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

Spencer M. Steinberg

University of Nevada, Las Vegas, spencer.steinberg@unlv.edu

David W. Emerson

University of Nevada, Las Vegas

Gary Cerefice

University of Nevada, Las Vegas, cerefice@unlv.nevada.edu

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Project Title:

**Annual Report: Immobilization of Fission Iodine by Reaction with a Fullerene
Containing Carbon Compound and Insoluble Natural Organic Matrix
October 28, 2003**

- Principal Investigator:** Dr. Spencer M. Steinberg (Chemistry)
4505 S. Maryland Parkway
Las Vegas NV 89154-4003
Phone: 702-895-3599
Email: spencer.steinberg@cmail.nevada.edu
- International Collaborator:** **V.G. Khlopin Radium Institute – Research-Industrial
Enterprise (KRI-KIRSI)** St. Petersburg, Russia
Dr. Boris E. Burokov (KRI-KIRSI, PI)
Dr. Michael Savopulo (Co-PI, KRI-KIRSI Director)
- Collaborators (UNLV):** Dr. David W. Emerson (Co-PI, Chemistry)
Dr. Gary Cerefice (HRC)
Gregory Schmett (Graduate Student, UNLV Chemistry)
Ginger Kimble (Graduate Student, UNLV Chemistry)
- AAA Project Collaborator:** Dr. James Laidler
Dr. George Vandegrift
Chemical Technology Division, Argonne National
Laboratory
- AAA Research Area:** Separations

Abstract:

The recovery of iodine released during the processing of used nuclear fuel poses a significant challenge to the transmutation of radioactive iodine. During the first year of this program we have examined the potential of Fullerene Containing Carbon compounds (FCC) developed by KRI, and natural organic matter (NOM) as sorbents for iodine released during the reprocessing of nuclear fuel. This work involved the development of bench-scale testing of the FCC and NOM material in a simulated process off-gas environment.

Research Objectives and Goals

- Develop bench-scale experimental set-up and procedures for simulating PUREX head-end vapor phase; Develop experimental procedures for evaluating I sequestering methods using bench scale procedures.
- Develop FCC-bearing material as potential I sequestration matrix.
- Determine binding of iodine to FCC and NOM.
- Examine alternate I sequestration matrices using techniques developed for FCC and NOM studies.
- Examine the effect of reaction conditions on binding.
- Elucidate the nature of the reaction products (volatile, hydrophobic, soluble, insoluble). See Figure 1 for example.
- Develop methodology and host matrix for converting sequestered I to solid matrix for evaluation as transmutation target and/or disposal matrix.
- Examine recovery of I from I sequestration matrices using combustion, hydrolysis and pyrolysis methods.

Work during the Academic Year 2003-2004:

During the first two quarters of this program we explored various analytical methods available for measurement of iodine, iodide, and iodate. We reproduced an analytical method proposed by Mishra et al., 2000 for measurement of trace levels of iodide and iodine in aqueous solution. Iodine or hypoiodic acid reacts with N,N-dimethylaniline to form p-iododimethylaniline. Iodide can be measured after selective oxidation of iodide with 2-iodosobenzoate to produce active iodine that is subsequently reacted with N,N-dimethylaniline. The product p-iodo-N,N-dimethylaniline can be quantified by GC/MS. This method gave excellent results in dilute aqueous solutions however; we did encounter some interference in the presence of NOM. The method should still be useful for quantifying low levels of iodine released by FCC or other sorbent materials.

We explored the use of an iodide selective electrode for routine measurement of iodide during binding studies. The electrode method has proven to be robust and can be used for measuring iodide and iodine (after reduction with NaHSO₃).

