CHARACTERISATION OF CHLORINE BEHAVIOR IN FRENCH GRAPHITE

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Abstract

Chlorine 36 is one of the main radionuclides of concern for French graphite waste disposal. In order to help the understanding of its leaching behaviour under disposal conditions, the respective impact of temperature, irradiation and gas radiolysis on chlorine release in reactor has been studied. Chlorine 36 has been simulated through chlorine 37 ion implantation in virgin nuclear graphite samples. Results show that part of chlorine is highly mobile in graphite in the range of French reactors operating temperatures in relation with graphite structural recovering. Ballistic damage generated by irradiation also promotes chlorine release whereas no clear impact of the coolant gas radiolysis was observed in the absence of graphite radiolytic corrosion.

1. INTRODUCTION

1.1. French graphite waste : inventory and management scenarios

The first generation of French nuclear plants (9 UNGG reactors, Natural Uranium Graphite Gas[1]) was operated from 1956 to 1994 by EDF and CEA. These reactors were moderated with graphite, cooled with carbon dioxide and fueled with natural uranium. This technology has generated large amounts of graphite waste - the current inventory is 23,000 tons – which are classified as Low Level Long Lived Waste (LLW-LL). Most of them are still within reactors. EDF has opted for a prompt dismantling of its 6 UNGG reactors. Dismantling will be performed under water for 4 reactors out of 9 to ensure radiological protection. As requested by the June 28th 2006 Planning Act on the suitable management of radioactive materials and waste, Andra is studying low-depth disposals concepts. Two alternative management solutions are also being considered [1]:

- Sorting prior to disposal. Within this scenario, graphite piles (18,000 tons featuring very low chlorine 36 inventory) would be disposed in a near-surface disposal together with radium-bearing waste while other graphite waste (5,000 tons including sleeves) would be disposed in the forthcoming deep geological disposal together with ILW-LL.

- Graphite waste treatment. The objective of graphite waste treatment is to retrieve part of graphite waste radionuclides so as to make graphite inventory acceptable for gasification, or for near surface disposal according to decontamination rates.

[1] "UNGG" technology is similar to that of Magnox reactors.

1.2. The specific issue of chlorine 36

Among the radiological inventory of French graphite waste, chlorine 36 is of particular concern because of its very long lifetime (302,000 years) and its low retention in cementitious materials and clay. A substantial clay thickness is thus required to mitigate its flow rate under disposal conditions. Alternatively a high ^{36}Cl decontamination rate would be needed to allow near-surface disposal - or even gasification – for all graphite waste.

French studies on graphite waste have also shown chlorine 36 peculiar behaviour, in particular when considering leaching experiments. In France, more than 60 leaching studies on chlorine 36 have been carried out for more than 20 years, mainly in CEA labs [2]. They all show that chlorine 36 is released in 2 stages, with a first very rapid chlorine 36 release kinetics (labile fraction) followed by a near stabilization. Surprisingly enough, such a labile fraction varies widely within the same pile as shown in Figure 1, ranging from few % to 90 % of the initial inventory.

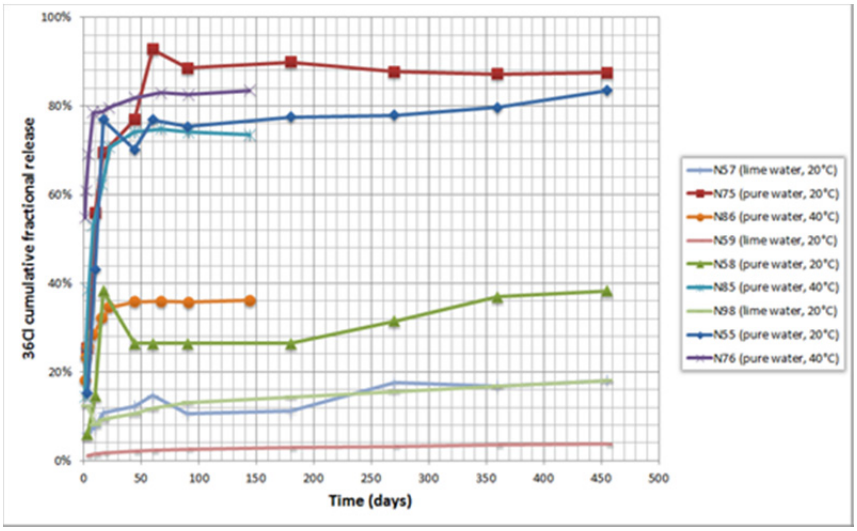


Figure 1 - Cumulative ^{36}Cl released fractions measured for Bugey reactor graphite pile samples.

Such a high variability has been correlated with graphite irradiation temperature in reactor. This is illutrated in Figure 2 for the G2 reactor, but a similar trend has been found for 2 other French graphite reactors. It is believed that in the reactor warmest areas, chlorine labile fraction has been more released than in the coolest areas, which may explain that the residual chlorine 36 labile fraction measured during leaching experiments is also lower and vice-versa. This has been supported by previous studies which have proved chlorine mobility in nuclear graphite under temperature above 200°C [3], [4]. In contrast, the origin of such a mobility, and its possible relation with chlorine speciation or graphite evolution under reactor operating conditions, has never been studied. We reckon such information would provide a more precise view of chlorine 36 behavior in graphite waste. It would support leaching models under disposal conditions and help in improving the treatment processes.

