Project No. 09-844

# Removal of 14C from Irradiated Graphite for Graphite Recycle and Waste Volume Reduction

## Reactor Concepts R&D

**Dr. Mary Lou Dunzik-Gougar**
Idaho State University

**In collaboration with**:
Furnaces Nuclear Applications Grenoble (FNAG)
Idaho National Laboratory
University of Manchester

Brian Robinson, Federal POC
Will Windes, Technical POC

Nuclear Energy University Programs
U.S. Department of Energy

**Final Report for 09-844: Removal of $^{14}C$ from irradiated graphite for graphite recycle and waste volume reduction**

PI: Mary Lou Dunzik-Gougar, Idaho State University

## ABSTRACT

The aim of the research presented here was to identify the chemical form of $^{14}C$ in irradiated graphite. A greater understanding of the chemical form of this longest-lived isotope in irradiated graphite will inform not only management of legacy waste, but also development of next generation gas-cooled reactors. Approximately 250,000 metric tons of irradiated graphite waste exists worldwide, with the largest single quantity originating in the Magnox and AGR reactors of UK. The waste quantity is expected to increase with decommissioning of Generation II reactors and deployment of Generation IV gas-cooled, graphite moderated reactors. Of greatest 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 a $^{14}C$ concentration in the outer 5 mm of the graphite structure. Characterization of irradiated graphite surfaces has been performed in parallel with treatment of the same material for removal of the labile $^{14}C$. Results of each process inform the other.

A nuclear-grade graphite, NBG-18, and a high-surface-area graphite foam, POCOFoam, were exposed to liquid nitrogen (to increase the quantity of precursor) and neutron-irradiated ($10^{13}$ neutrons/cm$^2$/s). Finer grained NBG-25 was not exposed to liquid nitrogen prior to irradiation at a neutron flux on the order of $10^{14}$ /cm$^2$/s. Characterization of pre- and post-irradiation graphite was conducted to determine the chemical environment and quantity of $^{14}C$ and its precursors via the use of surface sensitive characterization techniques. The concentration, chemical composition, and bonding characteristics of $^{14}C$ and its precursors were determined through X-ray Photoelectron Spectroscopy (XPS), Time-of-Flight Secondary Ion Mass Spectrometry (SIMS), and Energy Dispersive X-ray Analysis Spectroscopy (EDX). Results of post-irradiation characterization of these materials indicate a variety of surface functional groups containing carbon, oxygen, nitrogen and hydrogen. Specifically, aldehydes, carboxylics, lactones, ethers, ketones and quinones are indicated. Further, results of post-thermal treatment characterization suggest graphite surfaces are returned to pre-irradiation composition, if not structure.

During thermal treatment, irradiated graphite samples are heated in the presence of an inert carrier gas (with or without oxidant gas), which carries off gaseous products released during treatment. Graphite gasification occurs via interaction with adsorbed oxygen complexes. Lower temperatures and oxygen levels correlated to more efficient $^{14}C$ removal.

## OBJECTIVES and ASSOCIATED PUBLICATIONS

There were two major objectives of the work and both were successfully achieved.

- To determine the chemical form of $^{14}C$ on irradiated graphite surfaces.

This objective was met via extensive characterization of irradiated graphite surfaces and correlation of these data with the results of off gas composition data obtained during thermal treatment. It was determined that oxide complexes on irradiated graphite surfaces can be attributed directly to neutron irradiation. This conclusion is supported by the finding that concentrations of the oxide species decreased with depth below the surface. Ether-like groups dominated in the interlattice positions and carboxyl or quinone bonds dominated at plane edges, the site of dangling bonds. Post-thermal treatment surface characterization of the irradiated graphite revealed a composition virtually identical to pre-irradiation. These results combine to suggest that the identified oxygen-containing functional groups represent the most likely chemical forms of carbon-14.

The results of these analyses are presented in the following documents:

"Characterizing the Pathway to Formation of $^{14}C$ in Irradiated Graphite", Shilo M. McCrory, a Master of Science thesis in nuclear science and engineering, Idaho State University, Fall 2011.

"Characterization of $^{14}C$ in Neutron-Irradiated Graphite", Daniel Patrick LaBrier, a Doctor of Philosophy dissertation in nuclear science and engineering, Idaho State University, Fall 2013.

