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Recent advances in the treatment of irradiated graphite: A review

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A B S T R A C T

Graphite is used as a moderator and reflector in nuclear reactors. Fission products and activation of impurities in the graphite contaminated this graphite during reactor operation. Larger amount of irradiated graphite has to be considered as radioactive waste. The management of irradiated graphite waste is becoming an increasingly important issue worldwide. The objective of this paper was to briefly review the recent advances in the treatment and disposal of irradiated graphite to offer deep insight into a better understanding of the techniques for the management of irradiated graphite from nuclear reactors. The properties of irradiated graphite were briefly introduced. The formation of radionuclides, especially C-14, Cl-36 and H-3, in the irradiated graphite was summarized. The main features of Wigner treatment, thermal treatment, chemical treatment, conditioning, coating and impregnation, gasification were addressed. The final end point of the graphite and the final end point of the radionuclides were discussed and their influences on selection of treatment methods were compared.

Contents

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1. Graphite used in nuclear industry

1.1. Manufacture and properties of nuclear graphite

Graphite has been used as a moderator, reflector, or operational material in nuclear reactors. The irradiated graphite presents a major waste management challenge due to the presence of long-lived radionuclide species such as 14-C and 36-Cl, together with shorter-lived species including 3-H and 60-Co, and small quantities of fission products and actinides (Wareing et al., 2017).

Graphite is formed from a high temperature process combining raw coke particles and a binder that provides cohesion for the raw particles. Large quantities of irradiated graphite waste from graphite-moderated nuclear reactors exist and are expected to increase in the case of High Temperature Reactor (HTR) deployment (Smith et al., 2013). The irradiated graphite cannot be disposed of in a near surface repository because of large amounts of C-14 (Poskas et al., 2016; Wickham et al., 2017).

Nuclear graphite is manufactured from petroleum or natural pitch cokes selected for their crystallographic structure rather than an amorphous form of carbon (EPRI, 2006; IAEA, 2000, 2016; Marsden and Hopkinson, 2002; Ragan and Marsh, 1983). By heating the carbon materials to high temperatures, but below the melting point, in an air environment (calcination), impurities are removed from the petroleum products. These cokes are baked, blended and mixed with a binder and formed by extrusion, moulding or isostatic pressing into variously shaped blocks. Blocks intended for use as nuclear reactor moderator or reflector are then graphitized at 2500–3000 °C and may then be further impregnated with pitch, re-baked and re-graphitized in order to increase the density. Finally, the carbon material transforms into a crystalline layered structure.

1.2. Graphite used as moderator and reflector

Graphite, a low absorption neutron moderator, has been used as moderator and reflector of neutrons in more than 100 nuclear power plants and in many research and plutonium-production reactors (IAEA, 2006). Graphite moderated reactors include: air-cooled plutonium production graphite piles, light water cooled graphite-moderated piles, carbon dioxide cooled reactors and High-temperature helium cooled reactors (HTGR). There were also a small number of experimental reactors such as prototype molten salt or sodium cooled graphite-moderated reactors. Worldwide, there are more than 230,000 tons of radioactive graphite which will eventually need to be managed as radioactive waste (IAEA, 2006). Most of them are from irradiated graphite as moderator and reflector.

1.3. Graphite in fuel matrix

The fuel used in HTGRs is also contained in massive quantities of carbonaceous material. Three fuel bearing configurations have been used in HTGRs:

(1) Long, slender graphite prisms (in Peach Bottom-l);
(2) Graphite spheres about 6 cm in diameter in the German AVR, thorium high-temperature reactor(THTR), Chinese HTR-10 and HTR-PM;
(3) Hexagonal graphite prisms 35-cm wide and 76-cm long in Fort St. Vrain (FSV). FSV fuel is one of the most popular fuel, it is the prototype for future HTGR fuel in the U.S.;

The fuel of HTGR consists of small particles (spheres of the order of 0.5-mm diam) of uranium oxide or carbide. The particles are coated with thin layers of pyrolytic carbon (pyrocarbon) and silicon carbide, which serve as tiny pressure vessels to contain fission products and fuel. The ceramic-coated fuel particles are strong and highly resistant to irradiation and disintegrate.

In the case of the 6-cm spheres, the fuel particles are dispersed uniformly in the sphere, except in the outermost layer of the sphere that is a protective region of no-fueled graphite. In the case of the prism-shaped fuel, the fuel particles are first bound into rods that are subsequently carbonized. These fuel rods are placed into holes drilled in the prism graphite (Delage et al., 2004; DelCul et al., 2002; Lotts and Bond, 1992; Masson et al., 2006).

1.4. Other source of graphite waste

The majority of irradiated graphite is associated with reactor moderators and reflectors, however, there are a number of other routes from which radioactive graphite components requiring ultimate disposal can arise. For example, contaminated graphite tools from graphite crucibles and molds used in the production manufacture of nuclear fuel elements (Tian et al., 2010).

2. Analyses of irradiated graphite

The graphite materials are irradiated during reactor operation. The irradiation of graphite can potentially lead to physical, mechanical and thermal properties changes in the material. In addition to affecting operation of the plant, these changes may also subsequently impact upon dismantling, handling of the material during decommissioning, treatment and disposal. The irradiation of graphite could also lead to induced radioactivity of the graphite. Due to the production of long-lived radioisotopes within irradiated graphite, nearly all must be managed as radioactive waste.

Surface-sensitive analysis techniques (XPS, ToF-SIMS, SEM/EDS and Raman) can be applied to determine the chemical nature of C-14 on the surfaces of the irradiated graphite. Several C-14 precursor species were identified on the surfaces of irradiated graphite; their quantities decreased at sub-surface depths, suggesting that C-14 formation is predominantly a surface-concentrated phenomenon (LaBrier and Dunzik-Gougar, 2014).

X-ray microcomputed tomography (CT) was applied in characterizing the internal structures of a number of irradiated materials, including carbon-carbon fibre composites, nuclear-grade graphite and tristructural isotropic-coated fuel particles (Silva et al., 2015). The local cracks in carbon-carbon fibre composites can be observed using CT without any destructive sample preparation. They analyzed the pore distribution of graphite samples. The high-resolution CT can be used to probe internal layer defects of tristructural isotropic-coated fuel particles to elucidate the resulting high release of radioisotopes. They also used lay Description X-ray tomography to characterize a number of materials related to nuclear fuel industry, including carbon-carbon (C—C) fibre composites, nuclear-grade graphite and tristructural isotropic (TRISO)-coated fuel particles (Silva et al., 2015).

Raman spectroscopy is an appropriate technique to probe defects in carbon-based materials owing to its high sensitivity, most often focused on the commonly used I-D/I-G parameter. However, this ratio may be activated by various types of defects and in a completely independent manner. Ammar et al. (2015) discriminated the defect types using the combination of the I-D/I-G and FWHM(G). They used ion-beam irradiation as an effective way for creating defects that could be similar to those created by neutrons in the nuclear reactor.

Vulpius et al. (2013a) determined the locations and the chemical forms (chemical bonds) of radionuclides in neutron-irradiated nuclear graphite in order to develop principal strategies for the management of graphitic nuclear waste. Due to the relatively