Research Objective

The objective of this research is to measure the production of hazardous gases like molecular hydrogen and methane produced in the proton, helium ion, and carbon ion radiolysis of selected solid organic matrices such as polymers and resins. The environmental management of mixed waste containing transuranic radionuclei is difficult because these nuclides are alpha particle emitters and the energy deposited by the alpha particles causes chemical transformations in the matrices accompanying the waste. Basic gamma radiolysis studies have been performed on some organic matrices, however, the chemical changes induced by alpha particles and other heavy ions are typically very different and product yields can vary by a large magnitude. Helium ion radiolysis is used to mimic radiolytic conditions in waste materials containing alpha particle emitters while the other particles are useful for obtaining fundamental mechanistic information on the radiolytic decomposition of these materials. This knowledge can also be used to directly give reasonable estimates of explosive or flammability hazards in the storage or transport of transuranic wastes in order to enhance the safety of DOE sites.

Research Progress and Implications

This report summarizes the work after 30 months of a three-year project on determining the production of hazardous gases in transuranic waste materials. A major part of the project was to design and build an assembly to measure absolute radiolytic yields in solid organic matrices using accelerated ion beams. The very short range of ions such as alpha particles and the nature of the products place severe limitations on the experimental technique. A special beam exit window assembly coupled to a mass spectrometer has proven to be excellent for monitoring the desired products quantitatively. In addition, the apparatus allows one to determine the diffusion of various gases through polymers.

The first experiments focused on the hydrogen evolution in polyethylene because it is either associated with much of the transuranic waste or it can be used as a model of such waste. Hydrogen is the main gaseous product formed in polyethylene and the present work finds a radiation chemical yield of 3.3 molecules/100 eV of energy absorbed. A gradual increase in hydrogen yield is found with increasing particle linear energy transfer, LET (equal to the stopping power, -dE/dx). The yield of hydrogen with 5 MeV helium ions (LET=97 eV/nm) is 4.5 molecules/100 eV, which is about a 40% increase over that observed with gamma rays. Clearly, hydrogen yields with gamma radiolysis cannot be used to give accurate estimates of yields with alpha particles in the management of waste confinement.

The highest LET carbon ions (10 MeV, 840 eV/nm) give yields of hydrogen from polyethylene of 5.7 eV/100 eV. Methane yields in polyethylene are about two orders of magnitude less than that of hydrogen. The mechanism for gas formation in particle tracks is not well understood, and further experiments are examining the polymer cross-linking and scission in order to elucidate the formation processes. The hydrogen diffusion coefficient in polyethylene is found to be 2.2×10^{-6} cm^2/s, which is about an order of magnitude less than that found in typical hydrocarbon liquids. Diffusion of gases is a vital parameter in many engineering designs.

Gaseous product yields have also been determined in the proton, helium ion, and carbon ion radiolysis of polypropylene, poly(methyl-methacrylate) (Plexiglas), and polystyrene (Styrofoam). Gamma radiolysis of these materials gives hydrogen yields of 2.58, 0.24, and 0.04 molecules/100 eV, respectively. The large decrease in yields is obviously due to the nature of the side group connected to the main carbon-carbon polymer backbone, but the mechanism is not known. Irradiation with particles of higher LET can lead to dramatic increases in hydrogen yields. For instance, the molecular hydrogen yields for 5 MeV helium ions are 3.15, 0.62, and 0.15 molecules/100 eV for polypropylene, poly(methyl-methacrylate), and polystyrene, respectively. The increase for polypropylene is only about 20% while that for polystyrene is about 400% from gamma rays to 5 MeV helium ions. It is obvious that relative yields for one type of polymer cannot be reliably substituted for another. Such a result is completely unexpected and could lead to important engineering decisions concerning the management of radioactive materials containing these polymers.

Planned Activities

Many important experiments still need to be performed on the formation and evolution of gases in polyethylene, polypropylene, poly(methyl-methacrylate), and polystyrene. These materials are commonly found in construction materials and they invite interesting fundamental questions. Other products such as methane, acetylene, and carbon monoxide are observable in some of these materials. An examination of their dependence on particle LET may give information on the mechanisms involved. Hydrogen production in other important polymers, such as polyvinyl alcohol, polypyridine, and polybutylene are in progress. Polypyridine (Reillex) is a common resin used in the extraction of transuranic waste materials. Hydrogen yields from it show a large dependence on particle type, which is not currently being addressed.

Experiments are also underway to determine the source of the observed LET dependence on hydrogen yields. Polymer chain scission and crosslinking may give some indication of the reactions leading to and subsequent to the formation of hydrogen. Infrared and UV absorption experiments will also give some indication of the fate of the polymer chain following irradiation. These experiment are vital if one is to be able to predict the production of gaseous products in the radiolysis of polymers.

Information Access

Z. Chang and J. A. LaVerne, Molecular Hydrogen Production in the Radiolysis of High-Density Polyethylene, J. Phys. Chem. B, 103, 8267, 1999.

Z. Chang and J. A. LaVerne, Hydrogen Production in γ-ray and Helium Ion Radiolysis of Polyethylene, Polypropylene, Poly(methyl-methacrylate) and Polystyrene, J. Poly. Sci. in press.

J. A. LaVerne, Z. Chang and M. S. Araos, Heavy Ion Radiolysis of Organic Materials, Radiat. Phys. Chem. submitted.

Z. Chang and J. A. LaVerne, Hydrogen Production in the Heavy Ion Radiolysis of Polymers: I. Polyethylene, Polypropylene, Poly(methyl-methacrylate) and Polystyrene, Macromolecules, submitted.