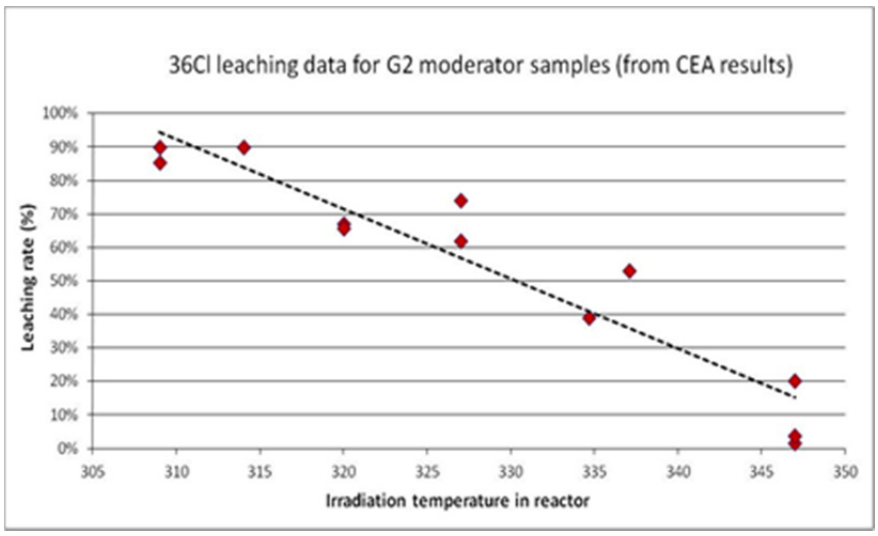


Figure 2 – Correlation between chlorine 36 leaching rate and the irradiation temperature of graphite leached samples for the G2 reactor.

Within this framework, a PhD work was started at the end of 2010 at the Institute of Nuclear Physics in Lyon (IPNL), France, in order to investigate chlorine 36 behavior under reactor operating conditions. More precisely, the objective of this PhD was to answer two main questions:

- What is the mechanism behing the impact of temperature on chlorine release?
- What is the impact of other reactor operating conditions – irradiation and coolant gas radiolysis – on chlorine behavior?

This PhD was defended at the end of 2013 and the reader is referred to the extensive manuscript for details [5]. Only a synthesis of the main results is proposed thereafter. It corresponds to the French EDF-CEA-Andra common project within IAEA CRP "Treatment of irradiated graphite to meet waste acceptance criteria".

2. OVERALL PROCEDURE

Studying chlorine 36 in irradiated graphite is rather difficult not only because it implies to handle radioactive materials but also because the amount of chlorine 36 is often below experimental detection limits. Such issues can be avoided by using simulating materials. In this regard, previous works have shown that ionic implantation of chlorine 37 can be used to simulate chlorine 36 behavior in nuclear graphite [3]. Indeed when chlorine 35 is activated in reactor to produce chlorine 36, the resulting recoil energy of chlorine 36 is generally high enough to displace it from its original equilibrium position. The implantation process, as sketched in Figure 3, simulates quite well chlorine 36 displacement. Moreover, structural alteration induced in the graphite matrix by implantation is also rather similar to that experienced in UNGG reactors [6].

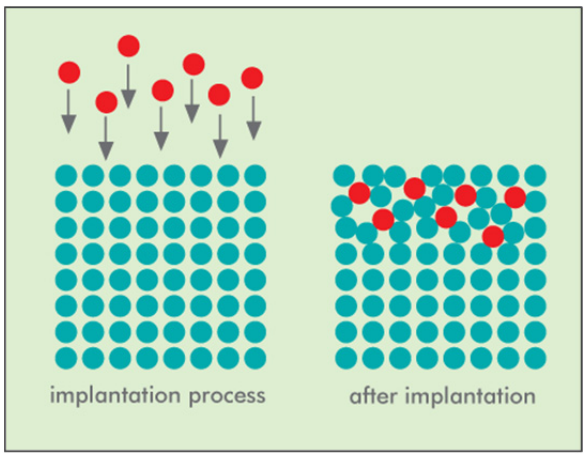


Figure 3 – Implantation process

In the present work, all experiments were performed on non irradiated nuclear graphite that was planned to be used as a moderator in the French UNGG reactor "Saint Laurent des Eaux A2". Chlorine 36 was simulated by chlorine 37 that was implanted in graphite samples at a fluence of 5.10^{13} at.cm^{-2}. The amount of chlorine 37 at the projected range is then in the order of 40 ppm, which is similar to the concentration of pristine chlorine in graphite. This fluence also allows limiting structural damage to 0.025 dpa (displacement per atom) whereas the common amount of displaced atoms found in irradiated UNGG graphite is in the order of 2 to 3 dpa [3], [7]. Other tests were performed with a higher fluence but are not detailed in the present report (see ref. [5] for more details).

Based on ^{37}Cl implanted graphite samples, the objective of the present work was to study the impact of reactor operating conditions - temperature, irradiation and gas radiolysis - on chlorine behavior. Each of these pararameters was investigated separately and is the topic of dedicated sections thereafter where specific experimental data are given. The evolution of chlorine 37 distribution within implanted samples is each time measured using Secondary Ion Mass Spectrometry (SIMS).

3. TEMPERATURE EFFECTS

Chlorine 37 thermal behavior in nuclear graphite has already been studied in a previous PhD [3], [4]. Such studies have shown the high mobility of implanted and pristine chlorine in nuclear graphite from low temperature (c. 200 °C). The objective was thus to complete these results by exploring longer thermal treatment durations and a higher temperature range.

In the following, thermal annealing experiments were performed either under a vaccuum or with an inert gas flux (Ar / He). Temperature range was explored from 200 °C up to 1600 °C so as to be representative of both reactor operating conditions (200-500 °C) and thermal treatment conditions (900-1600°C). Annealings were carried on for 8, 30 and 50 hours.

Chlorine 37 release was first assessed from 200 °C to 1100 °C. Results are synthesised in Figure 4. They show that chlorine 37 release always occurs in two steps, with a first fraction that is very mobile under thermal treatment followed by a near-stabilization. The mobile fraction is rapidly released during the first 8 hours and its proportion tends to increase up to 600 °C where a stabilization is observed at around 30%. Above 600°C and up to 1100°C, the mobile fraction does not increase significantly.

