Behavior of ^{14}C in irradiated nuclear graphite waste: consequences for inventory, decontamination and disposal

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Graphite is used in many types of nuclear reactors due to its ability to slow down fast neutrons without capturing them. Whatever the reactor design, the irradiated graphite waste management has to be faced sooner or later regarding the production of long lived radioactive species or radionuclides such as ^{14}C or ^{36}Cl that might be dose determining at the outlet after disposal. The first carbon dioxide cooled, graphite moderated nuclear reactors resulted in a huge quantity of irradiated graphite waste of around 23000 tons in the world. Many of these reactors are now being decommissioned. In case of disposal, a particular attention should be paid to ^{14}C due to its long half-life (T~5730 years) and as it is a major contributor to the radioactive dose. Thus, management solutions as graphite waste sorting or decontamination in order to reduce the initial radioactivity are also considered. In order to make informed decision about the best management process, it is necessary to assess the radioactive inventory and gain information on ^{14}C location and speciation in the irradiated graphite. Thus, our work aims at investigating the behavior of both ^{14}C and ^{14}N, one of its precursors. Indeed, ^{14}C has two main production routes: i) through transmutation of nitrogen ($^{14}N(n,p)^{14}C$) where nitrogen is mainly adsorbed at the surfaces of the irradiated graphite; ii) through activation of carbon from the matrix ($^{13}C(n,\gamma)^{14}C$). The predominance of one reaction versus the other depends on the nitrogen content in the graphite.

We used ^{13}C implantation into virgin nuclear graphite issued from SLA2 reactor and in some cases into model graphite such as HOPG (to simulate ^{14}C displaced from their original structural sites through recoil) and ^{14}N implantation to simulate the presence of nitrogen. Then, we investigated the coupled and decoupled effects of temperature and irradiation on their mobility. We also investigated the effects of radiolytic corrosion on ^{14}N and ^{14}C release at the graphite/gas interface, using a dedicated irradiation cell where a graphite sample was put in contact with a gas simulating the UNGG gas. Thus, using many complementary techniques for treatment (temperature annealing, irradiation) or analysis of the samples, (gas chromatography, SIMS, Raman microspectrometry, performed when possible *in operando*, XPS, SEM), following main information could be inferred.

Extrapolating our results on nitrogen to the behavior of ^{14}N as precursor of ^{14}C allows concluding that, prior to its activation, temperature and irradiation effects tend to induce nitrogen migration towards the graphite "surfaces" (as pores for instance) where it is partially released or tends to form carbon nitride complexes and several compounds such as C-N, C=N or C≡N. The migration and subsequent release occur all the more as the graphite structure is disordered (i.e. in the zones where the neutron flux is maximum) and the loss of ^{14}N may reach 65% of the initial amount.

Concerning the behavior of ^{13}C as precursor of ^{14}C, we may conclude that thermal annealing does not induce any migration of ^{13}C up to 1600°C (in inert atmosphere), even if the structure of the graphite is

initially disordered (around 6 dpa). A slight diffusion occurs from 1600°C. This diffusion might be linked to the reordering of the graphite structure and the "reorganization" of the implanted ^{13}C into carbon clusters for instance.

The impact of irradiation and its synergistic effects with temperature on ^{13}C release were also investigated. The collision of the impinging neutrons with the graphite matrix carbon atoms induces mainly ballistic damage. However, a small part of the recoil carbon atom energy is also transferred to the graphite lattice through electronic excitation. Thus, we simulated the effects of these different irradiation regimes in synergy with temperature using ion irradiation at different facilities with dedicated irradiation cells. The results show that "moderate" electronic excitations and ionizations, i.e. for electronic stopping powers S_e ranging up to 700keV/µm which corresponds to the usual range in UNGG reactors, do not promote ^{13}C release. Experiments carried out with S_e around 3700 keV/µm show that the implanted ^{13}C does not migrate even at 1000°C. In this latter case, Raman microspectrometry analysis evidenced a reordering of the graphite structure showing that ^{13}C presumably rearranges into new carbon structures. Ballistic damage was simulated by irradiating graphite samples heated at temperatures ranging from 200°C to 1000°C with 400keV C^+ ions. First results (that have to be confirmed) show that ^{13}C does not seem to be released.

The impact of gas radiolysis has also been investigated using ions. Graphite samples, heated at 500°C, put in contact with a gas representative of the UNGG gas were irradiated with $^4He^{++}$ ions. The results show that, in absence of methane, when the free radicals formed through gas radiolysis are produced at the gas/heated graphite interface, the radiolytic corrosion of the graphite surface proceeds, leading to a loss of the ^{13}C or ^{14}N implanted close to the interface.

Finally, extrapolating our results to the behavior of ^{14}C shows that nor UNGG reactor temperatures nor irradiation seem to favor ^{14}C migration or release, as far as the graphite surfaces are not oxidized. Indeed, radiolytic corrosion of graphite leads to the impoverishment of both ^{14}C (mainly issued from ^{14}N) and nitrogen inventory (that is more enriched close to free surfaces). The ballistic irradiation regime leads to bond breakage and fragmentation of the coke grains as well as the increasing disorientation of the crystallites in the grains that become smaller and smaller. But the typical UNGG temperatures (range ~ 200°-500°C) tend to reorder the graphite structure during irradiation, thereby probably stabilizing the ^{14}C into new carbon structures (that should be more or less ordered, depending on local irradiation and temperature conditions). Thus, radiolytic corrosion should therefore be a major factor that might be responsible for the ^{14}C depletion during reactor operation quoted by B. Poncet et al. [1]. Moreover, the nitrogen depletion we observed is fully in agreement with the conclusions of these authors who calculated that in irradiated graphite the remaining ^{14}C is mainly issued from ^{13}C activation of the graphite matrix.

Considering ^{14}C purification prior to disposal, our results show that annealing in inert gas would not lead to ^{14}C release, contrary to oxidizing conditions. However, it might be helpful to stabilize ^{14}C into new carbon structures which could therefore be beneficial for disposal.

[1] B. Poncet and L. Petit, J. Radioanal. Nucl. Chem (2013) 298:941-953 Method to assess the radionuclide inventory of irradiated graphite waste from gas cooled reactors

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