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Quarterly Report: January '02 to March '03

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


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**Scope:** The recovery of iodine released during the processing of used nuclear fuel poses a significant challenge to the transmutation of radioactive iodine. This proposal will develop and examine the use of Fullerene Containing Carbon (FCC) compounds as potential sorbents for iodine release from the reprocessing of nuclear fuel. This work will also include the development of bench-scale testing capabilities at UNLV to allow the testing of the FCC material in a simulated process off-gas environment. This experimental capability will also be used to test other potential sorption materials and processes, such as natural organic matter (NOM) and other promising alternatives. This work will also examine the development of a process to convert the sorbed iodine into a ceramic material with the potential for use as either a transmutation target or as a waste form in a partitioning and sequestration strategy.

Bench scale experimental apparatus and methodologies to simulate Iodine entrainment in the vapor phase released from the head end of the PUREX process (the 4M nitric acid dissolution of spent nuclear fuel) will be developed, along with procedures to test the sequestration of Iodine from the vapor mixture. Long term performance/suitability of FCC and NOM will be tested for sequestration of iodine released by nuclear fuel reprocessing. FCC-bearing materials will be prepared and evaluated under laboratory conditions by KRI-KIRSI. Simulated process evaluations will be done on the FCC-bearing materials, NOM, and other matrices suggested by the collaborators at UNLV. Conversion of the sequestered iodine to a ceramic-like material will be examined by the KRI-KIRSI team. Recovery of the Iodine from the sequestering matrices will also be examined (by both teams).

1. **Major Highlights:**

•Literature Search: We are continuing to search the chemical literature for references relevant to immobilization of iodine.

•Preparation of Test FCC and NOM: We are conducting experiments primarily with sphagnum peat moss and a commercial lignin preparation at this time. We have not received and FCC preparations at this time:

•Analytical Methods Testing: We are testing a using several analytical approaches aimed at characterizing iodine reactivity under conditions of the PUREX process.

•Set up Experimental Apparatus: We have obtained the glassware for assembling the both apparatuses that we will use to characterize iodine immobilization. The iodine generator is complete and undergoing testing. The second apparatus that will be used for simulating fuel rod dissolution is near completion.

•Iodine Binding Experiments (FCC): We have not received any materials for testing at this time.

•Iodine Binding Experiments (NOM): We have done some experiments with sphagnum peat moss and have demonstrated sequestration of iodine from the vapor phase.

**Technical Progress:**

Several additional analytical methods for measuring the speciation of iodine under vapor and aqueous conditions have been established in our laboratory.

> **Ion Chromatography:** $I^-$ and $IO_3^-$ have been quantified and separated by ion chromatography on a Dionex AS-9 column. We have used a Dionex AS-9 column for separation of iodide and iodate species. Under oxidative conditions iodate may be produced from iodide. As indicated in the chemical literature, iodate formation is not readily reversible (under these conditions). Formation of

iodate will prevent iodine sequestration by NOM. Furthermore, iodate salts are readily water soluble. We have also used and will use ion chromatography to monitor the uptake of iodine by NOM after conversion to reactive iodine ($I_2$ and IOH).

**Iodine Sensitive Electrode:** An iodide selective electrode has been used for quantifying iodide and iodine. The selective ion electrode measurement for iodide has been found to be promising. Results indicate that the method works well, even in the presence of high concentrations of natural organic matter. Active iodine (IOH and $I_2$) can be measured after reduction of with sodium bisulfite.

Formation of volatile iodine species (e.g. iodoform ) was examined in some aqueous phase experiments with sphagnum peat and alkali lignin. These experiments were performed in a head-space vial. Volatile iodinated compounds were extracted from the head-space using solid phase micro extraction (SPME). In addition, in several experiments, the aqueous phase was extracted with diethylether, and the extracts were analyzed by GC/MS. The formation of iodomethanes does not seem to be of great importance under these reaction conditions. We will continue this investigation.

Iodine uptake experiments from vapor phase and the aqueous phase on to NOM have been conducted and indicate favorable sequestration. We have conducted some experiments with the iodine generator. Iodine vapor was generated and measured by trapping in a sodium bisulfite solution and iodine was measured as iodide. Traps were prepared with sphagnum peat and break through was monitored. Results indicate that 97% of $I_2$ was trapped.

**Did we measure iodide remaining in solution?**

The materials for a device for simulating rod acid dissolution have been received and are and being assembled (figure 1).

