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Immobilization of Fission Iodine by Reaction with a Fullerene Containing Carbon Compound and Insoluble Natural Organic Matrix: Quaterly Report September-December 2003

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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 continuing to conduct experiments with sphagnum peat moss, a commercial lignin preparation and various model compounds. In addition we have continued to characterize the sorption of iodine on FCC preparations from KRI.

•Analytical Methods Testing: We have continued to characterization of volatile iodine species formed by reaction with NOM and by pyrolysis of NOM. We are quantifying unreacted iodine in solution by addition of N,N-dimethylaniline. The iodinated product is being measured by GC/MS.

•Iodine Binding Experiments: We are continuing to use the iodine generator to test sorption of iodine on FCC and NOM materials. We have conducted a series of experiments in a device constructed for simulating fuel dissolution. We have done additional work to characterize the iodine species produced under a variety of experimental condition. We have simulated the formation of NOx during fuel rod dissolution by addition of Cu metal. We have studied the influence of NOx on speciation of iodine on the FCC and NOM sorption and the speciation of iodine left in the reaction vessel.

•We are investigating iodine reaction kinetics with NOM and model compounds over a pH range of 2 –12. We have noted changes in reaction products with model compounds as a function of pH.

• Additional experiments were done with ion exchange resins for the purposes of sequestering iodide.

• Addition work was done characterizing resins containing ethylselenyl (CH_3CH_2-Se~, EtSe~) functional groups for the purposes of trapping methyl iodide released by pyrolysis of NOM.

Technical Progress:

The development of analytical methods for measuring the speciation of iodine under vapor and aqueous conditions are continuing. We have continued to use pyrolysis to examine iodine release from NOM. We have continued the experiments with iodinated sphagnum moss and have quantified the amount of iodine released as methyl iodide during pyrolysis.

We have developed a method for calibrating the GC/MS for methyl iodide. Gaseous methyl iodide standards are prepared by injecting neat methyl iodide into glass gas sampling bottles that had been previously purged with nitrogen. An aliquot of the standards (10 µL) was removed with a gas sampling syringe and injected into a small quartz tube filled with approximately 10 mg of Carbosphere™ (a carbon molecular sieve). This standard (in Carbosphere) was processed using the pyrolysis method described in previous reports. Desorption from the Carbosphere was accomplished by ballistic heating to 500 ^{o}C using the Pyroprobe 2000 instrument described in previous reports. Methyl iodide was quantified by monitoring the 142 (m/e) peak on the chromatogram. An example calibration is presented in figure 1.

Methyl Iodide Calibration

$y = 99743x + 4751$
$R^2 = 0.9992$

y-axis: area peak 142
x-axis: nmoles methyliodide
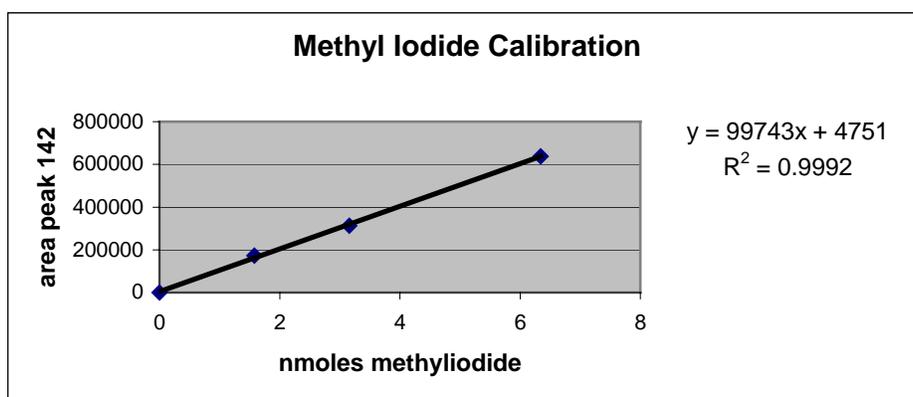
Figure 1: Example calibration for methyl iodide.

In order to address the formation of volatile and semi-volatile iodo-compounds we have exposed NOM solutions to iodine (at several pHs) and then fractioned the mixture as shown below (Figure 2).

Organic Matter → Dilute Acetic Acid Leach → Split

C_{18} → Aqueous → I_2 Analysis, I^- Analysis

Retained → Derivatize → GC/MS Analysis

Solids → NaHSO$_3$ Leach → I^-Analysis → NH$_4$OH Leach → I^-Analysis → Pyrolysis

Figure 2: NOM/I$_2$ fractionation.

