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Quarterly Report April 04-June '04

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

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- AAA Project Collaborator:** Dr. James Laidler
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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.
- Iodine Binding Experiments: We have conducted additional experiments in a device constructed for simulating fuel dissolution. We have corrected some artifacts and we are repeating some measurements in the experimental apparatus.
- Additional experiments were done with buffered sphagnum peat suspensions. Reaction rates of iodine with peat have been estimated at several pHs. We are continuing aqueous phase experiments at various pHs. We are determining the fraction of iodine that binds to NOM versus the fraction that is reduced to iodide. We are quantifying unreacted iodine in solution by addition of N,N-dimethylaniline. The iodinated product is being measured by GC/MS.

Technical Progress:

Summary Report:

We have reassembled the fuel rod simulator with the new parts and have eliminated greased fittings from the apparatus. With the exception of the trap material iodine will contact only glass and Teflon. We have demonstrated high recovery of iodine from this system. We have repeated simulated fuel rod dissolution experiments with a trap consisting of 0.01 grams of 70:30 Sphagnum Peat/Ca(OH)₂. The results of these experiments are shown in figure 1. Iodine (6 mg) was added to 55mL of 60% concentrated nitric acid. Sparging was started immediately. The amount of iodine remaining in the simulator was determined colorimetrically. The percent of the iodine removed from the system that escaped the trap was recorded as a function of sparging time. The results are presented as a graph of percent iodine against sparging time and trap bed volumes. No significant breakthrough was observed up to 20,000 bed volumes. Higher trapping efficiency could be obtained with a larger trap. The 0.01 grams of material was used to facilitate flow rate adjustments.

Iodine Breakthrough Fuel Rod Simulator (Glass and Teflon)

