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Immobilization of Fission Iodine by Reaction with a Fullerene Containing Carbon Compound and Insoluble Natural Organic Matrix: Quarterly Report August-September 2004

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Project Title: Immobilization of Fission Iodine by Reaction with a Fullerene Containing Carbon Compound and Insoluble Natural Organic Matrix - S. Steinberg, PI.

Area: Transmutation, TRP Program

Report: During first year of the project we were able to demonstrate iodine sorption by a sphagnum peat and $Ca(OH)_2$ mixture. We decided to explore varying the ratio of $Ca(OH)_2$ to sphagnum on the retention of iodine in both the iodine generator experiments and the fuel rod simulator experiments. Both of these experiments were described in earlier reports.

In Figure 1 we illustrate the effect of $Ca(OH)_2$: sphagnum ratio on iodine sorption by natural organic matter. These experiments are conducted with our iodine generator device at iodine concentrations of about ~10^{-5} mol/L in the presence of nitric acid fumes. In all of these experiments, the traps were packed with about 0.5 g of the sphagnum and $Ca(OH)_2$ mixture. The results indicate that the 30% $Ca(OH)_2$ mixture was most effective for sequestering iodine under these conditions.

We also constructed a device for simulating the dissolution of fuel rods. We expended a great deal of effort optimizing the fuel rod dissolution simulation experimental apparatus. Early experiments were impacted by sorption of iodine onto various components of the sorption train. We have eliminated or minimized iodine sorption by the system components. We retested both FCC and the sphagnum using this device. In these experiments a known quantity of iodine (3 – 6 mg) is placed into the system and nitric acid is added. The system is sparged with nitrogen through trap materials and through bisulfite filled impingers. Results for various $Ca(OH)_2$/sphagnum ratios are shown in Figure 2 and again indicate that the 30% mixture resulted in the smallest breakthrough. These experiments were conducted with very small quantities of sorbent (0.02 g)so that breakthrough could be observed in a reasonable amount of time. With larger amounts of material (~0.5 g) breakthrough was not observed under these conditions. We have conducted additional fuel rod simulation experiments on FCC and NOM to examine the effect of NOx. We are presently evaluating these results.

We have obtained additional data on the reaction of peat with iodine and iodate in aqueous suspension. Our results indicate that peat reacts with both iodate and iodine and for both species, reduction to iodide and incorporation into the organic matter occurs. Experiments over a range of pH values were conducted.

Experiments with iodine were conducted in aqueous buffered solution. All of the experiments were conducted with 350 mg of sphagnum suspended in 20 mL of solution

with an initial iodine concentration of ~10^{-4}M. We have been able to model the reaction with a simple kinetic scheme. We are conducting additional model reactions of compound at low pH to gain more insight into the reaction mechanism.

The kinetics of the reaction of iodine with peat is presented in Figure 3. These data were obtained by a combination of ion chromatography and the N,N-dimethylaniline method described in earlier reports. The reaction of peat with iodine obeys pseudo first order kinetics in the iodine concentration. The overall rate of reaction with the peat is increases with pH. The loss of iodine and the appearance of iodide can be modeled using the simple reaction scheme (P represents the reactive sphagnum and Pox has been oxidized by iodine). This scheme assumes two parallel reactions. The first is a reduction of iodine to iodide, while the second reaction is a substitution reaction (incorporation).

$$I_2 + P \rightarrow 2I^- + Pox$$

$$I_2 + P \rightarrow I^- + PI$$

This reaction scheme can be modeled as two parallel first order equations (1 and 2).

$$\frac{dI_2}{dt} = -(k_{red} + k_{sub}) * I_2 \qquad (1)$$

$$\frac{dI^-}{dt} = 2 * k_{red} * I_2 + k_{sub} * I_2 \qquad (2)$$

The rate constant k_{red} and k_{sub} are pseudo first order rate constants for the reduction of iodine and incorporation into the organic matrix (ring substitution?). The contribution of the two reactions can be calculated from the best-fit rate constants. These constants can be obtained by a numerical fit of 1 and 2 to time series data. Our results indicate that in the pH range of 6-8, these experiments indicate that 60-75% of the iodine reacted by incorporation (electrophillic substitution) into the organic matter.

