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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, transuranic 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).

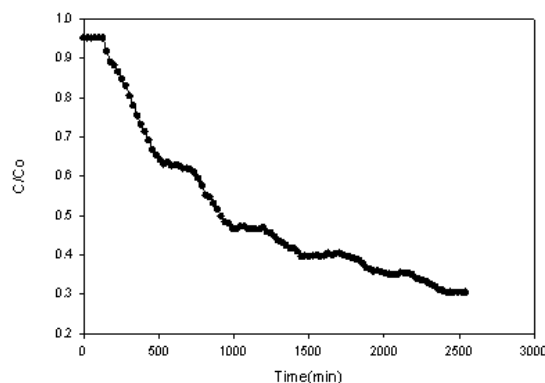
The primary goal of this research is to capture and immobilize the iodine released from these processes in a form that can easily be converted to a suitable target for neutron-induced transmutation. The investigators believe that iodine released during fuel reprocessing can be immobilized in a Fullerene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

NOM (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) in St. Petersburg, Russia, 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.

RESEARCH OBJECTIVES AND METHODS

The stability of the association of iodine with FCC and NOM products were 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.

Iodide Sequestration at pH 4
Continuous Flow method



Sequestration of iodide ($10^{-4}M$) in the presence of sphagnum peat and MnO_2 . The solution was circulated through a column at 5 mL/min.

The following are the specific research objectives and goals:

- Develop bench-scale experimental set-up and procedures for simulating plutonium extraction process (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 were developed and prepared by the KRI Research Industrial Enterprise (KIRSI). The KRI-KIRSI team researched the impacts of process parameters on sorption of iodine, and examined the material properties, such as how iodine attaches to the FCC compounds. The KRI-KIRSI team also examined 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.

RESEARCH ACCOMPLISHMENTS

Observations related to the oxidation of iodide to iodine (I_2) or hypoiodic acid (HIO) by MnO_2 were continued. The formation of triiodide presumably involves the adsorption of iodide onto the MnO_2 surface (perhaps displacing a surface hydroxyl group). The

iodide should be subsequently oxidized and released back into solution as IOH or I₂, which rapidly forms I₃⁻. The kinetic data has been modeled as a first order process. First order rate constants have been obtained for the formation of iodine in the presence of MnO₂. The increase in iodide oxidation rates with MnO₂ concentration is evident in the data. The reaction rate increases with iodide concentration although the dependence is not first order (an order of 1.4 appear to fit the data). The oxidation rate also increases with temperature and has a apparent activation energy of 16.2 kJ/mol.

The total yield of iodine from these materials was compared with the resulting Mn (II) concentration to estimate the oxygen to manganese ratio (MnO_x) for the starting material. This ratio (x) is a function of the average oxidation state of the material and is given by:

$$x = 1 + \frac{I_3^-}{Mn^{+2}}$$

The rate of iodide oxidation can be seen to vary significantly for the various preparations.

It is clear that some manganese oxide can oxidize iodide to iodine under mild pH and temperature conditions. By comparison, laboratory grade MnO₂ reacted sluggishly under these conditions. Because of the wide distribution of this mineral in nature, it is believed that the oxidation of iodide by manganese oxide may result in the formation of organic iodine bonds in sedimentary and soil organic matter.

TASK 15 PROFILE

Start Date: August 2002

Completion Date: October 2007

Theses Generated:

Gregory Tye Schmett, M.S., Department of Chemistry, "Immobilization of Fission Iodine by Reaction with Fullerene Containing Carbon Compounds or Insoluble Natural Organic Matter," August 2005.

James W. Dorman, M.S., Department of Chemistry, "Analysis of Iodide and Iodate in Soil and Water," December 2007.

Ginger Marie Kimble, M.S., Department of Chemistry, "Reactions of Iodine and Iodate with Sphagnum Peat: An Examination of Kinetics and pH Dependence," August 2008.

Journal Articles:

M.A. Cheney, N.R. Birkner, L. Ma, T. Hartmann, P.K. Bhowmik, V.F. Hodge, and S.M. Steinberg, "Synthesis and characterization of inor-

ganic double helices of cryptomelane nanomaterials," *Colloids and Surfaces A: Physicochemical Engineering Aspects* 289, pp 185-192, 2006.

S.M. Steinberg, B. Buck, J. Morton, and J. Dorman, "The speciation of iodine in the salt impacted Black Butte Soil Series along the Virgin River, Nevada, USA" Accepted for publication with minor revision.

Conference Proceedings:

G.T. Schmett, G.M. Kimble, S.M. Steinberg, D.W. Emerson and G.S. Cerefice. "Immobilization of Fission Iodine by Reaction with Insoluble Natural Organic Matter" Proceedings of the Actinide and Fission Product Partitioning & Transmutation, 8th Information Exchange Meeting, OCED/NEA: Las Vegas, Nevada. November 9-11, 2004.

S.M. Steinberg, G. Kimble, G.T. Schmett, and D.W. Emerson. "Abiotic Reaction of Iodine and Iodate with Sphagnum Peat," abstract and poster, American Chemical Society, Division of Environmental Chemistry, Vol 4, No 1, Spring 2005.

S.M. Steinberg, G.M. Kimble, G.T. Schmett, and D.W. Emerson, "Abiotic Reaction of Iodate and Iodine with Natural Organic Matter," American Chemical Society, 40th Western Regional Meeting, Anaheim, CA, January 22-25, 2006.

S.M. Steinberg, G.M. Kimble, G.T. Schmett, D.W. Emerson, M.F. Turner, and M. Rudin, "Immobilization of Fission Iodine by Reaction with Insoluble Natural Organic Matter," MARC VII, Honolulu, HI, April 3-7, 2006.

S.M. Steinberg, G.M. Kimble, G.T. Schmett, and D.W. Emerson, "Abiotic Reaction of Iodate with Sphagnum Peat and Other Natural Organic Matter," MARC VII, Honolulu, HI, April 3-7, 2006.

S.M. Steinberg, B. Buck, J. Morton, and J. Dorman, "Speciation of iodine in the salt-impacted Black Butte soil series along the Virgin River, NV," 234th American Chemical Society National Meeting, Boston, MA, August 19-23, 2007.

S.M. Steinberg and N.R. Birkner, "Formation of organic iodine in soil and sediment by reaction of manganese oxide with iodide," 234th American Chemical Society National Meeting, Boston, MA, August 19-23, 2007.

Mineral	O/Mn Ratio	K(sec ⁻¹)
Cryptomelane Type II	1.39	0.0328
Sodium Manganese Oxide Hydrate	1.87	0.0149
Black Birnessite + Cryptomelane	1.74	0.0137
Cryptomelane Type II	2.2	7.97 E-03
Cryptomelane Type II	2.47	1.49 E-03
Cryptomelane Type II	1.92	3.27 E-03
Manganes Oxide Hydrate	1.83	1.27 E-02

Rate constants for iodide oxidation (at pH 4 and solid concentration of 1 mg/mL) are tabulated along with the measured oxygen to manganese ratio of the manganese oxide. The mineral was identified by powder x-ray analysis.

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