The aqueous phase from these reaction mixtures was examined for semi-volatile species. The aqueous phase was passed through a solid phase ext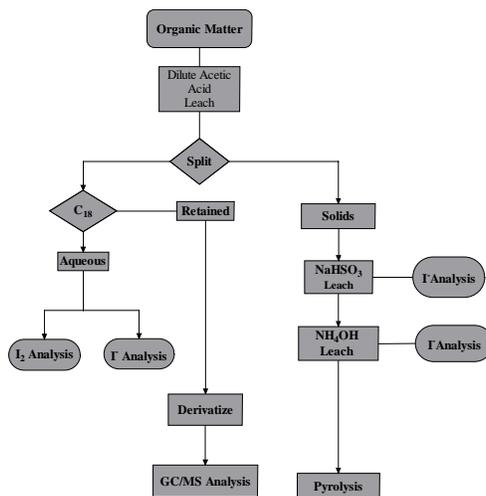raction (C_{18}) cartridge. Material retained by the solid phase cartridge was derivatized with BSTFA (silyation agent) and examined by GC/MS. Our previous observations indicate only minute formation of iodoform and other volatile iodinated alkanes were formed. We were not able to detect the formation of any semi-volatile organic iodides under these conditions.

The solid material remaining in the reaction mixture was leached with several reagents (ammonia and bisulfite) to determine the amount of iodine easily removed by hydrolysis or nucleophilic displacement. The solid was dried at subjected to pyrolysis and the amount of iodine released as methyl iodide was quantified. The amount of methyl iodide produced by pyrolysis was 5-8% and appeared independent of pH in the range of 4-12. A second series of experiments was conducted where 0.5 g of unbuffered sphagnum was treated with 1.5 to 6.0 mL of 250 ppm iodine. After 24 hours of exposure the samples were dried and pyrolyzed *without the leaching procedure outline above*. The results indicated that more than 40% of the applied iodine was converted to methyl iodide. There was no indication of iodine dose dependence in the methyl iodide yield in these experiments, which was certainly surprising. However, the methyl iodide formed was 20-25 times the apparent blank levels and so unambiguously related to the treatment. It may be that sampling of the treated sphagnum selected for iodinated "hot spot" because of textural changes induced by treatment. In other words iodine rich particles of sphagnum may be selectively sampled, for pyrolysis, because of differences in texture and density induced by the treatment. We are investigating this possibility.

We have conducted solution phase iodine binding experiments at various pHs with model organic compounds. Vanillin reacts with iodine at all pHs. However, at high pH the vanillin reduces I_2 to I^-, without incorporating any iodine into the aromatic ring. Under these conditions the reaction produces vanillic acid instead of iodovanillin. At all pHs the reaction kinetics are extremely rapid. In the presence of excess iodine the reaction is complete in less than 30 seconds (at pH 4-12). The rate of reaction is slower at pHs less than 3. We have examined other model NOM compounds such as gallic acid and tannic acid. Both of these materials may be components of NOM and are therefore relevant model compounds. Both gallic and tannic acid reduce iodide to iodide exclusively with no covalent C-I bond formation. The effect of pH on the reaction of iodine with vanillin are presented in figure 3.
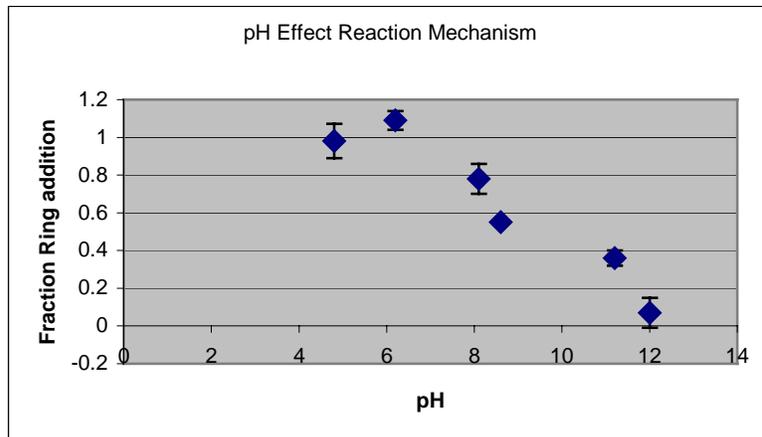
Figure 3: Fraction of iodine adding to aromatic ring in vanillin reaction. Reaction carried out with excess vanillin.