During the first year of this study it became apparent that iodine could be oxidized to iodate in the presence of nitric oxide and nitrogen dioxide. We have conducted a large number of experiments to determine the possible reaction of iodate with sphagnum peat moss. These experiments indicate that the natural organic material reacts with iodate and result in the formation of bound iodine (organo iodine) and/or iodide. The kinetics of this process is illustrated in Figure 4. This experiment was conducted at 60^{o}C. The reaction of iodate follows pseudo first-order kinetics. Iodide is formed by reduction of iodate in addition to organically bound iodine. The organically bound iodine appears to go through a maximum with reaction time indicating that it is eventually released into the solution as iodide. The reaction rate of peat with iodate decreases with increasing pH. The reaction rate of iodate is about one order of magnatude slower than that of iodine. We have obtained some data that indicates that iodate is first converted to hypoiodic acid, which in turn, can be further reduced to iodide, or react with peat resulting in sequestration into the organic matrix. This reaction presumably occurs as a substitution for hydrogen at phenolic rings. The reaction of iodate with peat appears to involve competition (parallel reactions) between sequestration and reduction to iodide. We are working on a model for this process.

For both iodine and iodate experiments we have verified the incorporation of iodine into the peat using the pyrolysis technique. Pyrolysis of sphagnum peat (at 500^{o}C) from either type of experiment results in the release of methyl iodide.

The formation of iodide from iodine during fuel rod dissolution would result in reduced fugitive iodine during fuel dissolution. However this iodide is also water soluble and highly mobile in the environment. We are exploring the potential use of ion exchange resins for temporarily sequestering this iodide. We are exploring several different types of resin for iodide sequestration. As noted in previous reports, after pyrolysis at 500^{o}C, iodide can be recovered from both ion exchange resins and sphagnum peat as methyl iodide. During the next contract year we will be exploring this phenomenon as well as developing a technique for converting methyl iodide to NaI. We have ordered the equipment necessary to begin the next phase of experiments.

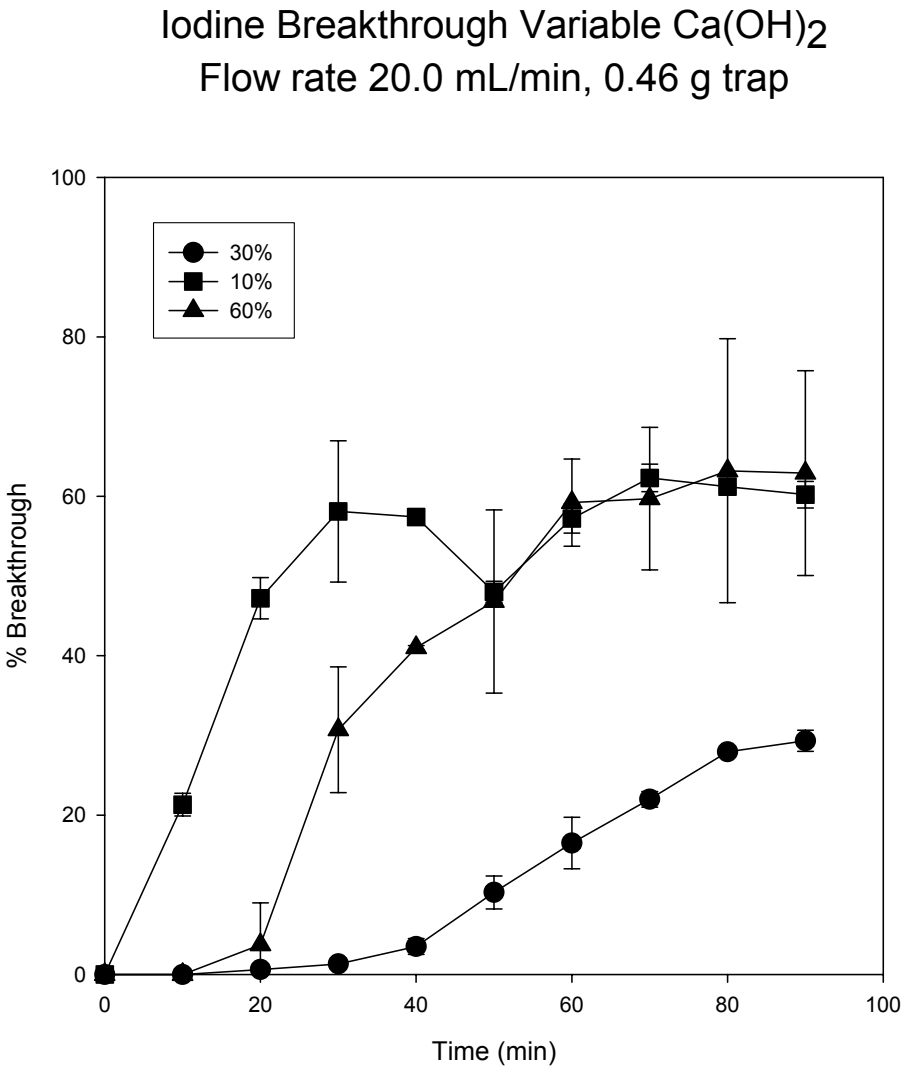

Figure 1: The breakthough of iodine using the iodine generator apparatus described in earlier reports. The trap consisted of 0.5 g of $Ca(OH)_2$: sphagnum mixtures. Three ratios were tested: 10, 30, 60%. The flow rates were 20.0 mL/min and the concentration of iodine was ~10^{-5} mol/L. The carrier was 50% saturated with nitric acid vapor.