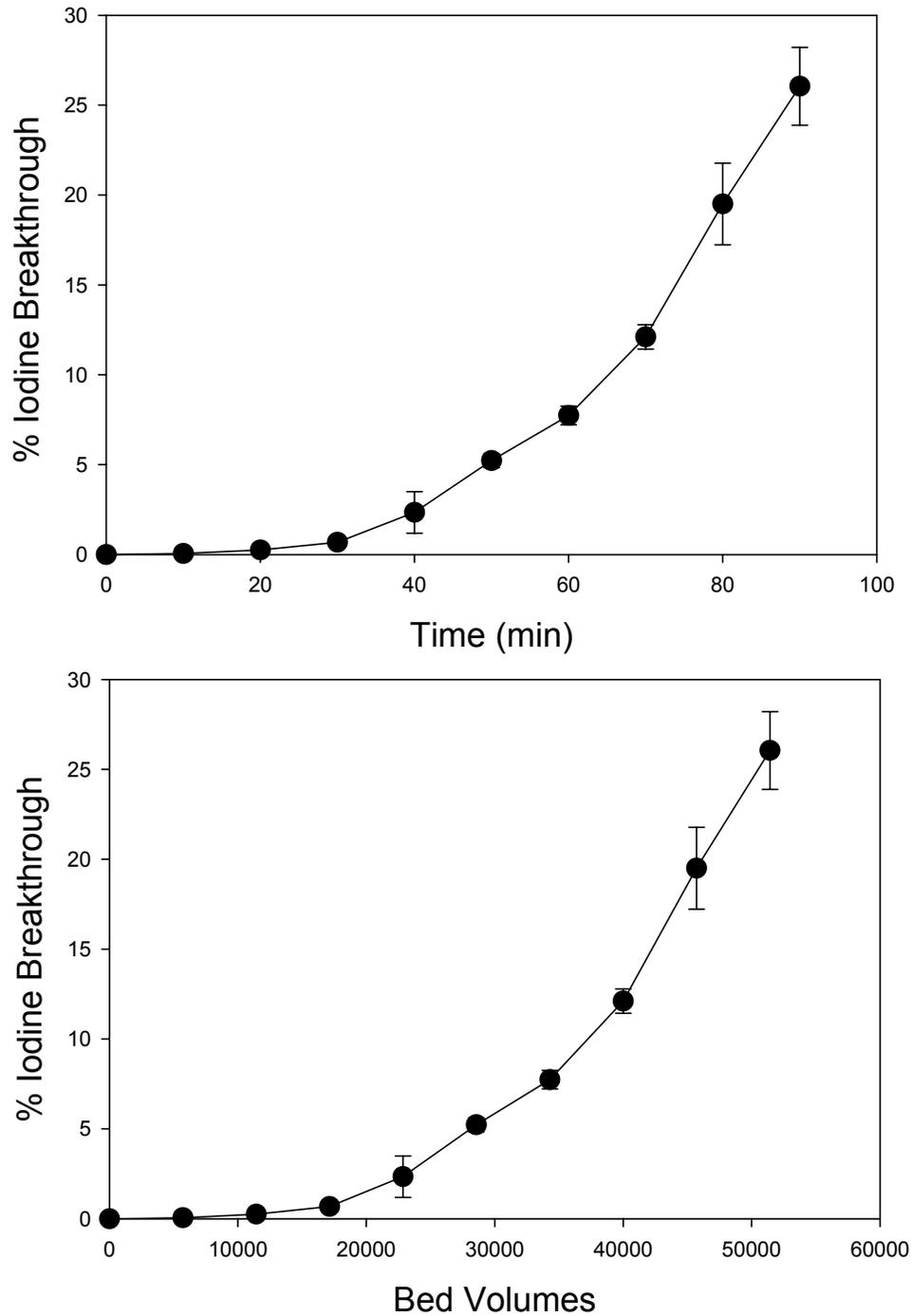


Figure 1: Fuel Rod Simulator Iodine Breakthrough for 0.01 grams of 70:30 Sphagnum/ $\text{Ca}(\text{OH})_2$ and a flow rate of 20 mL/min.

We have done additional experiments with the iodine generator and measured breakthrough curves for different ratios of peat to $\text{Ca}(\text{OH})_2$. Our results (Figure 2) indicate that $\text{Ca}(\text{OH})_2$ at 10% and 60% was less effective than 30%. We believe that the role of the base is two fold. First base deprotonates phenolic moieties making the peat more reactive toward iodine. Second, the base promotes the disproportionation of iodine, which immobilizes fugitive iodine. Disproportionation, may slow the reaction of iodine with the peat by trapping iodine in a less reactive form.

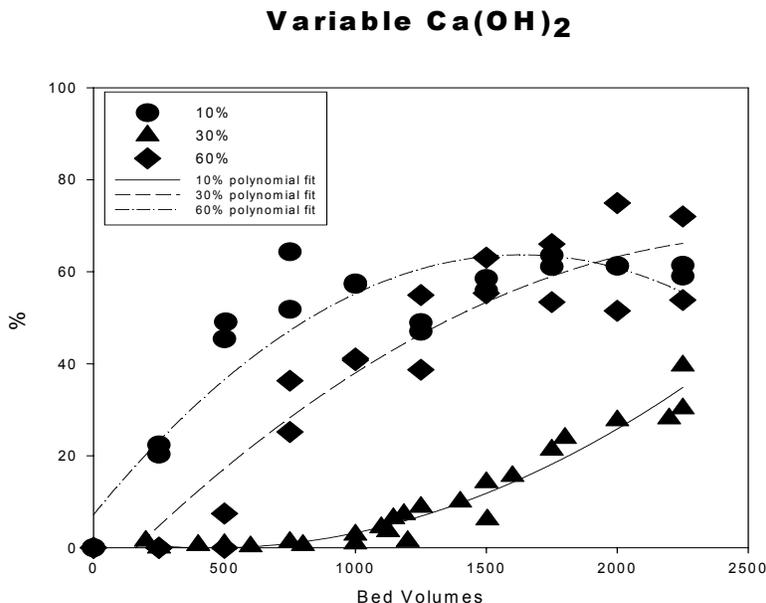


Figure 2: Percent iodine breakthrough for three different Sphagnum Peat/ $\text{Ca}(\text{OH})_2$ ratios. Flow rates were 20 mL/min. Iodine was generated from the vapor pressure of solid iodine and diluted by 50% with nitric acid vapor. The procedure was reported in earlier reports.

