

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

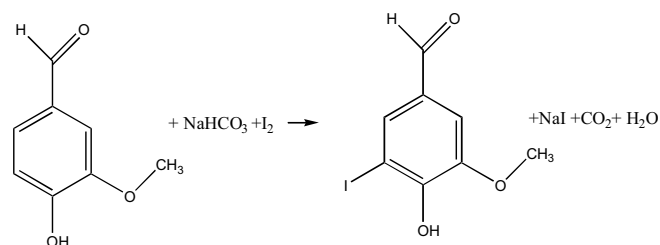
The recovery of iodine released during the processing of used nuclear fuel poses a significant challenge to the transmutation of nuclear waste. Iodine-129, a long-lived fission product formed by both commercial nuclear power generation and nuclear weapons production, is released when reprocessing nuclear 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. This involves decladding the used fuel rods and dissolving the fuel pellets with concentrated nitric acid. The elements of interest are then extracted from the acid solution and the spent acid solution is further processed to immobilize or recover other byproducts.

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. NOM contains a myriad of reactive functional groups such as phenols and α -methyl carbonyl groups that react with iodine or hypoiodite. 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, the researchers at KRI, now collaborators in this project, have proposed that the iodine-loaded FCC material, when combined with ceramics, is stable enough for use as a long-term storage form, and may be usable as a transmuter target matrix.



Ring addition of iodine to a phenolic compound.

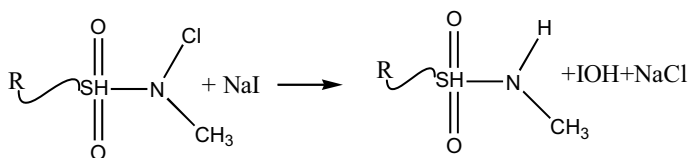
RESEARCH OBJECTIVES AND METHODS

The stability of the association of iodine with FCC and NOM products will be studied. Product distributions for the various matrices under various reaction conditions will be examined in order to maximize the binding of iodine. The recovery of the iodine from the sequestration matrices will also be 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 that have been identified:

- 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 Khlopin Radium Institute's Research Industrial Enterprise (KRI-KIRSI). The KRI-KIRSI team will research the impacts of process parameters on sorption of iodine, and will examine the material properties, such as how iodine attaches to the FCC compounds. The KRI-KIRSI team will also examine the 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.



Transformation of iodide to iodine by N-chlorosulfonamide resin.

UNLV will examine the FCC material, along with NOM and other potential sequestering agents, under simulated process conditions. Both teams will examine the recovery of the iodine from the sequestering matrices.

Initial experiments for FCC characterization will be performed following construction of an iodine (I_2) vapor generator. Additionally, a device will be constructed to simulate nuclear fuel dissolution using iodine sequestration under more realistic conditions. The reversibility of the sorption of iodine on FCC will be explored through a variety of experiments. The stability of the FCC to leaching with simulated groundwater and with solutions containing various reagents that can change the oxidation state of the iodine will be assessed.

Thermal stability of the iodine-FCC association will be measured using pyrolysis mass spectrometry on the FCC material exposed to iodine vapor in simulated fuel rod processing experiments. Information from this will be useful for assessing geological stability of FCC-iodine associations and for devising a method for recovery of iodine from FCC for transmutation. Additional studies using Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) may provide information to associate iodine loss with thermally induced physical and chemical transformations of the FCC sorbent.

Initial studies of iodine binding using NOM involve condensing the off-gas from nuclear fuel dissolution using a cooled trap. The role of pH in the conversion process will be examined. Iodine bound in insoluble organic matter will be measured after alkaline oxidation.

The potential production of volatile iodine species thermally released from charcoal and adsorbable organic iodide species will be measured and analyzed.

RESEARCH ACCOMPLISHMENTS

Highlights of accomplishments to date include the following:

- Several different NOM materials have been characterized.
- Iodine uptake experiments on NOM have been conducted and indicate favorable sequestration.
- The iodine vapor generator assembly was completed. Experimental results indicate that 97% of the iodine was trapped.
- Several tests of iodine sequestration/adsorption were conducted with a commercial peat moss. The results indicated extremely low breakthrough at iodine vapor concentrations close to saturation
- Ion chromatography methods to separate various iodine species were tested.
- A number of experiments have been conducted with alkali lignin and sphagnum moss to study iodide binding. The iodinated materials have been examined by pyrolysis. Researchers have discovered that pyrolysis releases the bound iodide as methyl iodide.
- The alkali stability of several model organic iodides was studied to see if base promoted hydrolysis will be useful in concentrating iodine from NOM
- Materials for a device to simulate rod acid dissolution have been received and assembly has begun on the apparatus that simulates nuclear fuel dissolution.
- The transfer of iodide to organic matter as facilitated by the chlorine sulfonamide resins was examined. Using NOM analogs, iodine was shown to become associated with organic matter in the presence of the active chlorine sulfonamide resins.

FUTURE WORK

Trials with NOM will be continued in the second year of the project. Additional sequestration experiments with the iodine generator will be performed. The effects of nitric acid vapor on the binding of iodine will be explored. Investigation into the speciation of iodine in the NOM in an exposed trap will be implemented. The role of active chlorine in iodine binding will be examined. Additionally, rate constants for the formation of iodate and for the formation of iodophenols will be estimated.

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

Gregg Schmett, Graduate Student, 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