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Immobilization of Fission Iodine by Reaction with a Fullerene Containing Carbon Compound and Insoluble Natural Organic Matrix: Quarterly Report September-December 2002

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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 sorbtion 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 have concentrated on characterizing several sources of organic matter as candidates for immobilization of iodine. 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 apparatuses that we will use to characterize iodine immobilization. The pyrolyzer for use with ICP has been ordered.

•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 in aqueous suspensions.

Technical Progress:

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

> **Colorimetric**: A method based on N,N-diethyl-p-phenylene diamine reaction with active halogens. This reaction is standard analytical approach for analysis of active chlorine and other active halogen reactions. It is not particularly selective. The reaction is based on the formation of a colored products with N,N-diethyl-p-phenylene diamine (DPD). DPD reacts with active chlorine producing a pink reaction product (Würster Dye). This product is not stable and does fade with

time. All active halogens produce this color. This method was used to demonstrate the reactivity of active chlorine with the NOM. Rapid loss of active iodine was demonstrated with a number of substrates. The technique cannot prove binding of NOM with the active iodine. For this reason we are resorting to IC and iodine selective electrode methods.

Gas Chromatography: A method based on the formation of p-iodo-N,N-diethyanaline (a volatile compound) has been reproduced. The limitations of this method are being explored. The method relies of reaction of active iodine with N,N-diethylaniline. This reaction results in formation of p-iodo-N,N-dimethylaniline. This compound is sufficiently volatile for analysis by GC/MS. Iodide can be rendered reactive by reaction with 2-iodosobenzoic acid. This compound selectively oxidizes iodine to active iodine (I_2 and IOH). Results indicate that the method did work in standard solutions. There does appear to be difficulty in applying the method in the presence of soluble NOM (alkali lignin). Results were erratic. Application may require cleanup of solution (removal of humic like compounds).

Several different NOM materials have been characterized. These materials are all mosses, peat moss, lignin and commercially available humic acid. We have used chemo-pyrolysis methods and CHN analysis to characterize these materials. Chemo-pyrolysis involves heating organic matter to 350^{o}C in the presence of tetramethylammonium hydroxide. The process results in the formation of volatile methylated degradation products that are characteristic of the material being examined. This study has verified the phenolic nature of these materials. We believe these phenolic materials are excellent candidates for iodine immobilization.

In addition to the chemo-pyrolysis we have done some routine carbon hydrogen nitrogen (CHN) analysis using Exeter Analytical CDS 440.

We have conducted some immobilization experiments under aqueous conditions. For batch studies, iodine solutions were prepared by equilibrating solid iodine with distilled water. Batch experiments have demonstrated that iodide reacts rapidly with NOM, and we are in the process of determining the nature of the adducts. To this end, we have conducted some experiments with active iodine in the presence of low molecular weight phenolic compounds that are analogous to the moieties on NOM that we feel will be responsible for iodine bonding. The phenolic "model compounds" were dissolved in a 0.05 M $NaHCO_3$ solution. We have examined iodine reactivity with phenolic compounds such as vanillin, p-hydroxy coumaric acid and acetophenone and demonstrated reactivity with iodine compounds. These compounds are the phenolic building blocks of lignin and are produced by TMAH chemopyrolysis of many types of NOM.

When an aliquot of iodine is added to a bicarbonate buffered solution of the model phenol, the iodine "color" rapidly fades. For these experiments, the reacted solution was extracted with diethyl ether. The either was removed with a N_2 stream and the residue

was treated a silylating reagent. Trimethylsilyl (TMS) derivatives were separated analyzed by GC/MS and iodinated compounds were confirmed by their mass spectra. With p-hydroxyacetophenone only ring iodination was achieved under these reaction conditions.

We assembled an iodine generator as shown in figure 1. 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 (add bicarb) and break through was monitored. We expect to generate some results for vapor sequestration very soon.

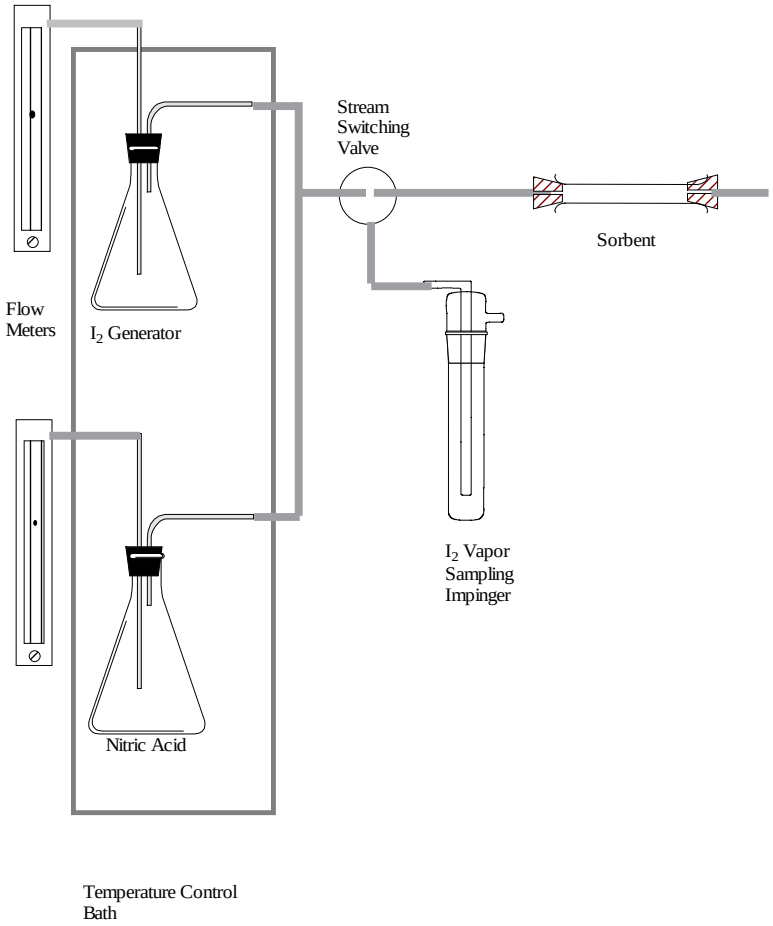

Figure 1

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 begin measuring the sequestration of iodine from the vapor phase using the iodine generator experiments. We will begin testing the effect of added chlorine on iodine reactivity to NOM.

We expect to continue trials with the NOM. We will explore the role of active chlorine in iodine binding.