We have obtained additional data on the reaction of peat with iodine at pH 2, 6, 8, 10. As will be discussed below the data indicates a pseudo first order reaction of iodine with peat. A plot illustrating the disappearance of iodine (as $\ln [I_2]$ vs. time) is shown below in figure 3. The method was presented in a previous report. The reaction rate at pH 10 was too fast to follow by our method.

I₂ and Peat

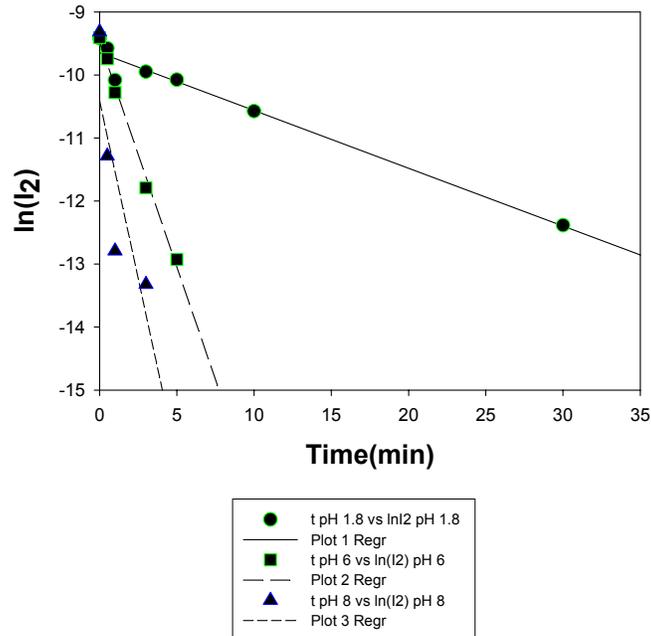


Figure 3: Apparent first order reaction of iodine with Sphagnum peat in aqueous suspension.

The reaction of iodine (I₂) with a suspension of Sphagnum Peat (350 mg/10 mL of Buffer) appears to be pseudo first order in I₂. The pH dependence of the pseudo first order rate constant (k_t) is illustrated in Figure 4. This rate constant represents the sum of the reduction and peat addition (ring addition) reactions.

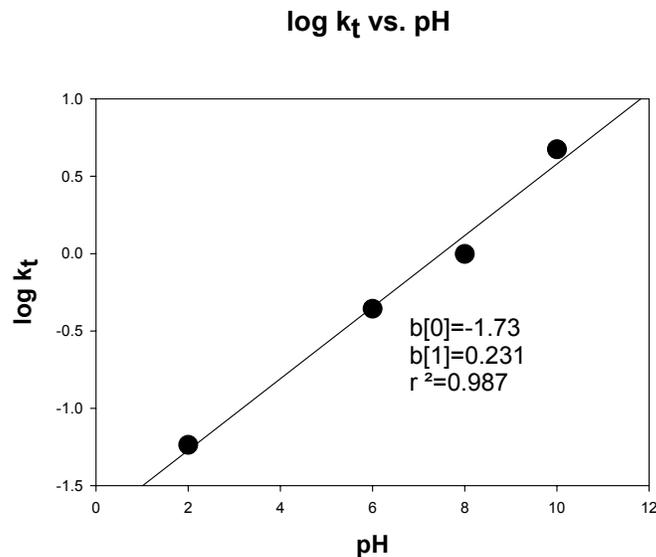
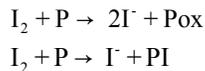


Figure 4: The pseudo first order rate constant for iodine binding as function of pH.