Labrier, D. and Dunzik-Gougar, M.L., "Characterization of Thermally Treated Neutron-Irradiated Graphites NBG-18 and NBG-25, Journal of Nuclear Materials, Submitted Jan (2014). (Attached)

LaBrier, D. and Dunzik-Gougar, M.L., "Characterization of $^{14}C$ in Neutron Irradiated NBG-25 Nuclear Graphite," In Press, Journal of Nuclear Materials, Available online 4 February (2014). (Attached)

- To develop a method of thermal treatment for removing $^{14}C$ from irradiated graphite surfaces.

This objective was met via thermal treatment of irradiated graphite samples under various temperature and pressure conditions. The efficiency of carbon-14 removal was determined via timed sampling of off gas collection solutions and subsequent analysis of carbon-14 content via liquid scintillation counting. In addition to specific analysis of carbon-14 release, off gas speciation was monitored to provide insight to the dominant surface species. The overall conclusion was that removal of carbon-14 from all graphites was most efficient at the lower temperature (700°C) without addition of oxidant ($O_2$) to the flow gas. In other words, oxidation of surface species occurred most efficiently (<90% carbon-14) with sources of oxygen already adsorbed or bonded to the surface before treatment. This result has led to post-NEUP testing with pre-loading of oxygen to the graphite surface at low temperature (150°C), followed by thermal treatment in argon at 700°C.

The results are presented in the following documents:

"Thermal Treatment of Irradiated Graphite for the Removal of $^{14}C$", James Cleaver, a Master of Science thesis in nuclear science and engineering, Idaho State University, Fall 2011.

"Removal of $^{14}C$ from Irradiated Graphite for Waste Volume Reduction and Bulk Graphite Recycle: Thermal Treatment", Tara Elizabeth Smith, a Master of Science thesis in nuclear science and engineering, Idaho State University, Fall 2012.

Dunzik-Gougar, M.L. and Smith, Tara E., "Removal of Carbon-14 from Irradiated Graphite", In Press, Journal of Nuclear Materials, Available online 18 April (2014). (Attached)

Smith, Tara E., McCrory, Shilo, Dunzik-Gougar, M.L., "Limited Oxidation of Irradiated Graphite Waste to Remove Surface Carbon-14", Journal of Nuclear Engineering and Technology (JoNET), Vol. 3, No. 1 (2013) (Attached)

**OTHER PUBLICATIONS and PRESENTATIONS**

Dunzik-Gougar, M. L., Cleaver, J., LaBrier, D., Smith, T. E., and Nelson, K., Chemical Characterization and Removal of $^{14}C$ from Irradiated Graphite - III. Waste Management Symposium 2014. (Peer-reviewed full paper and oral presentation)

IAEA Coordinated Research Project (CRP) entitled "Treatment of Irradiated Graphite to Meet Acceptance Criteria for Waste Disposal, IAEA, Vienna, Austria, Irradiated Graphite: Treatment and Characterization of $^{14}C$, Dunzik-Gougar, M. L., Workshop, International, Invited, December 2013. (Oral presentation)

LaBrier, D. and Dunzik-Gougar, M. L, "Characterization of $^{14}C$ in Neutron-Irradiated NBG-25 Graphite," Transactions of the 2013 Winter Meeting of the ANS, Washington, D.C. November 2013 (Peer-reviewed summary and oral presentation)

VHTR Technology Development Office, 6th Annual Technical Review Meeting, DOE, Idaho Falls, ID, Characterization and Treatment of $^{14}C$ on Irradiated Graphite Surfaces, Dunzik-Gougar, M. L. (Presenter & Author), Cleaver, J. (Author Only, Graduate), LaBrier, D. (Author Only, Graduate), McCrory, S. (Author Only, Graduate), Nelson, K. (Author Only, Graduate), Smith, T. E. (Author Only, Graduate), Workshop, National, Not Published in Proceeding, April 2013. (Poster)

Dunzik-Gougar, M. L., Cleaver, J., LaBrier, D., McCrory, S., Smith, T. E. (2013). Chemical Characterization and Removal of $^{14}C$ from Irradiated Graphite - II. Waste Management Symposium 2013. (Peer-reviewed full paper and oral presentation)

