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Removal of carbon-14 from irradiated graphite

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ABSTRACT

Approximately 250,000 tonnes of irradiated graphite waste exists worldwide and that quantity is expected to increase with decommissioning of Generation II reactors and deployment of Generation IV gas-cooled, graphite moderated reactors. This situation indicates the need for a graphite waste management strategy. On of the isotopes of great concern for long-term disposal of irradiated graphite is carbon-14 (^{14}C), with a half-life of 5730 years. Study of irradiated graphite from some nuclear reactors indicates ^{14}C is concentrated on the outer 5 mm of the graphite structure. The aim of the research presented here is to develop a practical method by which ^{14}C can be removed. In parallel with these efforts, the same irradiated graphite material is being characterized to identify the chemical form of ^{14}C in irradiated graphite.

A nuclear-grade graphite, NBG-18, and a high-surface-area graphite foam, POCOFoam®, were exposed to liquid nitrogen (to increase the quantity of ^{14}C precursor) and neutron-irradiated (10^{13} neutrons/cm^2/s). During post-irradiation thermal treatment, graphite samples were heated in the presence of an inert carrier gas (with or without the addition of an oxidant gas), which carries off gaseous products released during treatment. Graphite gasification occurs via interaction with adsorbed oxygen complexes. Experiments in argon only were performed at 900 °C and 1400 °C to evaluate the selective removal of ^{14}C. Thermal treatment also was performed with the addition of 3 and 5 vol% oxygen at temperatures 700 °C and 1400 °C. Thermal treatment experiments were evaluated for the effective selective removal of ^{14}C. Lower temperatures and oxygen levels correlated to more efficient ^{14}C removal.

1. Introduction

For the past 50 years graphite has been widely used as a moderator, reflector, and fuel matrix in a variety of gas-cooled reactors. The result is approximately 250,000 metric tons of irradiated graphite waste [1]. The U.S. and other countries are developing advanced nuclear systems coined "Generation IV concepts" as established by the Generation IV International Forum, which institutes protocol for individual countries to lead the development of a reactor concept in which they have particular interest [2]. The U.S. has pursued research and development of the high temperature gas-cooled reactor (HTGR) under the U.S. Department of Energy's Next Generation Nuclear Plant (NGNP) initiative. The HTGR uses helium coolant, graphite-coated fuel particles, a graphite reflector, and other graphite core structural components [3]. Operational HTGRs would dramatically add to the present quantity of irradiated graphite waste.

Characterization of existing irradiated graphite indicates that a most significant long-lived radioisotope from graphite reactors similar to the HTGR is carbon-14 (^{14}C). With a half-life of 5730 years this species is of concern for deep geologic disposal of irradiated graphite because it is readily mobile in groundwater and atmospheric systems [4]. Removal of ^{14}C from large irradiated graphite reactor components may reduce disposal cost, while also allowing the possibility of recycling this very pure nuclear grade material [2]. An understanding of the bonding characteristics, functional groups, location, and concentration of ^{14}C would contribute to optimizing its removal from irradiated graphite.

1.1. Formation of ^{14}C

As graphite is bombarded by neutrons, ^{14}C is produced through neutron capture by carbon-13 (^{13}C), nitrogen (^{14}N), and oxygen-17 (^{17}O) as seen in Eqs. (1)–(3) [4].

$$^{14}N + n \rightarrow {}^{14}C + p \quad (1)$$

$$^{13}C + n \rightarrow {}^{14}C + \gamma \quad (2)$$

$$^{17}O + n \rightarrow {}^{14}C + \alpha \quad (3)$$

Characterization of existing irradiated reactor graphite revealed that there is a concentration of ^{14}C on the surfaces of graphite blocks [5]. The concentration of ^{14}C on the surface is dependent

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on its location within the reactor, core design, flux, manufacturing, and environment. The inhomogeneous distribution of ^{14}C is indicative of the neutron capture of ^{14}N and ^{17}O. Graphite naturally adsorbs air; consequently, ^{14}N and ^{17}O are readily found on the graphite surface. Oxygen and nitrogen adsorption occurs during graphite manufacturing, component assembly and storage, and as a result of air leaks into the reactor coolant gas. The neutron capture cross sections and isotopic abundances of ^{14}N and ^{17}O indicate the neutron activation of ^{14}N is likely the main source of ^{14}C on the surfaces of irradiated graphite [5] (see Table 1).

Neutron absorption by ^{13}C can also be a significant contributor to the overall ^{14}C content of irradiated graphite; however, ^{14}C from this source is more likely homogeneously distributed throughout a graphite component than concentrated on its surface.

1.2. Thermal treatment

When graphite is heated at a constant temperature under forced convection with an inert gas it oxidizes due to the presence of adsorbed air, thus releasing gasified carbon–oxygen compounds (expected primarily as carbon monoxide) [6]. An oxidizing species also can be added to the carrier gas. If optimized, this process could be a viable strategy for graphite waste management given that the ^{14}C enriched surface oxidizes first.

