-	0%	0,0	0%
01/12/2008	0,021	34±10	5,1±1,5	24±7%	11±10	1,7±1,5	15±14%	6±2	22±8%
01/12/2008	0,043	44±10	6,6±1,7	31±8%	11±10	1,8±1,7	17±15%	8±3	28±9%
01/12/2008	0,14	34±10	6,3±1,8	29±8%	12±10	2,1±1,8	20±17%	7±3	27±10%
01/12/2008	0,25	38±10	7,4±2,0	35±9%	12±10	2,3±2,0	21±18%	9±3	32±11%
02/12/2008	1	57±10	11±2	51±10%	12±10	2,5±2,1	23±19%	12±3	45±12%
02/12/2008	1,25	56±10	12±2	54±11%	11±10	2,5±2,3	23±21%	13±3	48±13%
03/12/2008	2	65±10	14±2	64±11%	10±10	2,5±2,4	23±22%	15±4	56±14%
03/12/2008	2,25	55±10	13±3	62±12%	10±10	2,7±2,6	25±23%	15±4	54±14%
04/12/2008	3	58±10	14±3	68±13%	12±10	3,1±2,7	29±25%	16±4	60±15%
05/12/2008	4	58±10	15±3	72±13%	54±10	9,6±2,9	88±26%	**20**±4	75±16%
08/12/2008	7	60±10	16±3	77±14%	45±10	9±3	83±28%	21±5	79±17%
11/12/2008	10	52±10	16±5	76±21%	15±10	5,3±3,2	48±29%	19±6	70±23%
17/12/2008	16	49±10	17±6	78±28%	15±10	5,5±3,3	50±30%	19±8	72±29%
22/12/2008	21	49±10	17±8	81±35%	15±10	5,7±3,5	52±32%	20±9	75±34%
05/01/2009	35	47±10	18±9	83±42%	11±10	5,3±3,6	49±33%	20±11	76±40%
19/01/2009	49	14±10	20±11	93±49%	14±10	7,4±5,1	68±47%	24±13	88±49%
02/02/2009	63	10±10	21±12	100±56%	12±10	9,2±6,6	85±61%	26±15	97±57%
04/05/2009	154	< 10	21±12	100±56%	11±10	10,9±8,1	100±74%	27±16	100±60%
30/06/2009	211	< 10	21±12	100±56%	< 10	10,9±8,1	100±74%	27±16	100±60%

Balance test G2-46

G2-46-5a		Chloride			Chlorite			Total chlorine	
date	days	[Cl-]mes (µg/l)	Cl- µg	% leached	Chlorite (µg/l)	Chlorite (µg)	% leached	(µg)	% leached
13/10/2008	0	0	0	0%	0	0	0%	0,0	0%
13/10/2008	0,05	27±10	4,1±1,5	8±3%	16±10	2,4±1,5	22±14%	5±2	9±4%
13/10/2008	0,10	21±10	3,2±1,7	6±3%	13±10	2,2±1,7	20±15%	4±3	7±4%
13/10/2008	0,14	22±10	4,0±1,8	8±3%	11±10	2,1±1,8	19±16%	5±3	9±5%
13/10/2008	0,25	21±10	4,2±2,0	8±4%	11±10	2,3±2,0	20±18%	5±3	9±5%
14/10/2008	1	31±10	6±2	12±4%	15±10	3,0±2,1	27±19%	8±3	13±6%
14/10/2008	1,25	30±10	6±2	12±4%	14±10	3,1±2,3	28±20%	8±3	14±6%
15/10/2008	2	35±10	8±2	14±5%	14±10	3,3±2,4	30±22%	9±4	16±6%
16/10/2008	3	46±10	10±3	19±5%	15±10	3,7±2,6	33±23%	12±4	20±7%
16/10/2008	3,25	41±10	10±3	19±5%	11±10	3,3±2,7	30±25%	11±4	20±7%
17/10/2008	4	49±10	11±3	22±5%	12±10	4±3	33±26%	13±4	23±8%
20/10/2008	7	109±10	21±3	41±6%	12±10	4±3	34±27%	23±5	40±8%
23/10/2008	10	145±10	28±5	54±9%	15±10	4±3	40±29%	31±6	53±11%
29/10/2008	16	205±10	39±6	76±12%	15±10	5±3	42±30%	42±8	72±13%
03/11/2008	21	196±10	41±8	79±14%	14±10	5±3	43±31%	44±3	75±16%
10/11/2008	28	198±10	44±9	85±17%	24±10	6±4	58±33%	48±11	83±19%
17/11/2008	35	173±10	44±11	84±20%	22±10	6±4	59±34%	47±12	81±33%
01/12/2008	49	180±10	47±12	91±23%	20±10	7±4	59±35%	51±14	88±24%
15/12/2008	63	19±10	50±14	96±26%	16±10	9±4	81±37%	55±16	95±27%
16/03/2009	154	13±10	52±15	100±29%	14±10	11±6	100±50%	58±118	100±31%
12/05/2009	211	10±10	52±15	100±29%	< 10	11±6	100±50%	58±18	100±31%