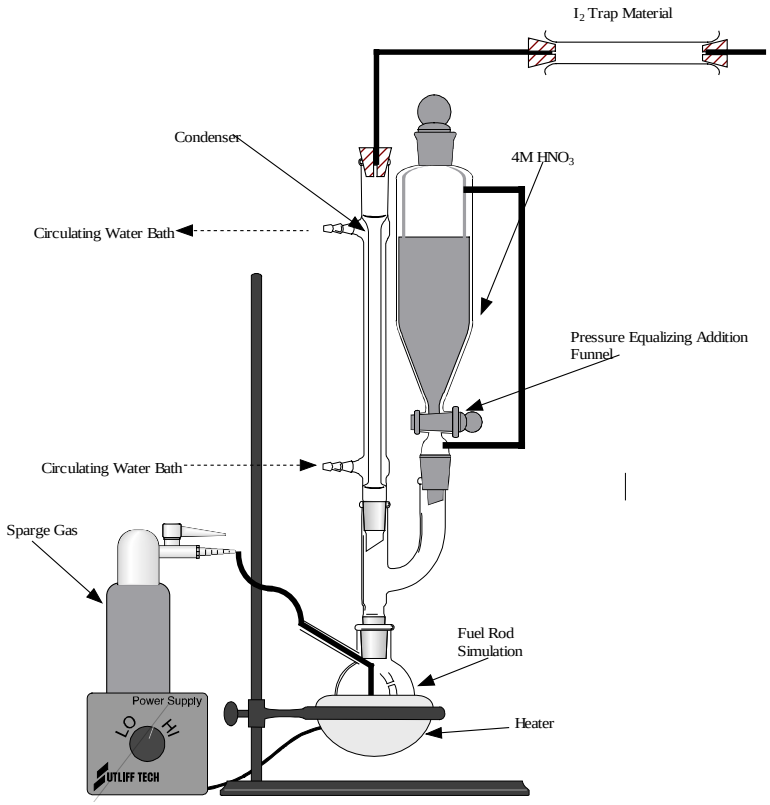


**Figure 1**

## Investigation of Active Chlorine Resin:

Reprocessing of fuel rods may release iodine as HI as well as $I_2$. To capture and immobilize HI (iodide species) we need to effect a change in oxidation state. As noted in our proposed study the chloramines are known to promote the binding of iodide by NOM. Chlorination may also result in the formation of iodate. Iodate will not be immobilized in high molecular weight organic matter. We have therefore undertaken an investigation of this process. We have chosen to examine the behavior of an active chlorine donating resin instead of chloramination. These resins are straightforward to manufacture and have been characterized by a number of investigators. We have done some experiments with a chlorinated sulfonamide resin that was prepared and characterized by Dr. David Emerson during a previous investigation. In the presence of iodide these resins should produce active iodine species that can react with NOM. The chlorinated resin was exposed to buffered KI solutions (pH 8). Ion chromatography was used quantify the formation of iodate. We have used our NOM analogs to demonstrate the formation of reactive iodine. We are monitoring iodate production as a function of time in order to understand the kinetics of these processes and to determine if this reaction would be important under the conditions that we anticipate NOM immobilization will be used.

It is clear that the addition of KI to the resin produces active iodine species almost immediately. $I^-$ has been shown by other investigators to rapidly displace chloride from sulfonamide resins. Experiments with the resin in the presence of vanillin demonstrated the formation of iodovanillin. (4-hydroxy-3-methoxy-5-iodo benzaldehyde). We are also investigating the extent that these resins will produce oxidation byproducts by reaction of active chlorine with the NOM.

We are in the process of conducting experiments with these resins in the presence of complex NOM. We will use IC and the iodine selective electrode method to determine if the resin promoted binding of iodine under these conditions. We are exploring ways to incorporate the resin into the NOM iodine trap train.

**Management Issues:**

**a. Are you spending according to your proposed schedule?**

Spending for the expendable materials are approximately on target. We have not received and FCC material for testing at this time. The pyrolysis instrument is on order. We will need to purchase expendable supplies for this instrument. We are unaware of the status of the ICP instrument.

**b. How are your completion goals tracking with your proposed timeline?**

The development of the analytical methods is proceeding on schedule. NOM studies are on track. As noted above we are unclear on the status of FCC.

**c. What problems have you encountered? Do you need assistance from the UNLV program management on any of these issues? From the national program?**

There have been no significant problems.

**d. Has the proposed schedule/timeline changed?**

No major changes from our prospective. We are unsure of the status of our collaborators at Khlopin.

**e. What do you expect to accomplish in the next quarter?**

We expect to continue trials with the NOM. We expect to do more sequestration experiments with the iodine generator. We will explore the effect of nitric acid vapor on the binding of iodine. We also plan to investigate the speciation of iodine in the NOM (soluble, insoluble, volatile, etc.) by fractionating the NOM in an exposed trap. We will

explore the role of active chlorine in iodine binding. We will estimate rate constants for formation of iodate and for the formation of iodophenols.