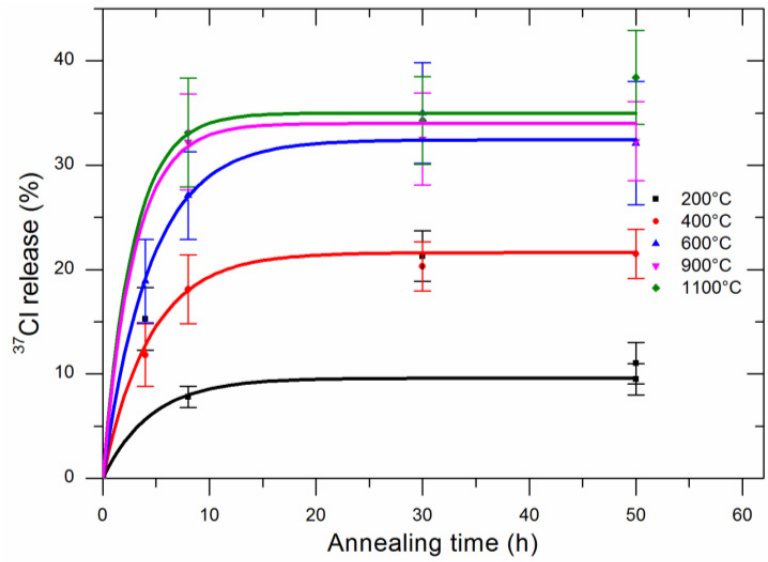


Figure 4 – Chlorine 37 release for implanted and annealed samples as a function of the annealing time

It is then needed to heat above 1100°C to observe a resumption of chlorine 37 release. Chlorine 37 depth profiles were indeed measured as a function of temperature from 1300°C to 1600°C and annealing time from 6 to 8 hours. They are compared in Figure 5 to the as implanted profile ie. without thermal annealing treatment. At 1300°C after 8h of treatment, chlorine release reaches 78.2±20.0%, together with a shift of the Rp value. At higher temperature (1450°C and 1600°C), chlorine is completely removed.

Graphite structure evolution was then studied with Raman spectroscopy in order to check the relation between chlorine release and graphite structure recovering. Figure 6 (a) shows that graphite structure does not change above 8h of thermal treatment, in agreement with the stabilisation of chlorine 37 release observed in Figure 4. Figure 6 (b) represents the evolution of Raman spectra in the range of 200-600°C after 8 hours of thermal treatment, using 514 nm laser excitation. All the spectra, normalised to the G band of the virgin sample, display four main bands: the G band centred at around 1580 cm^{-1} corresponding to the "graphite" band (E2g mode) and three "defect" bands - D1, D2 and D3 - centred respectively around 1350 cm^{-1}, 1620 cm^{-1} and 1500 cm^{-1}[6], [8], [9]. As expected the implantation process results in a strong increase of such"defect" bands but the annealing temperature clearly reorders the graphite structure corresponding to a decrease of the defect bands intensity. The higher the temperature, the higher the graphite structure recovery [4], [6].

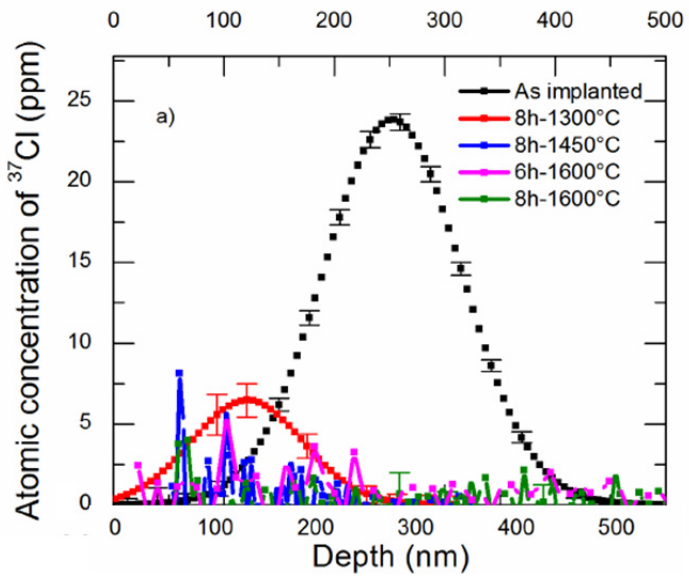


Figure 5 - *Chlorine 37 profile for implanted and annealed samples in the range of 1300-1600°C*

However, even at 600°C and after 8h annealing, the original structure is not completely recovered. Full structural recovering is only observed after annealing at 1600°C (not shown). The Raman spectrum can then be superimposed on the virgin sample spectrum. However, in all these expriments, the implantation fluence was low so that initial structural damages were low as well. Full recovering is indeed not observed, even after thermal treatment at 1600°C, for higher implantation fluences and more disordered samples.

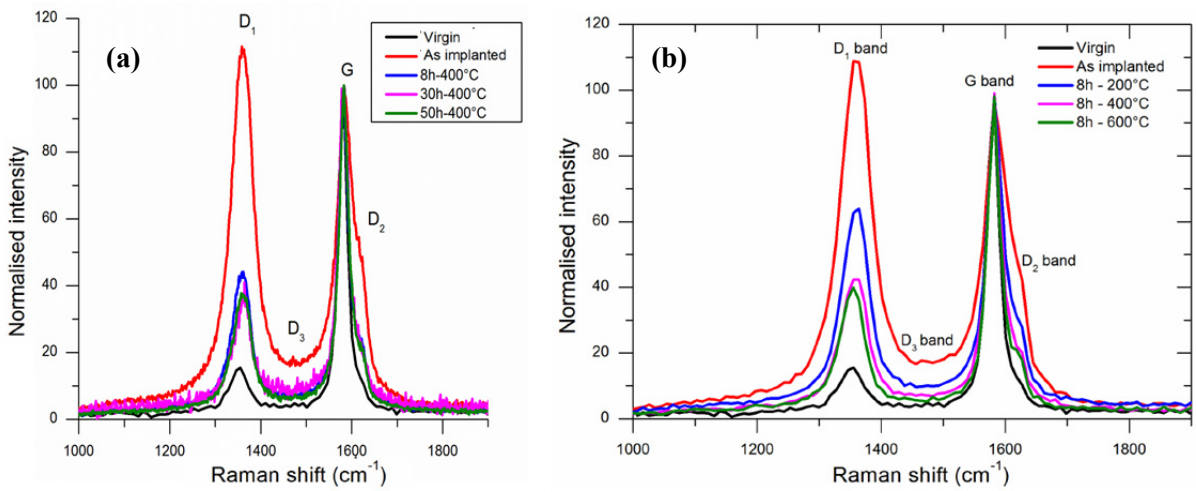


Figure 6 – Raman spectra of annealed samples compared to virgin and as implanted samples.