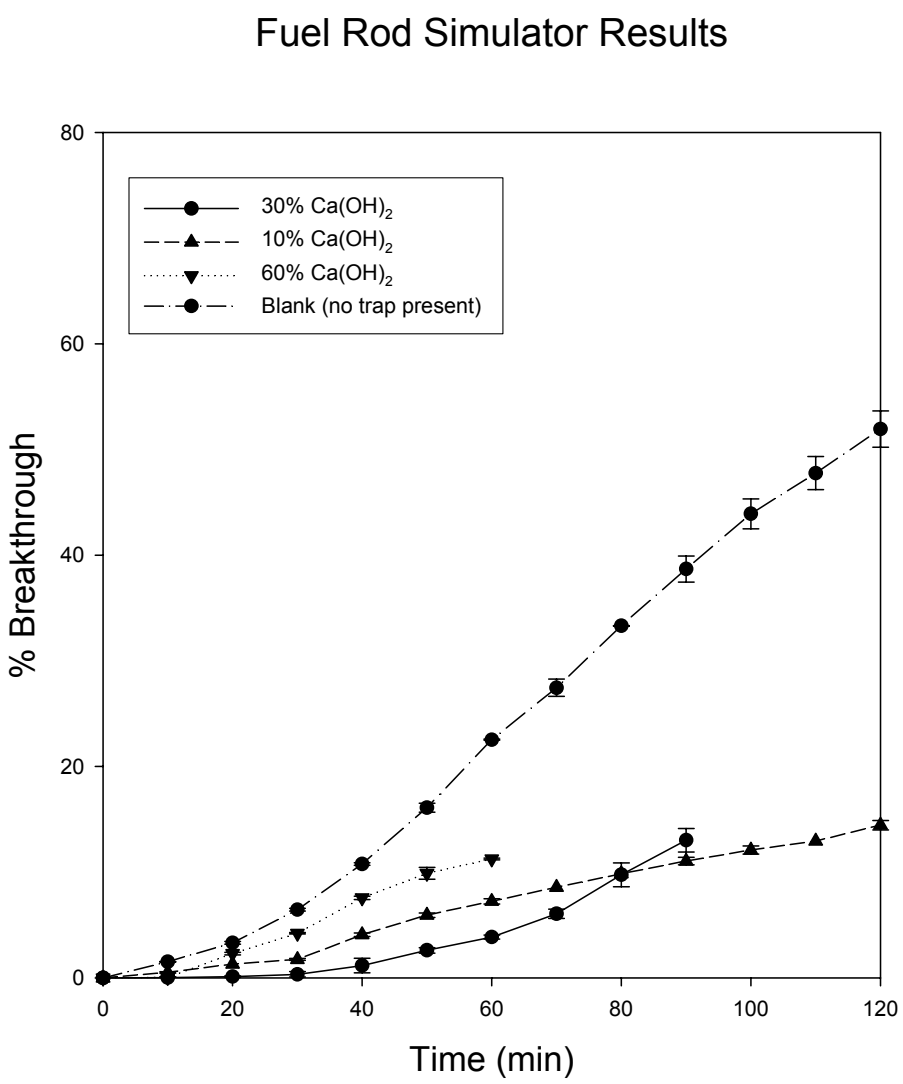

Figure 2: The breakthough of iodine on 0.0.02 g of $Ca(OH)_2$:sphagnum mixtures using the fuel rod simulator experiment described in earlier reports. The flow rates were 20.0 ml/min.