Graphite oxidation rate is controlled by 3 reaction mechanisms determined largely by temperature. At lower temperatures (less than about 600 °C), oxidation kinetics is controlled by the chemical rate of reaction and at higher temperatures (above about 900 °C) kinetics is dominated by diffusion of reactants and products through the product boundary layer. At intermediate temperatures, oxidation rate is controlled by diffusion of reactants and products through graphite porosity. The temperatures of transition between oxidation kinetic regimes are highly dependent on the particular graphite properties and experimental conditions. The estimated transition temperatures are displayed in Table 2 [7]. The optimal temperature, and oxidation regime, for maximum ^{14}C removal must be determined experimentally.

Table 1
Properties of ^{14}C precursors.

Species	Capture cross section (Barns)	Isotopic abundance (%)
^{14}N	1.8	99.63 (^{14}N:N)
^{13}C	0.0015	1.07 (^{13}C:C)
^{17}O	0.235	0.04 (^{17}O:O)

Table 2
Expected graphite oxidation kinetics regime temperature boundaries.

Regime 1 (°C)	Regime 2 (°C)	Regime 3 (°C)
<(500–700)	>(500–700), <900	900

Table 3
Graphite Irradiation.

Graphite	Pre-irradiation liquid N_2 exposure	Facility	Time (days)	Flux (n/cm^2/s)
NBG-18 POCOFoam®	Yes	MURR	120	10^{13}–10^{14}

2. Method

Irradiated and unirradiated samples of nuclear-grade graphite NBG-18, a German-produced medium-grain graphite, and POCOFoam®, a highly porous graphite foam, have been analyzed. The non-nuclear grade foam was chosen for its significant surface area [8]. NBG-18 and POCOFoam® samples were immersed in liquid nitrogen (LN) for 24 h immediately prior to being placed and sealed into a container in ambient air for neutron irradiation. The purpose of LN immersion was to promote nitrogen adsorption and subsequent neutron-induced production of ^{14}C to ensure measurable quantities on sample surfaces. Typical ^{14}C concentrations in existing irradiated reactor graphite are on the order of parts-per-billion, which is too low for meaningful characterization. Sample irradiation took place at the MURR research reactor at the University of Missouri for 120 days in a thermal neutron flux of 6.7×10^{13} neutrons/cm^2/s.

Graphite sample irradiation conditions for this project are summarized in Table 3.

2.1. Thermal treatment

During thermal treatment experiments a pre-weighed graphite sample was placed in the center of the main furnace (Fig. 1). Experimental temperatures (700 °C, 900 °C and 1400 °C) were chosen with the intent of facilitating oxidation via different mechanisms that may affect the selective release of ^{14}C. Argon carrier gas was flowed through the furnace to transport gasified oxidation products released from the graphite through the system to a collection bottle. In some experiments, the carrier gas was doped with 3 vol% (1.5 sccm) or 5 vol% (2.6 sccm) oxygen gas to increase the amount of graphite oxidation. Argon gas was flowed through the system at 50 standard cubic centimeters per minute (sccm) to carry gasified oxidation products released from the graphite.

A small portion of gas leaving the furnace was diverted to a Hiden quadrupole mass spectrometer gas analyzer before returning to the main gas flow path. The gas analyzer was programmed to monitor for CO, CO_2, Ar, O_2, N_2, H_2O, CH_4, ^{14}CO, and $^{14}CO_2$. After this analysis all gas flowed through the 800 °C oxidizing furnace where any CO oxidized to CO_2 via reaction with granular copper

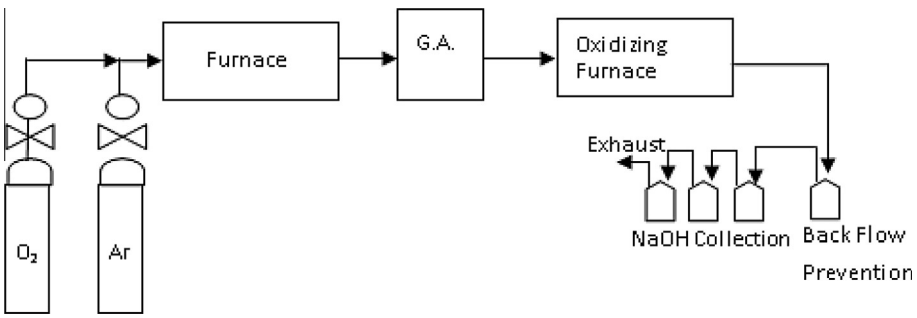

Fig. 1. Experimental design for thermal treatment of nuclear graphite to remove ^{14}C (G.A. is gas analyzer).