(a) Effect of annealing duration
(b) Effect of temperature

Figure 7 allows synthesising all of these effects. Chlorine 37 release is shown in red. In this plot, it is clear that chlorine 37 starts to be released at low temperature and increases c. 30% at 600°C. There is then a stabilisation until 1200°C where release starts again, even more strongly, until full release around 1500°C. There is thus evidence that there is two chlorine fraction featuring different thermal behaviors. In the same figure, the black curve compares chlorine release with the evolution of Raman D3 band height and shows a very nice correlation. In the literature, Raman D3 band is often associated with sp^3 hybridized carbon atoms although this is still debated [10]. Chlorine release would then be

related to sp^3 carbon atoms disappearance (possibly C-Cl bonds), in line with graphite structural recovering.

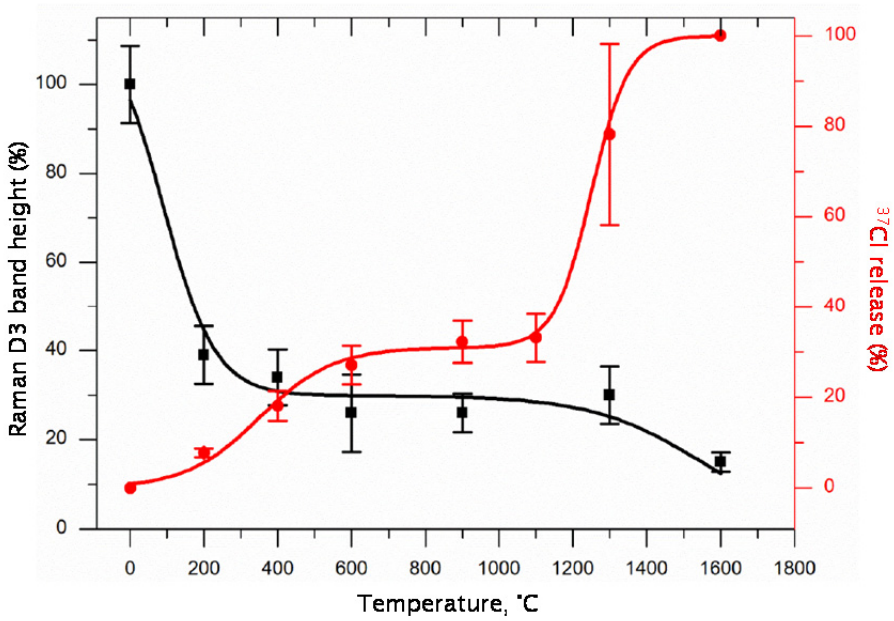


Figure 7 – Evolution of Raman D3 band height and of chlorine 37 release as a function of annealing temperature. Solid lines are only displayed to help interpretations.

4. IRRADIATION EFFECTS

In UNGG reactors, irradiation effects are two fold:

- Electronic effects related to ionizations and electronic excitations generated by photons and electrons (gamma and beta beams)

- Ballistic damages, in particular due to neutrons generated by fission reactions

Moreover carbon atoms may be displaced within the crystal network by neutron bombardment. These atoms mostly loose their energy through ballistic damages, but for the most energetic ones, electronic effects are also possible. For instance, for a 10 MeV neutron –the maximum energy of neutrons produced by ^{235}U fission [11] – the resulting carbon atomsmay have an energy as high as 2.84 MeV, which implies an electronic stopping power of graphite of 1600 keV.μm^{-1} [12]. For a 2 MeV neutron – mean energy of neutrons produced by nuclear fission reaction – carbon atoms mean energy is 284 keV, which means an electronic stopping power of 700 keV.μm^{-1}. This is the most frequent case faced in UNGG reactors, whereas 10 MeV neutrons are hardly produced.

In the present work irradiation effects have been studied through the effect of carbon atoms on graphite matrix. Both electronic effects and ballistic damages have been considered, with the objective to study their impact on implated chlorine release. To do so, irradiation experiments have been performed in a vaccuum using various ion beams (He, I and C) on nuclear graphite implanted samples. Irradiation parameters are detailed in Table 1.

Table 1 – Electronic and nuclear stopping power in the implanted area for irradiations performed with He, I and C ion beams [12].

Ion beams	Helium		Iodine	Carbon
Energy	900 keV	7,5 MeV	200 MeV	400 keV
Electronic stopping power	420 keV/µm	135 keV/µm	13 MeV/µm	400 - 600 keV/µm
Nuclear stopping power	< 1 keV/µm	< 1 keV/µm	< 40 keV/µm	15 - 30 keV/µm
Displacement per atom (ballistic damages)	negligible	negligible	< 0.1 dpa	1 dpa (in the ^{37}Cl implanted area)

These data are compared to UNGG irradiation conditions in Figure 8 [13], [14] and Figure 9 [3], [7].They show that helium irradiation simulates low electronic stopping powers found in UNGG reactors with no ballistic damages. There is no ballistic damage for iodine irradiation either, but electronic effects are then very large (13 MeV.µm^{-1}). Carbon irradiation couples both electronic and ballistic effects and is close to UNGG irradiation conditions.