We have conducted additional experiments with the iodine generator and the fuel rod dissolution simulator in order to examine the effects of nitric acid fumes and NOx (at 40°C) on iodine sequestration.   Previously we demonstrated that our NOM traps, prepared with sphagnum peat and $Ca(OH)_2$, were able to trap iodine vapor in the presence of nitric acid vapor. Only a small fraction of the iodine was released by water leaching as iodide or iodate (<10%). If the main reaction was addition of iodine to the aromatic ring one iodide should be produced for each reacted iodine. The iodide should be leachable from the column.   In the absence of nitric acid fumes less than 15% of the adsorbed iodine was desorbed from the column with water. This is significantly less than the 50% we would predict if addition to aromatic rings were the primary reaction. It is interesting to compare this result with the reaction of a suspension of sphagnum moss with an aqueous solution of iodine. At high pH (~12) about 30% of the iodide is converted to iodide in solution. At pHs of 5.7 most of the iodine was apparently reduced to iodide. The difference in behavior between gas phase sequestration and the solution reaction is puzzling and we are continuing to investigate. Experiments with the fuel rod dissolution simulator indicate that both FCC and NOM are capable of trapping iodine.

For many of our trapping experiments we rinsed trapped "iodine" from the columns using a KI solution. The purpose of the KI solution was to convert trapped I_2 to I_3^-. We observed that with the fuel rod simulations that the eluted iodine exceeded the starting material. It is known that nitric acid can oxidize iodide to higher oxidation states. Experiments with concentrated nitric acid and KI indicated rapid formation of I_2. Because significant quantities of nitrate and nitrite are measurable in both the bisulfite solutions and in aqueous extracts of the NOM and FCC traps we believe that KI was being oxidized by the nitric acid fumes thus creating the artifact. Buffering the KI solution with sodium bicarbonate subsequently eliminated this artifact. Because nitric acid can apparently oxidize iodide we thought it would be important to try to examine speciation of iodine on the trap materials. We did a number of experiments to determine the speciation of trapped iodine on FCC and NOM. These experiments involved rinsing the trapping media with distilled water, which was subsequently analyzed by ion

chromatography. Ion chromatography indicates that a significant amount of iodine trapped by FCC is converted to iodate. In the case of FCC 50-60% of the iodine could be desorbed as iodate. For NOM 20-30 % of the iodide was converted to iodate during simulation of fuel rod dissolution. In the presence of NOx the 50-60% was converted to iodate. We repeated experiments with the iodine generator to see if iodate was formed during these experiments. Ion chromatography indicated that iodate formation of NOM was not significant under these conditions. Using the iodine generator 3-4 mg of iodine is transferred to the trap over 1-2 hours. In the case of the fuel rod simulation all of the iodine is placed in the flask where the dissolution process is simulated by warming and addition of Cu. It may be that this second procedure results in more rapid transfer to of iodine from the system and increases the importance of oxidative side reactions.

Unfortunately quantification of iodate by ion chromatography can be somewhat difficult. Iodate elutes very rapidly from the column and emerges very close to the "water dip" in the ion chromatogram. This makes integration of small peaks difficult. In addition, the potential for co-eluting interference is very high for iodate. We will try to address this problem by improving the chromatography or reducing iodate to iodide for analysis.

The generation of NOx by the addition of copper metal may has some important consequences for iodine speciation. Our results indicate that NOx oxidized trapped iodine on the FCC material to IO_3^-. The iodate was easily leached from the column by a water wash (and detected by ion chromatography). Rinsing the column with KI resulted in the generation of an equivalent quantity of I_2. Significant iodate was also produced by the NOM under these reaction conditions.

The formation of iodate has important implications for iodide binding by FCC material. NOx generation also complicates the determination of breakthrough volumes for iodine in the fuel rod dissolution simulator. NOx gas fills the reaction vessel and reacts with the bisulfite trapping solution. This limits the time available for monitoring breakthrough. In addition, the NOx oxidizes iodine that has been previously trapped by the bisulfite. We have examined the transfer of iodide (in the form of KI) in the fuel rod simulator experiments. We believe that iodide released from fuel rods could be transferred from the sparging vessel as HI or some other volatile form of iodine. Since we wanted to focus on the possible volatile forms of iodine created from KI and nitric acid, these experiments were conducted without out a solid phase absorbent. Iodine transfer was quantified by examining the composition of the bisulfite trapping solution. One possibility is that I^- could be oxidized to I_2 by the nitric acid, which would subsequently be sparged from the system. Other possible volatile forms of iodide are NOI (nitrosyl iodide) which we believe may be formed under these conditions. Several experiments were conducted with KI and nitric acid. Transfer rates were generally less than 25 % over 90 minutes of sparging. In the presence of NOx (Cu experiments) I^- was oxidized to iodate (in the reaction vessel). NOx carried over to the trapping solution depleted the bisulfate concentration. After one experiment conducted with 8 mg of KI, 500 mg of Cu in 25 mL of concentrated nitric acid, it was noted that the bisulfite trap took on a iodine like color. The trap solution reacted positively to KI starch paper indicated that I_2 was probably present in the solution. In order to confirm the presence of iodine we added a known