The loss of iodine and the appearance of iodide can be modeled using the simple reaction scheme (P represents the reactive Sphagnum).



This reaction scheme can be represented as two parallel first order equations.

$$\begin{aligned} \frac{dI_2}{dt} &= -(k_{red} + k_{sub}) * I_2 \\ \frac{dI^-}{dt} &= 2 * k_{red} * I_2 + k_{sub} * I_2 \end{aligned}$$

The rate constant k_{red} and k_{sub} are pseudo first order rate constants for the reduction of iodine and substitution of iodine for hydrogen on the organic matrix (ring substitution?). The concentrations of I_2 and I^- are plotted as a function of reaction time in figure 5. The two differential equations presented above have been fit to the data using a numerical method (Simple Runge-Kutta Integrator). The lines in figure 5 represent the least square fit results. The reaction of iodine with sphagnum proceeds partially by reduction and partially by reaction of iodine with the organic material resulting in a substitution of iodine for hydrogen. The top horizontal line represents the iodide concentrations for complete reduction. The bottom horizontal line represents the predicted iodide concentration for ring substitution.

Peat pH 6 I_2 Kinetics

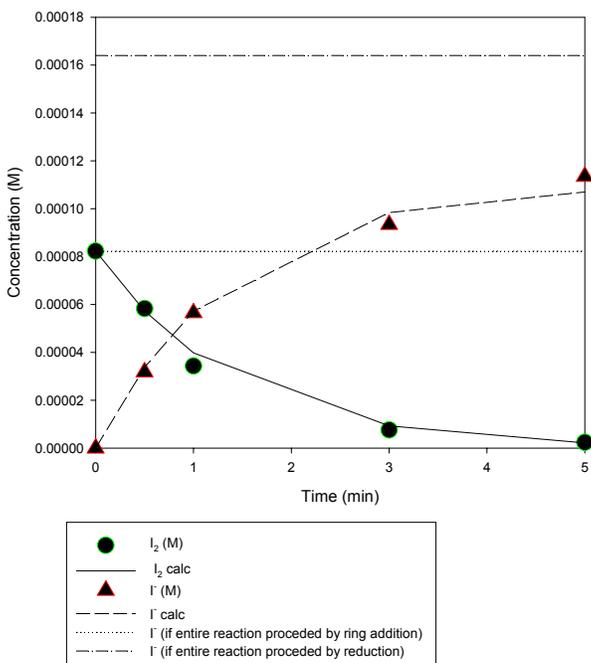


Figure 5: Iodine and Iodide concentrations as a function of time the presence of a suspension of Sphagnum peat (at pH 6). The lines represent best-fit results.

The best-fit values for the rate constants at pH 6 and 8 are as follows.

pH	k_{red}	k_{sub}
6	.25	.48
8	.95	2.91

The fraction of iodine that reacts by addition can be calculated from the rate constants:

$$\%Addition = \frac{100 * k_{sub}}{k_{sub} + k_{red}}$$

About 65% of the iodine reacted by “ring substitution” at pH 6, and 75% at pH 8.

Because it is clear from experiments that simulate the dissolution of fuel rods that some iodine is converted to iodate, we have also investigated the reaction of iodate with Sphagnum peat. 12 hour heating experiments were conducted over a range of pHs. These experiments were conducted with 350 mg of Sphagnum peat in 10 mL of 57 μ M iodate. It is clear from these results that much of the iodate is reduced to iodide. Experiments at pH of 2-9 and demonstrated that 5-30% of the iodine (from the iodate) is incorporated into the peat. The incorporation of iodine from iodate has been quantified by pyrolysis GC/MS. We have quantified the amount of iodine released as methyl iodide during pyrolysis (Figure 6). In addition, we have measured the concentration of residual iodate and iodide produced by the treatment (Figure 7).