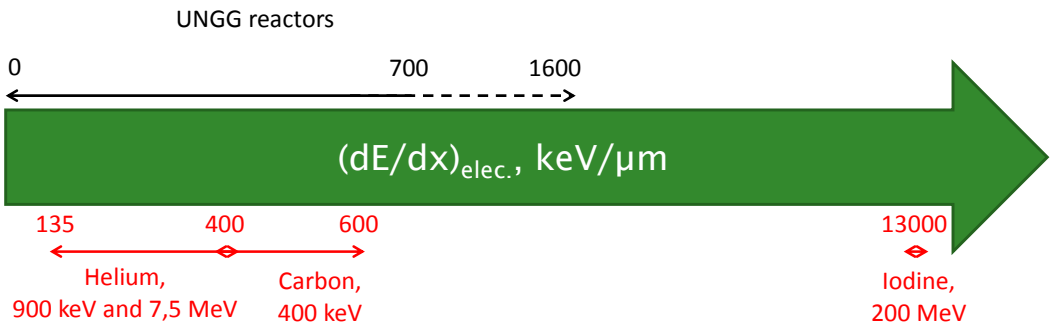


Figure 8 – Comparison of graphite electronic stopping powers for irradiation experiments with that in UNGG reactors

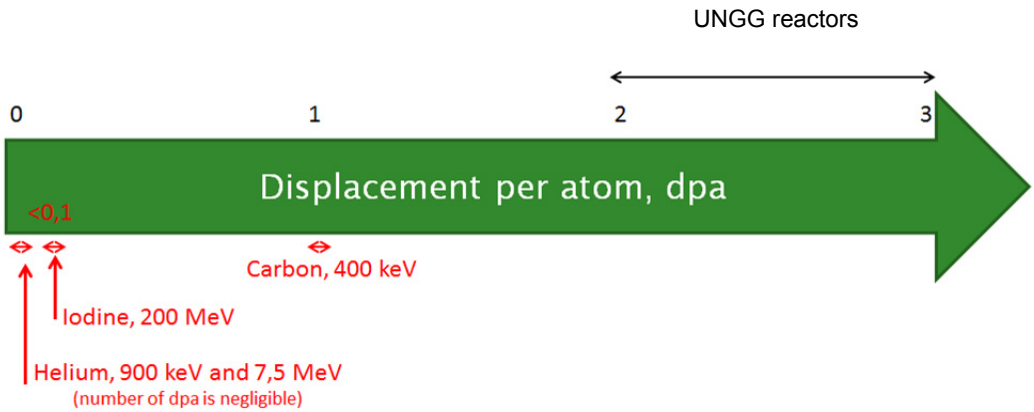


Figure 9 - Comparison of displacements per atom values for irradiation experiments with that in UNGG reactors

For each kind of ion irradiation, experiments were performed both at room temperature and under thermal annealing. Chlorine 37 release was systematically measured and graphite structure was checked by scanning electron microscopy (SEM) and Raman spectroscopy. Results were compared to data collected in section 3. Figure 10 gathers resulting chlorine 37 release data for the 3 ion irradiation conditions tested.

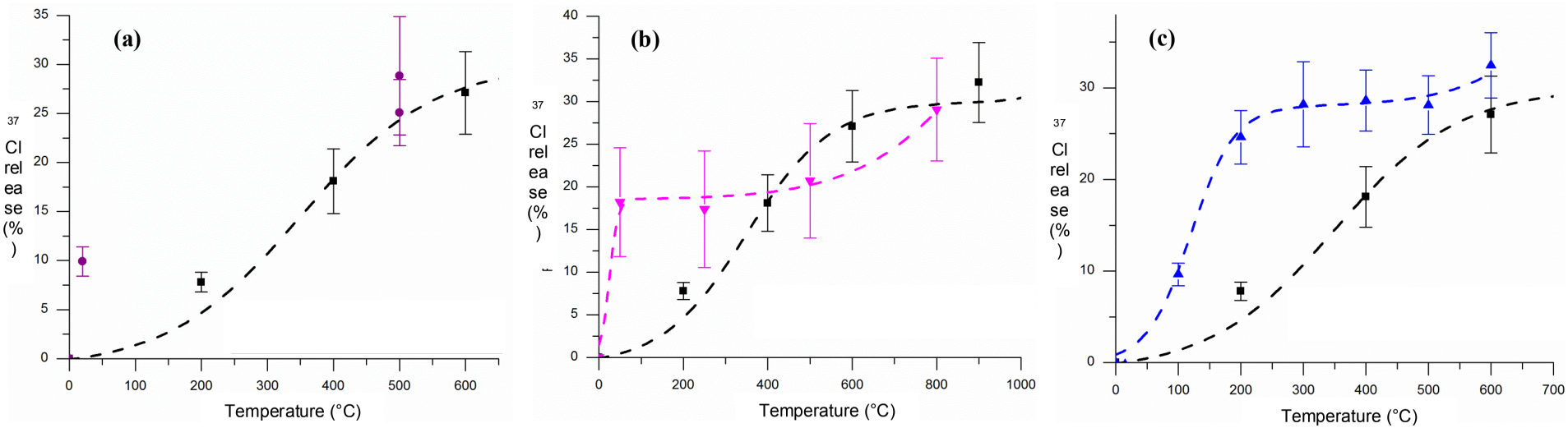


Figure 10 – Comparison of chlorine 37 release for implanted samples with and without ion irradiation as a function of temperature. Non irradiated samples are plotted in black., irradiated samples in colour.

(a) He irradiation, 900 keV
(b) I irradiation, 200 MeV
(c) C irradiation, 400 keV

For helium irradiation (case (a), Figure 10), electronic effects are low, in the range of 135-420 keV.µm^{-1}. They do not significantly increase chlorine 37 release compared to temperature effects alone. No alteration of the graphite structure due to irradiation has been observed either.

For iodine irradiation (case (b), Figure 10), electronic effects are very high and an increase in chlorine 37 release is observed below 400°C whereas no change is found for higher irradiation temperatures compared with thermal annealing experiments alone. Irradiation also induces an alteration of the graphite structure. It has been previously mentioned in the literature that high energy ion irradiation may generate a local increase of temperature related to the tranfer of the ion energy to the electronic network of the matrix (valence electrons). This effect is known as the "thermal spike model" [15] and could explain a local annealing of the graphite structure under iodine irradiation, which could in turn increase chlorine release. Its has already been observed by Liu et al. [13] for irradiation of HOPG[2] samples with 3 MeV Xe ions at 500 and 800 K. Similar results were also obtained on graphite sample using 8.6 MeV Au ions irradiation [16]. In this regard, the increase in chlorine 37 release could be more related to thermal effects than to irradiation effects.