APPENDIX 4

Geometric characteristics of samples

Piece No.	Weight	Mean size (cm)			ρ_G	Ptot	Remark
	(g)	L	l	H		%	
G2-27-7A	12,1629	1,53	1,53	3,02	1,72±0,03	24,1±0,3	Balance test
G2-27-7B	10,0860	1,62	1,51	2,46	1,67±0,04	26,2±0,3	
G2-27-7C	12,0563	1,61	1,51	3,01	1,65±0,04	27,0±0,3	
G2-27-7D	6,1674	1,52	1,52	1,67	1,60±0,04	29,2±0,3	SIMS -initial
G2-27-7E	1,0933	0,91	0,47	1,52	1,68±0,08	25,8±0,6	½ cut for SIMS measurement
mean					*1,67±0,05*		
Min					*1,60±0,04*		
max					*1,72±0,03*		
G2-32-6A	10,5228	1,47	1,46	3,12	1,58±0,04	30,0±0,4	Balance test
G2-32-6B	8,2873	1,46	1,41	2,51	1,61±0,04	28,7±0,4	
G2-32-6C	10,6187	1,48	1,42	3,15	1,61±0,04	29,1±0,4	
G2-32-6D	10,3788	1,48	1,41	3,12	1,60±0,04	29,4±0,4	SIMS –initial
G2-32-6E	1,0243	0,82	0,53	1,41	1,67±0,08	26,2±0,6	½ cut for SIMS measurement
mean					*1,61±0,04*		
Min					*1,58±0,04*		
max					*1,67±0,08*		
G2-42-6A	13,2756	1,61	1,52	3,12	1,74±0,06	23,3±0,4	Balance test
G2-42-6B	9,8308	1,48	1,53	2,57	1,70±0,04	25,1±0,3	
G2-42-6C	13,1417	1,53	1,64	3,12	1,68±0,04	25,8±0,3	
G2-42-6D	3,6458	1,43	1,01	1,53	1,66±0,05	26,9±0,4	SIMS –initial
G2-42-6E	1,1327	0,78	0,55	1,53	1,73±0,08	23,8±0,6	½ cut for SIMS measurement
mean					*1,70±0,05*		
Min					*1,66±0,05*		
Max					*1,74±0,06*		
G2-46-5A	11,9283	1,6	1,48	3,02	1,67±0,03	26,4±0,4	Balance test
G2-46-5B	9,6695	1,62	1,47	2,49	1,64±0,04	27,7±0,3	
G2-46-5C	11,9511	1,62	1,49	3,06	1,62±0,04	28,6±0,3	
G2-46-5D	11,5513	1,58	1,46	3,05	1,65±0,04	27,3±0,3	SIMS -initial
G2-46-5E	1,0066	0,79	0,48	1,59	1,67±0,08	26,3±0,3	½ cut for SIMS measurement
mean					*1,65±0,04*		
Min					*1,62±0,04*		
Max					*1,67±0,08*		

G2 prismatic irradiated samples

Core	Sample (see cutting drawing)	Mean diameter cm (±0,02)	Mean thickness (cm) (±0,02)	Weight (g)	Density (±0,02)	Ptot %) (±0,4%)	Wear % (±0,8%)
G2-27	3	6,32	1,10	56,3001	1,62±0,02	28,51	5,26
	4	6,33	0,96	49,6919	1,65±0,02	27,18	3,51
	5	6,32	3,02	157,2170	1,66±0,02	26,74	2,92
	6	6,32	1,53	80,0304	1,67±0,02	26,4	2,5
G2-32	3	6,33	1,08	54,8243	1,62±0,02	28,51	5,26
	4	6,32	2,91	147,8640	1,62±0,02	28,51	5,26
	5	6,32	1,40	72,0947	1,64±0,02	27,6	4
G2-42	3	6,32	1,09	58,6864	1,71±0,02	24,54	0,00
	4	6,32	3,04	164,6040	1,73±0,02	23,65	-1,17
	5	6,32	1,50	82,044	1,74±0,02	23,1	-2
G2-46	2	6,33	1,05	55,4287	1,69±0,02	25,42	-0,60
	3	6,34	3,03	159,2290	1,67±0,02	26,30	0,60
	4	6,32	1,56	80,8629	1,65±0,02	27,1	1,6

G2 cylindrical irradiated samples

To calculate the wear rate of the reference special A coke: 1.71- ref Lockport coke: 1.68

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