Dunzik-Gougar, M.L., "Characterization and Treatment of $^{14}C$ on Irradiated Graphite Surfaces," project reports presented at the 11th, 12th, 13th and 14th International Nuclear Graphite Specialists' Meeting, Eastbourne, UK, Jeju, South Korea, Meitingen, Germany, and Seattle, WA, September (2010, 2011, 2012 and 2013) (Peer-reviewed summaries and oral presentations)

"Chemical Characterization and Removal of $^{14}C$ from Irradiated Graphite" presented at research coordination meeting of IAEA project Treatment of Irradiated Graphite to Meet Acceptance Criteria for Waste Disposal, Vienna, Dec 2012 (Oral presentation)

"Chemical Characterization and Removal of $^{14}C$ from Irradiated Graphite" presented (by research partner Johannes Fachinger) at 11th EPRI Decommissioning & Rad Waste Workshop, Rome, Oct 2012 (Peer-reviewed summary and oral presentation)

Smith, T., Cleaver, J. and Dunzik-Gougar, M.L., "Removal of 14C from Irradiated Graphite for Waste Volume Reduction and Bulk Graphite Recycle: Thermal Treatment," Transactions of the 2012 Annual Meeting of the ANS, Chicago, June 2012 (Peer-reviewed summary and oral presentation)

Cleaver, J., McCrory, S., Smith, T. and Dunzik-Gougar, M.L., "Characterization and treatment of 14C on irradiated graphite," poster presented at DOE's VHTR Annual Review meeting, Salt Lake City, May 2012. (Poster presentation)

Cleaver, J., McCrory, S., Smith, T., and Dunzik-Gougar, M.L., "Chemical Characterization and Removal of Carbon-14 from Irradiated Graphite," WMS 2012, Phoenix, February 2012 (Peer-reviewed full paper and oral presentation)

Dunzik-Gougar, M.L., " Irradiated Graphite: Chemical Characterization of $^{14}C$ and Treatment for Radionuclide Removal " presented at research coordination meeting of IAEA project Treatment of Irradiated Graphite to Meet Acceptance Criteria for Waste Disposal, Vienna, Dec 2013 (Oral presentation)

Smith, T., Cleaver, J. and Dunzik-Gougar, M.L., "Removal of $^{14}C$ from Irradiated Graphite for Waste Volume Reduction and Bulk Graphite Recycle: Thermal Treatment," Transactions of the American Nuclear Society, October-November 2011 (Peer-reviewed summary and oral presentation)

Smith, T. and Dunzik-Gougar, M.L., "The Removal of 14C from Irradiated Graphite Waste for Waste Volume Reduction and Recycle," presented at DOE's Office of Nuclear Energy, Fuel Cycle R&D Review Meeting, Argonne National Lab (U.S. Department of Energy Innovations in Fuel Cycle Research Award, November (2011) (poster)

Smith, T., McCrory, S., and Dunzik-Gougar, M.L., "Removal of $^{14}C$ from Irradiated Graphite for Waste Volume Reduction and Bulk Graphite Recycle," Transactions of the American Institute of Chemical Engineers, October 2011 (Full paper, oral presentation and winner of the Nuclear Engineering Division OUTSTANDING STUDENT PAPER AWARD)

Dunzik-Gougar, M.L., Cleaver, J., McCrory, S., and Smith, T., "Characterization and Treatment of $^{14}C$ on Irradiated Graphite Surfaces," presented at the annual review meeting of the U.S. Department of Energy's Next Generation Nuclear Plant Program, April 2011 (poster)

McCrory, S. and Dunzik-Gougar, M.L., "Characterization of the Chemical Form of $^{14}C$ in Irradiated Graphite", presented at the 2011 Student Conference of the American Nuclear Society, Georgia Tech (AWARD for Best Presenter in the Environmental Sciences & Decommissioning, Decontamination, and Reutilization Technical Track) (2011) (Summary and Oral presentation)

McCrory, S.M., Dunzik-Gougar, M.L., "A Study to Remove $^{14}C$ From Irradiated Graphite for Graphite Waste Volume Reduction and Recycle," Proceedings of the Annual Student Conference of the American Nuclear Society, University of Michigan, Ann Arbor, MI, April, 2010 (Summary and Oral presentation)