Finally, for carbon irradiation where both electronic and ballistic effects are combined, there is a clear increase in chlorine 37 release under irradiation. However, the electronic stopping power in these tests is in the same range as for helium irradiations (c. 400 keV/µm) for which no impact of electronic effects was found. Thus, such an increase should be related to ballistic damages.

5. RADIOLYSIS EFFECTS

Radiolysis is the interaction between radiations (electrons, neutrons, photons) and matter, resulting in the dissociation of molecules. In UNGG reactors, the CO_2 coolant radiolysis was mainly due to gamma irradiation. Oxidative species were produced resulting in premature wear of graphite called "radiolytic corrosion". To prevent graphite mechanical weakening, methane and carbon monoxide were added to inhibit radiolysis but their own radiolysis produced carbonaceous deposits in the reactor (polymerization of C_3O_2, C_2H_6 and C_3H_8). The main radiolysis products are shown in Table 2 as a reminder.

In 1973, irradiation experiments were performed in France on Osiris research reactor in order to produce such carbonaceous deposits. The experimental conditions were representative of UNGG Bugey reactor operating conditions. Nuclear graphite sleeve samples were irradiated at 300°C under gamma radiation in contact with 40 bar CO_2. Two kinds of deposits – black and rust-coloured – were observed. Their composition was analyzed and a high amount of chlorine was detected, suggesting that chlorine could be preferentially trapped in these deposits.

Table 2 – Main molecules produced by UNGG coolant radiolysis.

Radiolysed molecules	**Carbon dioxide (coolant)**	**Carbon monoxide (coolant radiolysis inhibitor)**	**Methane (coolant radiolysis inhibitor)**
Radiolysis consumption yield (molecules.100 eV^{-1})	0.005 (1 atm.)	4 to 5.5	7 to 7.6
Radiolysis products	CO, O_2, C, O_3	CO_2, C_3O_2, C	H_2, C_2H_6, C_3H_8

In order to study radiolysis effects on chlorine behavior in graphite, several experiments of gas irradiation were performed. As a first step, the objective was to check the impact of gas radiolysis, and thus of resulting radiolysis products, on chlorine release. The possible trapping of chlorine within carbonaceous deposits was then studied. Carbonaceous deposits were synthetised and their structure was characterised. Unfortunately, possible chlorine trapping could not be investigated owing to time contraints. Only gas radiolysis experiments are thus described below.

[2] Highly Oriented Pyrolytic Graphite

Gas radiolysis experiments were performed either with gamma or alpha radiations. Although in UNGG reactors the coolant was mainly radiolysed by gamma rays, helium ions were also used as they lead to similar radiolysis products as gamma rays but with higher reaction yields. The dose obtained in a few hours of experiments could then be similar to that occuring in reactor after several years of operation.

A specific irradiation cell has been designed in order to allow dissociating gas radiolysis effects from graphite irradiation. Several configurations were allowed as illustrated in Figure 11.

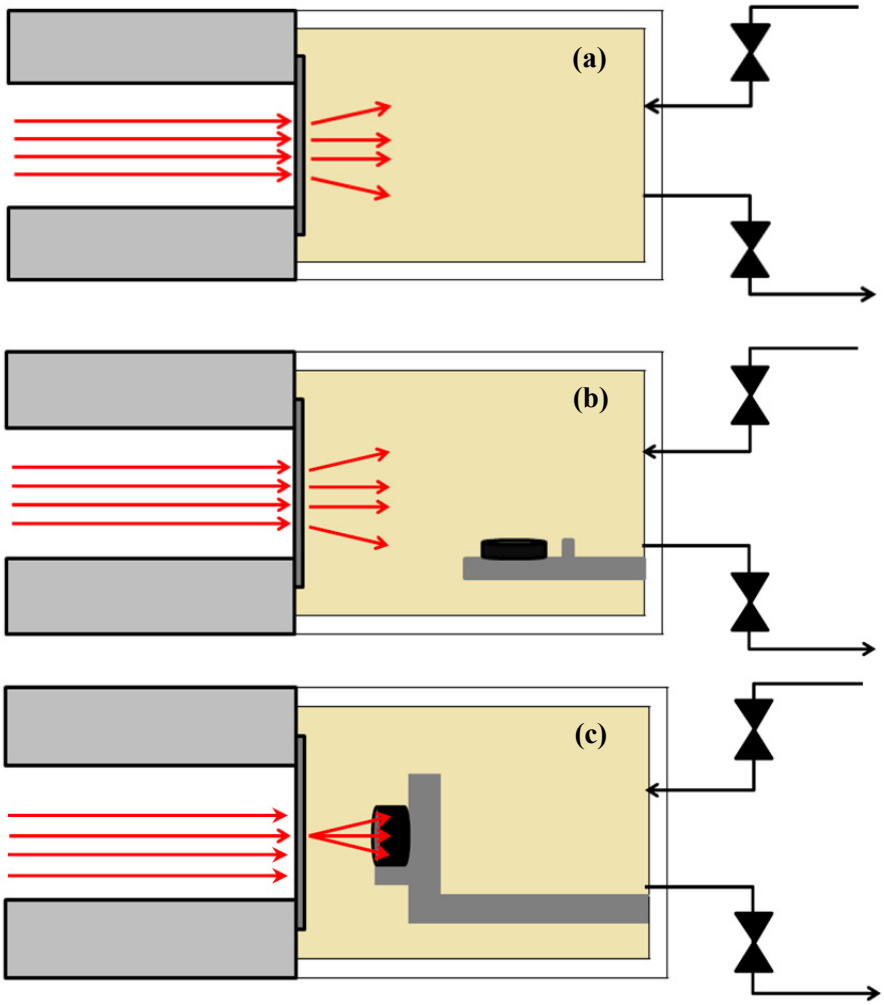


Figure 11 – Irradiation cells configurations used in gas radiolysis experiments

(a) Coolant radiolysis alone
(b) Coolant radiolysis in contact with a graphite sample (with/without heating)
(c) Combined effect of gas radiolysis and graphite irradiation (with/without heating)

In the first set of experiments (case (a) in Figure 11), the gas composition was monitored using gas chromatography–mass spectrometry (GC-MS). The initial gas composition was choosen to be as close as possible to the coolant gas composition that was used in UNGG reactors, as detailed in Table 3. It is mainly made of carbon dioxide, with very low amounts of carbon monoxide, oxygen and hydrogen.