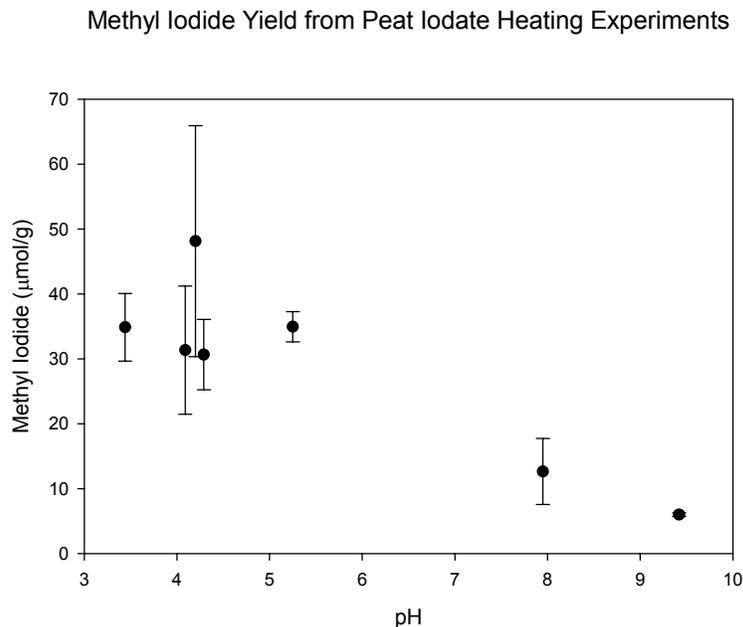


Figure 6: Methyl iodide generation from iodate treated peat (12 hours at 60°C).

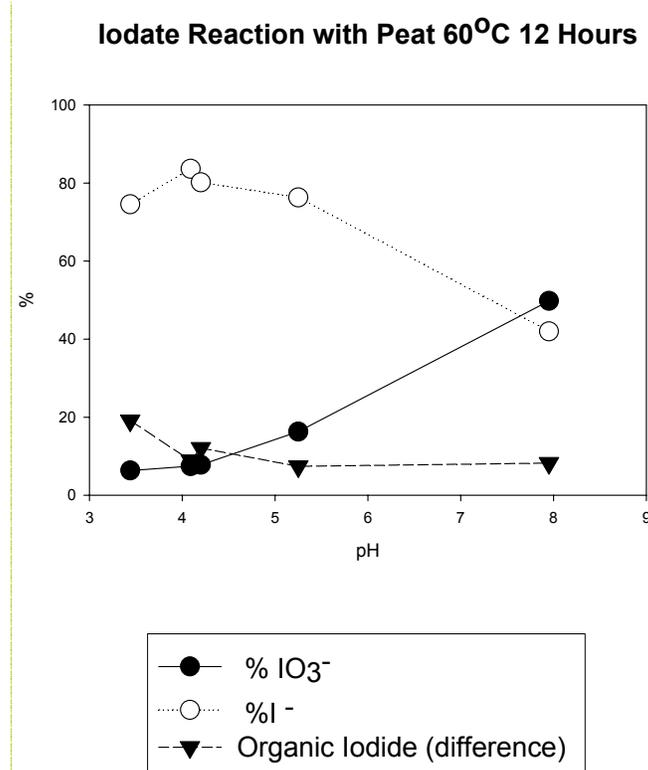


Figure 7: The amount of iodate and iodide in peat suspensions after 12 hours of heating. The amount of organic iodine was calculated by difference.

Management Issues:

a. Are you spending according to your proposed schedule?

Yes.

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

All of our proposed work is 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 experiments with the NOM and FCC. We will repeat more experiments with the modified fuel rod simulator. We still would like to use the pyrolysis ICP to confirm some of our previous observations. We will continue to measure pH effects on NOM iodine bonding with the purpose of gaining more insight into the reaction mechanism. We will continue to examine the reduction of iodate to iodide by NOM. Gregg Schmett and Ginger Kimble are writing their MS theses.