

Task 15

Immobilization of Fission Iodine by Reaction with a Fullerene Containing Carbon Compound and Insoluble Natural Matrix

S.M. Steinberg, G.S. Cerefice, and D.W. Emerson

BACKGROUND

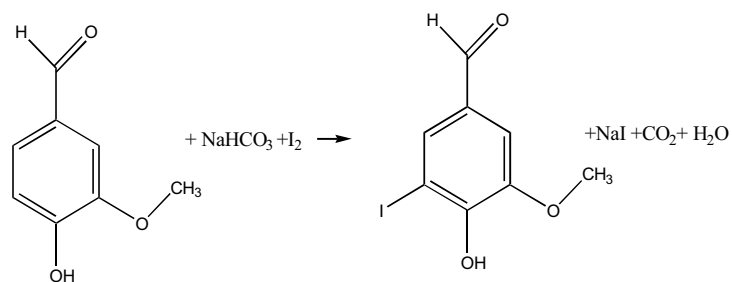
The recovery of iodine released during the processing of used nuclear fuel poses a significant challenge to the transmutation of nuclear waste. Iodine-129, a long-lived fission product formed by both commercial nuclear power generation and nuclear weapons production, is released when reprocessing nuclear fuel. Since iodine can be concentrated in the human thyroid, any uncontrolled release of iodine may result in an increased rate of thyroid cancer in the exposed population. For this reason, recovery of iodine is important for implementing any nuclear transmutation strategy.

The first step in any transmutation strategy is the processing of the used nuclear fuel. This step involves separating the used fuel into its constituent elemental components, allowing the recovery of the uranium, actinides, long-lived fission products, and other components, depending on the strategy and processes involved.

When used fuel rods are dissolved in concentrated nitric acid in preparation for actinide recovery, iodine is released from the fuel. A significant fraction of the iodine is lost to the vapor phase during this process, where it may potentially become a fugitive emission and be released from the plant. To avoid this, specialized filtration systems are used to try to trap and sequester the released iodine (and other fission product gases).

The primary goal of this research is to capture and immobilize the iodine released from these processes in a form that can easily be converted to a suitable target for neutron-induced transmutation. The investigators believe that iodine released during fuel reprocessing can be immobilized in a Fullerene Containing Carbon (FCC) compound or a Natural Organic Matter (NOM) matrix.

Natural organic matter (such as sphagnum moss, peat or brown coal) is an inexpensive and a renewable resource. Further processing of the trapped iodine using simple desorption or combustion processes should be able to produce iodine in a form suitable for transmutation. Furthermore, collaborators at the Khlopin Radium Institute (KRI) have proposed that the iodine-loaded FCC mate-



Ring addition of iodine to a phenolic compound. This reaction is an analogy for reaction with NOM.

rial, when combined with ceramics, is stable enough for use as a long-term storage form, and may be usable as a transmuter target matrix.

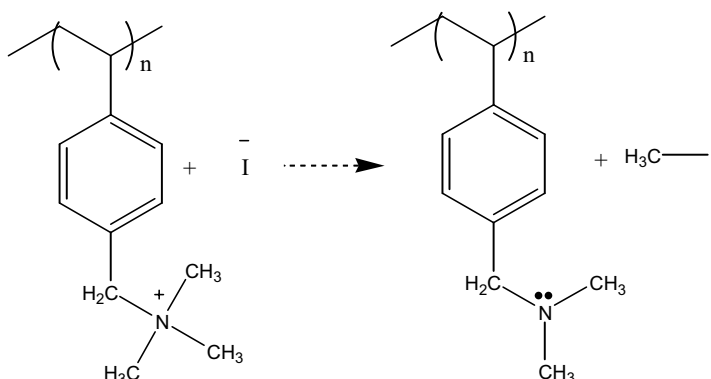
RESEARCH OBJECTIVES AND METHODS

The stability of the association of iodine with FCC and NOM products are studied. Product distributions for the various matrices under various reaction conditions were examined in order to maximize the binding of iodine. The recovery of the iodine from the sequestration matrices was also examined, along with the conversion of the iodine to matrices more suitable for geological storage and/or use as transmutation targets.

The following are the specific research objectives and goals:

- Develop bench-scale experimental set-up and procedures for simulating PUREX head-end vapor phase.
- Develop experimental procedures for evaluating iodine sequestering methods using bench-scale procedures.
- Develop FCC bearing material as potential iodine sequestration matrix.
- Determine binding of iodine to FCC and NOM.
- Examine alternate iodine sequestration matrices using techniques developed for FCC and NOM studies.
- Examine the effect of reaction conditions on binding.
- Elucidate the nature of the reaction products (volatile, hydrophobic, soluble, insoluble).
- Develop methodology and host matrix for converting sequestered iodine to solid matrix for evaluation as transmutation target and/or disposal matrix.
- Examine recovery of iodine from sequestration matrices.