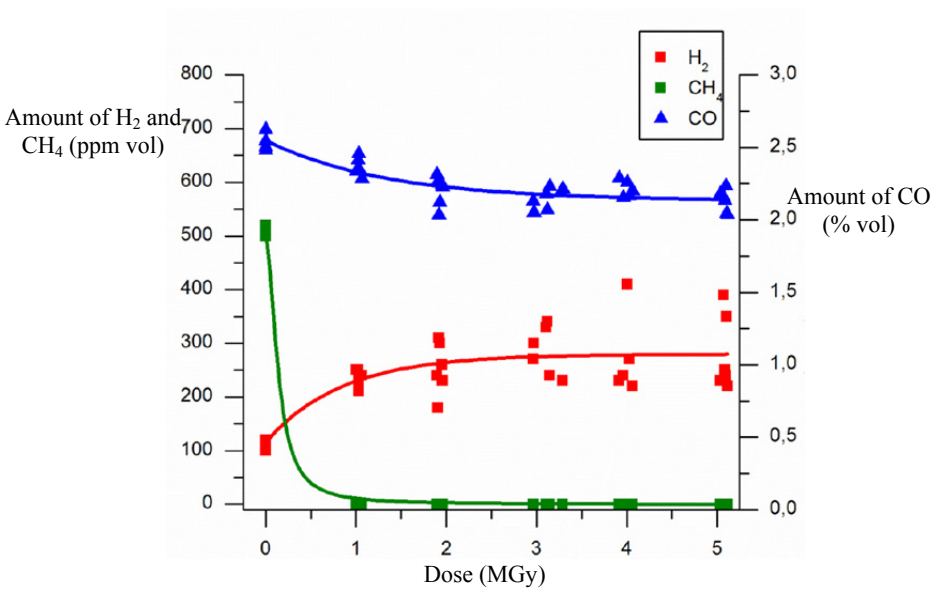
Table 3 – Specifications for UNGG coolant and gas composition used in our experiments

Molecule	Specification for UNGG reactors	Concentrations used in our experiments		
		Bottle 1	Bottle 2	Bottle 3
Carbon monoxide (CO)	2.5 % vol.	2.25±0.05 % vol.	2.49±0.05 % vol.	2.67±0.05 % vol.
Dioxygen (O_2)	100 vol.ppm	91.0±4.5 ppmvol	98.0±5.0 ppmvol	119.7±6.0 ppmvol
Dihydrogen (H_2)	100 vol.ppm	88.1±1.8 ppmvol	102.0±2.0 ppmvol	96.8±1.9 ppmvol
Methane (CH_4)	500 vol.ppm	478±9 ppmvol	511±10 ppmvol	536±11 ppmvol
Carbon dioxide (CO_2)	Balance	Balance	Balance	Balance

The objective was to check that the evolution of the gas composition was consistent with theoretical expectations. Results are shown in Figure 12 for gamma irradiation, but similar trends were observed for alpha irradiation. Logically, methane is consummed very fast and there is no methane left beyond 1 MGy. This goes hand in hand with hydrogen production, as reminded in Table 2. Oxygen concentration is in contrast very stable whatever the dose whereas carbon dioxide concentration slightly increases, up to 97.7%vol.

In the second cell configuration (case (b), Figure 11), a graphite sample implanted with chlorine 37 was put in contact with the gas, but was not submitted to irradiation to control whether radiolysis products, in particular oxidative species, could impact chlorine release and/or graphite structure. On the whole, no evolution was found in comparison to the initial implanted graphite sample, whether on graphite structure or on chlorine distribution profiles.

Ultimately gas radiolysis and graphite irradiation were combined (case (c), Figure 11). The evolution of the chlorine 37 concentration is shown in Figure 13: it does not show any change compared to the graphite implanted sample before irradiation whatever the dose considered.



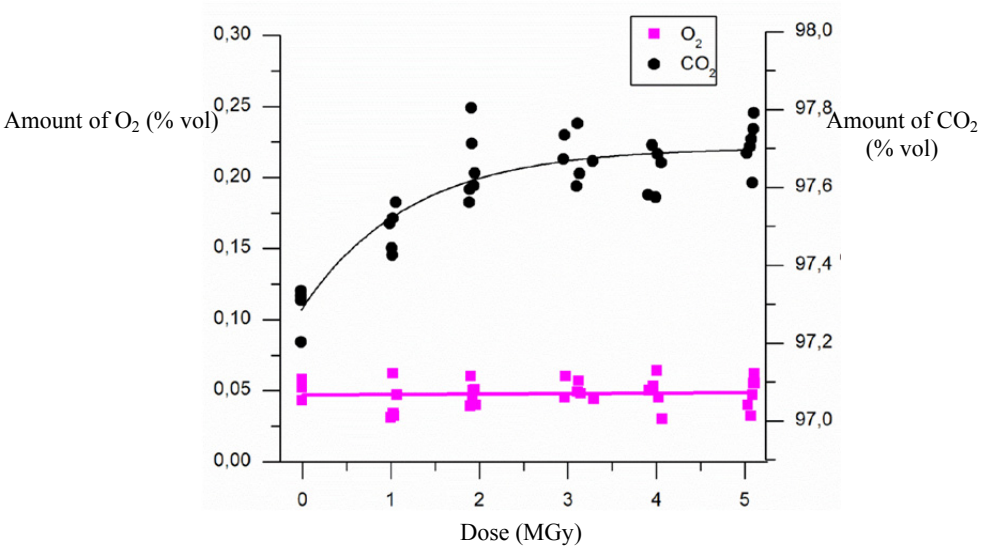


Figure 12 – Evolution of species concentration as a function of the dose (gamma) absorbed by the coolant gas