quantity of N,N-dimethyl aniline. This compound reacts quickly with molecular iodine to form 4-iodo-N,N-dimethyl aniline. The solution was extracted and complete iodinization was confirmed by GC/MS. The same experiment was conducted in the absence of copper. Without the NOx generation active iodine was not observed in the bisulfite trap. Apparently the NOx acts to deplete bisulfite and oxidize any iodide present to a "reactive" form (I_2, IOH, NOI). NOx likely contributes to oxidation of iodine on FCC and NOM traps as well.

From the work we have concluded so far we believe that iodine reacts with the NOM/$Ca(OH)_2$ by several mechanism.

1. Ring addition reactions
2. Reduction to iodide
3. Disproportionation in strong alkali ($Ca(OH)_2$)

We believe that FCC adsorbs iodine as molecular iodine and thermal or chemical desorption from this material is facile.

The presence of NOx and nitric acid in these experiments has several effects. Both reagents are capable of oxidizing iodide. This may occur in the reaction vessel during the dissolution of fuel rods or after transfer to the FCC or NOM trap. The formation of highly water-soluble iodate would compromise the sequestration of iodine by either material.

Some additional experiments were performed using ion exchange resins to sequester iodide ions. One line pursued consisted of studying the affinity of various ion exchange resins for iodide ions in potassium iodide solutions. The resins that showed some potential were of the quaternary ammonium type P~$CH_2N(CH_3)_3^+OH^-$, (A-641) and AG-1 P~$CH_2N(CH_3)_2CH_2CH_2OH^+ OH^-$, neither having been used before. "P~" is a cross-linked polysyrene with a position on the phenyl groups to attach a functional group in place of a hydrogen atom. AG-1 retained 1.38 millieqivalents of iodide per g (meq/g) of resin and A-641 retained 2.03 meq/g. Eluting the iodide from AG-1 proved difficult. Solutions containing both sodium chloride and sodium perchlorate were required.

Iodine trapping experiments showed that when natural organic matter (NOM) was used to trap iodine, pyrolysis of the NOM released a substantial amount of iodomethane, MeI. We experimented briefly with trapping MeI on a resin having an ethylselenyl (CH_3CH_2-Se~, EtSe~) functional group that should react readily with the EtSe~ group to form P~$Se(Et)(Me)^+I^-$. A simple experiment to test this was carried out by placing 0.3 g of the resin in a bottle, introducing either 20 or 40 µL of MeI, capping the bottle with a septum cap, and sampling the head space for MeI after a period of time. No solvent was used. With both sample sizes, 58% of the MeI was removed by the resin. Pyrolysis of the resin produced both MeI and EtI as anticipated (Umemura et al., *Bull. Chem. Soc. Jpn.* **1990**, *63*, 2593-2600) showing that P~$Se(Et)(Me)^+I^-$ was formed. This finding is important because if it becomes necessary to trap iodine from Me[129]I, it can likely be done using a resin P~SMe that will trap Me[129]I to form P~$S(Me)_2^+$ [129]I^-. It should then be possible to treat this sulfonium salt, P~$S(Me)_2^+$ [129]I^-, with sodium hydroxide to form P~SMe,

methanol, and sodium iodide thus regenerating the trapping agent P~SMe and producing a water solution of Na^{129}I, and volatile methanol.

Management Issues:

a. Are you spending according to your proposed schedule?

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?
All of our proposed work in on track with the exception of pyrolysis ICP studies.

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. Except we may not be able to utilize pyrolysis/ICP in this funding year.

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

We expect to continue trials with the NOM and FCC. We would like to use the pyrolysis ICP to confirm some of our previous observations. We expect to do more sequestration experiments with the iodine generator. We will continue to measure pH effects on NOM iodine bonding with the purpose of gaining more insight into the reaction mechanism.

Gregg Schmett and Ginger Kimble will begin writing the MS theses'. We will also begin planning our renewal proposal.