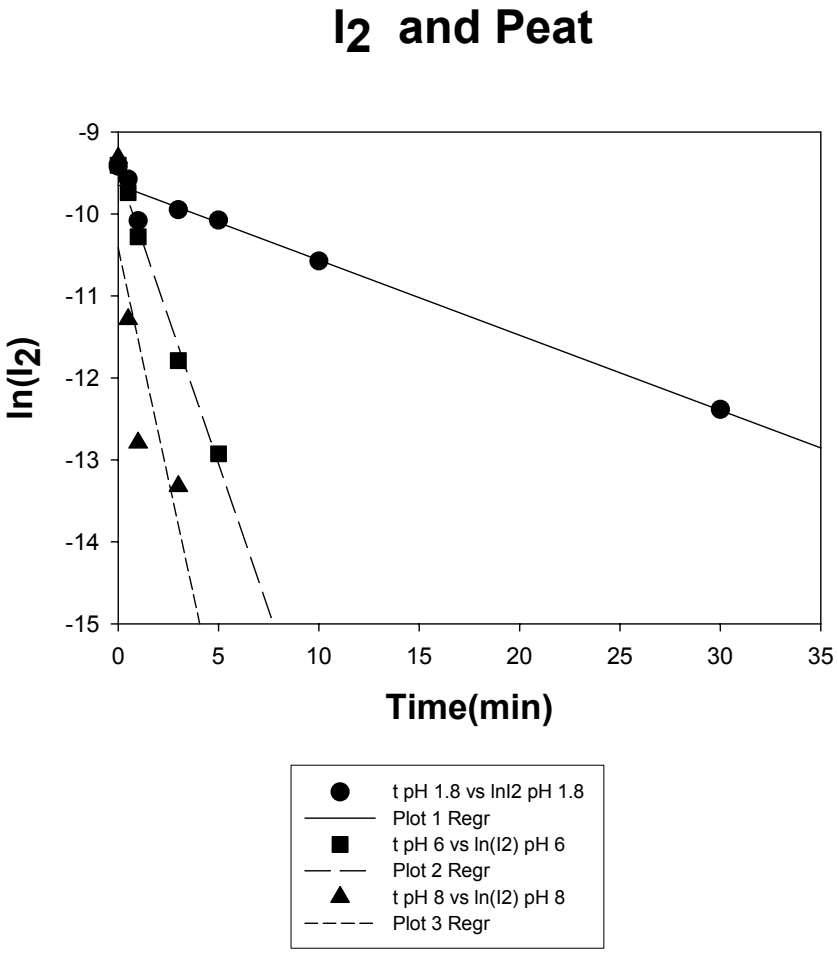

Figure 3: Pseudo fist order kinetics for the batch reaction of iodine with suspensions of sphagnum peat. The reactions were carried out in buffered solutions with initial iodine concentrations of ~10^{-4} M (20 mL volume) and 350 mg of sphagnum.

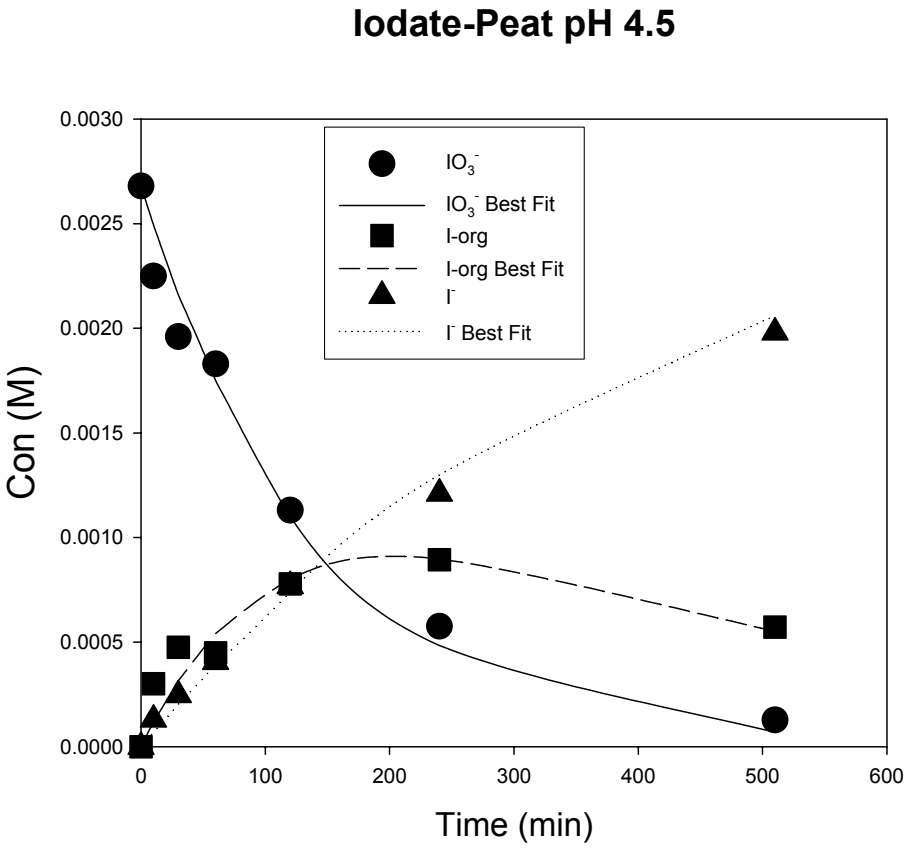

Figure 4: Reaction of iodate with a suspension of sphagnum peat. The reactions were carried out in buffered solutions with initial iodine concentrations of ~$3*10^{-3}$ M (20 mL volume) and 350 mg of sphagnum.