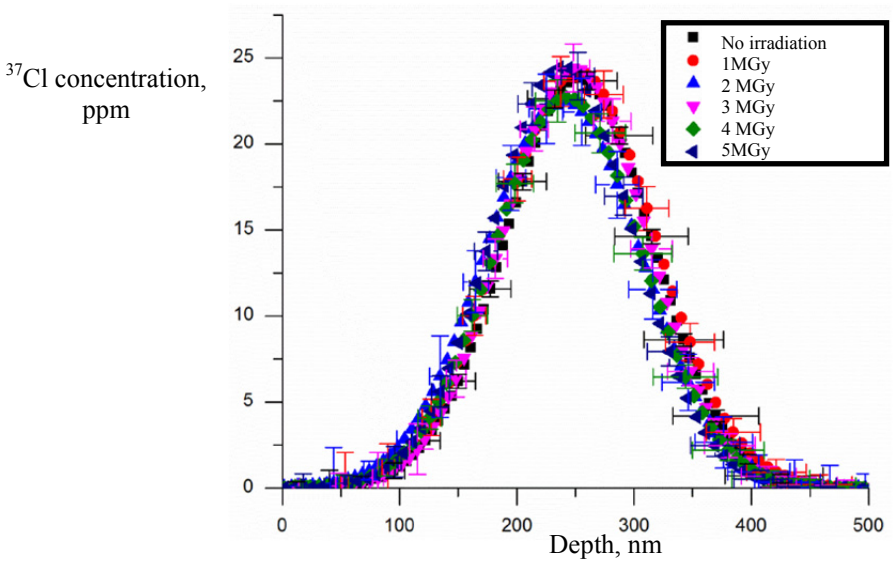


Figure 13 – Mean chlorine 37 profiles of implated graphite samples after gamma irradiation between 1 and 5 MGy and comparison with a non irradiated sample.

6. CONCLUSION

Chlorine 36 is one of the main radionuclide of concern for French graphite waste disposal. Numerous leaching experiments on French irradiated graphite have been performed since the end of the 80's in order to precise its behavior under disposal conditions. All these experiments have led to similar conclusions showing a high variability in chlorine leaching rates even for samples retrieved from the same reactor. A correlation between chlorine release rate and the irradiation temperature in reactor has been proposed and confirmed for 3 different reactors. However, no clear explanation about thermal effects in reactor was available, as well as on the effect of other operating parameters such as irradiation and gas radiolysis on chlorine release.

In this regard, EDF, CEA (graphite waste owners) and Andra (French radioactive waste management agency) have been working since several years with the Institute of Nuclear Physics in Lyon (IPNL)

in order to clarify the respective impact of temperature, irradiation and coolant gas radiolysis on chlorine behavior in graphite under UNGG reactors operating conditions. Chlorine 36 was simulated with chlorine 37 ion implantation in virgin nuclear graphite samples. The present paper is a synthesis of a PhD work performed from 2010 to 2013 and proposed as an input to the IAEA CRP "Treatment of irradiated graphite to meet waste acceptance criteria" as the French EDF-CEA-Andra common project.

The first objective was to specify the impact of temperature on chlorine release in UNGG reactors. Various thermal annealing experiments were performed, from 200 to 1600 °C and from 8 to 50 hours. Results show that chlorine 37 features two different thermal behaviors. A first fraction is very mobile and starts to be released at low temperature, c. 200°C. In contrast, the second fraction release is observed at high temperature, c. 1200°C. Chlorine release process is directly related to graphite structural recovering under temperature effects and possibly with the disappearance of C-Cl bonds.

As a consequence, in the range of UNGG reactors temperatures (200-500°C), only the most labile fraction of chlorine 36 should have been released. In the range of [200-500]°C, this amount increases with temperature, which is in agreement with our previous conclusions drawn from leaching experiments and thus explains high variability in leaching rates: chlorine labile fraction has been more released in the reactor warmest areas, thus explaining lower leaching rates.

It has been sometimes assumed that chlorine 36 could have been trapped within the graphite matrix due to the thermal recovering process which could explain why the resulting labile fraction in leaching tests is lower in samples trepanned from warmest areas of the reactors. On the contrary, the present work shows that graphite reordering promotes chlorine release.

Moreover, for decontamination purposes higher temperatures should be needed but full decontamination in chlorine 36 seems possible.

The second step of our study was to check whether irradiation and gas radiolysis could also impact chlorine release in reactor as for temperature. Irradiation effects have been studied by simulating electronic and ballistic damages due to carbon atoms displaced by neutron bombardment by ion irradiation experiments:

- Low electronic effects were simulated with helium ions irradiations but no significant increase in implanted chlorine release was observed.

- High electronic effects were simulated with iodine ions irradiations. They lead to an increase in implanted chlorine release from ambient temperature. No difference with thermal regime alone is in contrast observed above 400°C. It is assumed that it could be related to local heating as suggested by the "thermal spike model".

- A major result was obtained when combining both electronic and ballistic effects with carbon ions irradiation. It was shown that in the range of UNGG reactors operating conditions, irradiation tends to promote chlorine release compared to thermal effects alone which seems to be mainly related to ballistic damages.

Graphite irradiation and coolant gas radiolysis effects were also studied, alone or in combination with both alpha ions and gamma photons. On the whole, no significant effect on chlorine release was observed.

Complementary studies on combined effects of irradiation and temperature are already planned. They include tests on HOPG samples in order to define the chlorine release mechanism in graphite more precisely.

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