The FCC compounds are developed and prepared by the KRI Research Industrial Enterprise (KIRSI). The KRI-KIRSI team research the impacts of process parameters on sorption of iodine, and examine the material properties, such as how iodine attaches to the FCC compounds. The KRI-KIRSI team also examines the



Transformation of iodide to methyl iodide by pyrolysis of anion exchange resin.

conversion of the iodine loaded FCC compound to a stabilized matrix (similar to ceramic) for potential use as a disposal form, acceptable transportation material, or potential target material.

RESEARCH ACCOMPLISHMENTS

Highlights of accomplishments to date include the following:

- Fuel rod dissolution experiments were conducted and it was demonstrated that FCC and NOM can sequester iodine under these conditions.
- Nitrogen dioxide (NO₂) impact on iodine sequestration: Using the fuel rod simulator it was demonstrated that NO₂ (generated by metal dissolution in nitric acid) reduces iodine sorption for both FCC and NOM.
- Iodate Reduction studies: NOM was demonstrated to convert iodate to iodide and organoiodide at moderate pH. IOH was demonstrated to be an intermediate in the reduction process. Pyrolysis of NOM demonstrated that a large fraction of the iodate is converted to organoiodine.
- Efforts were continued to prepare methyl pyridinium resin. Methods were developed to prepare larger quantities of the methyl pyridinium resin in the chloride form. Recovery studies will be initiated.
- A preparative pyrolysis method was developed for forming methyl iodide. This technique will be used to recover sodium iodide. Using the preparative method, increased



Iodine System

ACADEMIC YEAR HIGHLIGHTS

- ◆ “Immobilization of Fission Iodine by Reaction with Insoluble Natural Organic Matter” by G.T. Schmett, G.M. Kimble, S.M. Steinberg, D.W. Emerson and G.S. Cerefice, was published in the Proceedings of the Actinide and Fission Product Partitioning & Transmutation, Eighth Information Exchange Meeting, OCED/NEA, Las Vegas, Nevada, November 9-11, 2004.
- ◆ “Abiotic Reaction of Iodine and Iodate with Sphagnum Peat” by S.M. Steinberg, G. Kimble, G.T. Schmett, and D.W. Emerson was presented as an extended abstract and poster at the American Chemical Society, Division of Environmental Chemistry (Volume 4, No. 1 - Spring 2005).

methyl iodide during pyrolysis was demonstrated as a function of reaction time for the case of the iodate-peat reaction.

- The reaction rate of iodine (as triiodide) was quantified in aqueous solutions. Using model compounds, it was demonstrated (as previously proposed) that the reaction is first order in the phenol and in I₃⁻. The effects of temperature and pH on the reaction kinetics were measured. Iodine reaction measurements were made on a soluble alkali lignin a commercial humic acid and several model organics (vanillin, vanillic acid, syringic acid, p-hydroxy benzoic acid, and coumaric acid).

FUTURE WORK

Trials with NOM will be continued in the third year of the project. Additional sequestration experiments with the fuel rod simulator will be performed. Investigation into the speciation of iodine in the NOM in an exposed trap will be continued. Additionally, rate constants for the formation of iodate and for the formation of iodophenols will be estimated. The effect of pH on the reaction of iodine with NOM will continue to be investigated. Conversion of trapped iodide (via methyl iodide) to potential target materials will be studied and a bench scale method will be developed.

Research Staff

Spencer M. Steinberg, Principal Investigator, Professor, Chemistry Department
Gary S. Cerefice, Research Scientist, Harry Reid Center for Environmental Studies
David W. Emerson, Emeritus Professor, Chemistry Department

Students

Ginger Kimble and Gregg Schmett, Graduate Students, Chemistry Department

Collaborators

James J. Laidler, Senior Scientist, Chemical Technology Division, Argonne National Laboratory
George F. Vandergrift, III, Senior Scientist, Chemical Technology Division, Argonne National Laboratory
Michael Savopulo, V. G. Khlopin Radium Institute—Research-Industrial Enterprise, St. Petersburg, Russia
Boris E. Burakov, Head of Mineralogical Group, V.G. Khlopin Radium Institute—Research-Industrial Enterprise, St. Petersburg, Russia