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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 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 any FCC preparations from KRI. We have obtained a commercially available fullerene preparation from Aldrich and we will conduct some experiments with this material in preparation for the FCC studies.

• Analytical Methods Testing: We have established our primary analytical methods for iodide, iodine and iodate. We are establishing method for volatile iodine species formed by reaction with NOM and by pyrolysis of NOM.

• Set up Experimental Apparatus: The iodine generator is complete and undergoing testing. We have made some additional modifications of the device that should substantially improve reproducibility. We have constructed a device for simulating fuel dissolution and we are performing some preliminary tests.

• Iodine Binding Experiments (FCC): We have not received any materials for testing at this time. We have obtained what we believe to be analogous material from Aldrich Chemical, and will conduct some preliminary tests with this material.

• Iodine Binding Experiments (NOM): We are continuing experiments with sphagnum peat moss and have collected additional data on sequestration of iodine from the vapor phase. We are examining the effect of flow rate and nitric acid fumes on recovery of iodine.

Technical Progress:

Analytical methods for measuring the speciation of iodine under vapor and aqueous conditions are continuing to be developed.
**Ion Chromatography:** In the second quarterly report we reported that $\Gamma$ and $\text{IO}_3^{-}$ have been quantified and separated by ion chromatography on a Dionex AS-9 column. We discovered some interference with this method and have switched to a Novasep A1 anion column (from Alltech Associates) that has been optimized for hydrophobic anions. The new column has resolved the interference problem.

**Pyrolysis GC/MS:** We have done some experiments with iodinated sphagnum moss and have discovered that during pyrolysis the major iodinated organic compound released is methyl iodide. We are in the process of calibrating this method so that we can quantify the amount of methyl iodide released during pyrolysis. Some additional glassware had to be ordered to this end. We believe that this process can serve as a basis for concentration iodine from NOM sequestering agents and processing this iodine into a form suitable for accelerator processing.

We are continuing experiments to determine if the formation of volatile iodine species (e.g. iodoform) occurs during the reaction of iodine with Sphagnum peat and alkali lignin. We are optimizing the headspace solid phase micro extraction (SPME) method for iodoform and other volatile iodinated species.

We have conducted additional experiments with the iodine generator. We have examined the effects of nitric acid fumes (at 40°C) on iodine sequestration. Traps were prepared with sphagnum peat and Ca(OH)$_2$ and breakthrough was monitored. Results indicate that at up to 1000 column volumes trapping efficiency for $\text{I}_2$ was greater than 95%.

In Figure 1 the composite of a number of peat column studies is shown. The fraction of iodine (concentration ~$1.2 \times 10^{-5}$ mol/L) removed from the flowing gas stream is graphed against the number of bed volumes of nitrogen passed through the column. The nitrogen steam was split so that half the flow was saturated with iodine and half with nitric acid. The flow streams were combined and passed though the peat column. Using the criteria of 5% (for breakthrough), it appears that 1000 bed volumes can be passed through these columns under these conditions before the column is effectively exhausted. The column used in this study had a bed volume of 0.9 mL ± 0.1 mL.
Figure 1: Percent of iodine in sorbed by Peat columns. The vapor phase was concentration of iodine was $1.2 \times 10^{-5}$ mol/L and was about 50% saturated with nitric acid fumes.

Upon completion of the breakthrough experiment the contents of the column were leached with distilled water (24 hours). The iodide and iodate content of the leachate was measured using ion chromatography. The results of this exercise indicate only a small fraction of the iodine (<10%) was removed by the water leaching leaching. This observation has interesting mechanistic implications that we will continue to investigate.

The materials for a device for simulating rod acid dissolution have been received and are and being assembled and tested.

**Investigation of Active Chlorine Resin:**

In our previous report we discussed the use of active chlorine donating resins for trapping iodide. Experiments with several model compounds indicate rapid reaction of iodide. Using model compounds such as vanillin we have demonstrated rapid transformation of iodide to iodo-vanillin by a sulfonamide resin. In these experiments we have monitored both the loss of iodide from solution and the appearance of iodo-vanillin. Iodo-vanillin was confirmed by GC/MS analysis. The results of one experiment that demonstrates the rapid kinetics of this process are shown below. This experiment was conducted with 10.0 mM NaI and 13.0 mM vanillin in a NaHCO₃ buffered solution. The reaction was initiated by addition of 50 mg of a sulfononamide resin with approximate 1 meq/gram (wet) of active chlorine.
We are in the process of conducting experiments with these resins in the presence of complex NOM.

In order to demonstrate the presence of iodine in the treated organic matter we have pyrolyzed (400-700°C) iodine treated NOM, and examined volatile and semivolatile products. The results of this study indicate that bound iodine is released from the pyrolyzed organic matter predominantly as methyl iodide. Trace quantities of ethyl iodide were detected. A total ion chromatogram generated by pyrolysis of 0.9 mg of lignin treated with iodine (~40 μmoles of iodine per mg of lignin) is shown in the Figure 2a. This pyrogram is dominated by methyl iodide, which elutes at scan 350. A single ion chromatogram (142 m/e) is presented for the sample in Figure 2b. Pyrolysis leaves most of the starting material as an organic residue.
Figure 3b: Specific ion chromatogram (142 m/e) corresponding to the molecular weight of methyl iodide. The integrated peak area is shown in the figure.

Figure 4a: Pyrogram of lignin that was not exposed to iodine treatment.

Figure 4b. Single ion chromatogram that indicates the presence of methyl iodide in untreated lignin.
In comparison, the chromatogram of pyrolysis products for untreated lignin had numerous peaks corresponding to phenolic compounds (Figure 4a). These peaks are largely missing from the iodine treated sample. It is interesting that methyl iodide can be identified in the untreated lignin, however, its abundance as illustrated by the integrated area of the 142 (m/e) peak is much lower (Figure 4b).

Methyl iodide can easily be hydrolyzed to methanol and sodium hydroxide. We propose that this reaction may be conducted on a macroporous strongly basic anion exchange resin (in hydroxide form). The results of this process would leave the iodide associated with the anion exchange resin, from which it could be recovered for further processing. One can envision a reaction such as:

\[ CH_3I + (Pol \sim N(CH_3)_3^+OH^-)_{solid} \rightarrow (Pol \sim N(CH_3)_3^+I^-)_{solid} + CH_3OH \]

The hydrolysis process leaves iodide associated with the anion exchange resin from which it could be eluted with a strong base such as sodium or ammonium hydroxide. Many suitable resin are commercially available for testing. Pyrolysis may therefore present a useful approach for recovering and concentrating sequestered iodine for further treatment such as transmutation or incorporation into a ceramic.

**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 has arrived and we are awaiting the installation of the ICP instrument.

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

NOM studies are on track. We hope to begin the FCC studies in the near future.

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.

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 begin some experiments with the commercial fullerene materials. We do some preliminary simulations of fuel rod dissolution. 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 continue to explore the role of active chlorine in iodine binding. We will quantify the production of methyl iodide during pyrolysis of iodinated NOM. We will attempt to trap and hydrolyze methyl iodide using a OH⁻ loaded anion exchange resin.