Project ID: **59934**

Project Title: **Hazardous Gas Production by Alpha Particles in Solid Organic Transuranic Waste Matrices**

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Research Objective

Fundamental radiation chemical techniques are used to elucidate the basic processes occurring in the heavy-ion radiolysis of some of the solid hydrocarbon matrices such as polymers that are associated with many of the transuranic waste deposits or the transportation of these radionuclides. The environmental management of mixed waste containing transuranic radionuclides 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. The objective of this research is to measure the production of hazardous gases such as molecular hydrogen and methane produced in the proton, helium ion, and carbon ion radiolysis of selected solid organic matrices in order to obtain 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 21 months of a three-year project on determining the production of hazardous gases in transuranic waste materials. The first stage 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 window assembly was constructed allowing the beam to pass consecutively through a collimator, a vacuum exit window and into the solid sample. Two types of sample configurations are necessary. Either a solid sheet of sample is sealed a short distance from the exit window or small pellets of sample are confined to a sample holder. A stream of gas, such as nitrogen, flows between the sample and the beam exit window or between the pellets to flush away gaseous products that evolve from the sample surface. The gas steam is sampled with a quadrupole mass spectrometer. By monitoring the desired mass peak with the spectrometer it is possible to quantitatively determine a number of different products on line.

The first experiments have 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 3.1 molecules/100 eV of energy absorbed, in agreement with the literature. (1) A gradual increase in hydrogen yield is found with increasing particle linear energy transfer, LET. The yield of hydrogen with 5 MeV helium ions (LET=97 eV/nm) is 4.5 molecules/100 eV. The highest LET carbon ions (10 MeV, 840 eV/nm) give yields of hydrogen of up to 5.7 eV/100 eV. The mechanism for hydrogen formation in particle tracks is not well understood. Increased radical-radical combination reactions in the particle tracks are probably allowing more hydrogen atoms to undergo abstraction reactions with the bulk material to form

molecular hydrogen. Excited state chemistry may also be a factor at the highest LET. Further experiments are examining the polymer cross-linking and scission in order to elucidate hydrogen formation processes. Hydrogen yields have also been determined in the gamma and helium ion radiolysis of polypropylene, polystyrene, and polymethyl-methacrylate.

Both gamma and heavy ion radiolysis studies have shown that thick samples of polyethylene appear to give low hydrogen yields because of the time necessary for diffusion of the gas from the bulk polymer. The online experimental technique in combination with a suitable model has found the diffusion coefficient of hydrogen in polyethylene to be about 2.2×10^{-6} cm^2/s. The diffusion of hydrogen from the bulk can have a large consequence on the management of waste material and will be examined further. It is very important to note that the observed yield of molecular hydrogen may not be equivalent to its true yield, which is important in the long-term management of waste materials.

1. H. Mitsui and Y. Shimizu *J. Polym. Sci.* **1979**, *17*, 2805.

Planned Activities

The series of experiments to be performed in the next year will thoroughly examine the formation and evolution of hydrogen in polypropylene, polystyrene, and polymethyl-methacrylate. These materials are commonly found in construction materials and they invite interesting fundamental questions. Experiments with gamma rays and helium ions have shown a decrease in hydrogen in the order of polyethylene, polypropylene, polymethyl-methacrylate, and polystyrene. Other products such as methane 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 will also be examined under different atmospheric conditions. Initial experiments in the presence of oxygen have found very little influence on hydrogen yields. Most of the hydrogen is formed in the bulk material and surface reactions apparently give a minor contribution. Nevertheless, the influence of oxygen and water vapor will be examined because of the possible practical implications.

Hydrogen diffusion in the bulk material appears to play a major role in the observed radiation chemistry. A simple diffusion model has been used to extract diffusion coefficients and more complicated models will be developed for multidimensioned applications. The bulk material following irradiation will be examine for cross-linking and scissions. This information will give a more thorough understanding of the radiolytic processes involved and enable better prediction of outcomes in systems that are not possible to be examined experimentally.

Information Access

The results obtained from this project and a discussion of their significance will be submitted for publication in peer reviewed journals.