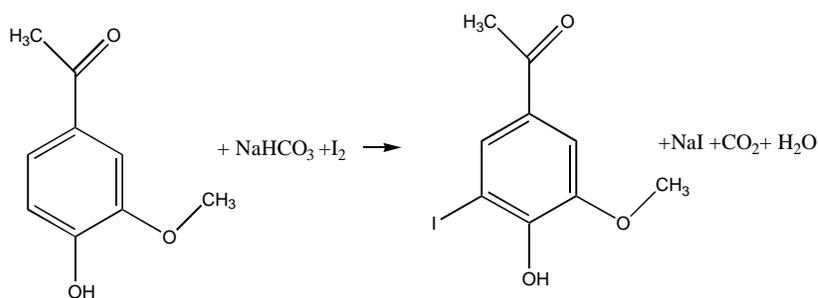
The DPD (N,N-diethyl-p-phenylenediamine) colorimetric method has also been demonstrated to be useful for routine monitoring of iodine. We employed the DPD method for batch reaction studies and for monitoring breakthrough in sequestration tests.

An ion chromatography method was employed for monitoring iodide and iodate during binding studies with natural organic matter. During the first few months of the project we evaluated several anion exchange columns for analysis of iodide and iodate in solution. A Novasep A-1 column was selected for routine separations. Using ion chromatography with suppressed conductivity detection it is possible to follow the changes in iodine speciation during the various experiments conducted with FCC, NOM and other iodine sequestering materials (e.g. activated carbon).

Model Compounds:

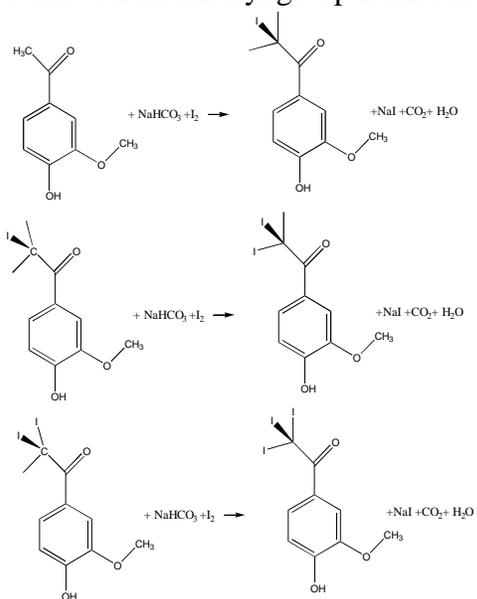
Organic chemical reactions of iodine with NOM have been investigated for decades. Many researchers have demonstrated the incorporation of iodine into naturally occurring high molecular weight organic matter (natural organic matter such as humin, humic acids and fulvic acids). Oktay et al., investigated the speciation of iodine (^{129}I and ^{127}I) in the Mississippi river. Their work indicated that 70-85% of the iodine was associated with colloidal organic matter. Heumann et al., (2000) and Rädlinger and Heumann (2000) demonstrated that iodine becomes associated with higher molecular weight organic matter as a result of microbiological influences. Warner et al., (2000) studied the rapid interaction kinetics of aqueous I_2 with phenols and humic substances. Bischel and Von Gunten (2000) investigated the reaction of iodide with various model phenols and α -methylcarbonyl compounds during oxidative treatment of iodide containing waters with ozone, chlorine and chloramine. Oxidizing reagents react rapidly with dissolved iodide converting it into hypiodous (HIO) acid and hypiodite (IO^-), depending on the pH. Hypiodous acid reacts rapidly with organic matter resulting in formation of iodine carbon bonds. Iodination reactions are most favorable with chloramines because chloramines selectively oxidize iodide to hypiodite. Other oxidants, including hypochlorite, can convert iodine to iodate (IO_3^-) (Vel Leitner et al., 1998).

Model compound studies indicate that phenolic and α -methyl carbonyl groups in natural organic matter (NOM) should be especially reactive toward active iodine (I_2 and IOH). The reaction mechanism with phenols is reasonably well understood. The reaction is promoted by both H^+ and OH^- ions. At low pH the IOH_2^+ is the iodinating species. At extremely alkaline conditions the reaction of iodine with organic matter will be complicated by the disproportionation of iodine to iodate and iodide. At pHs in the range of 7-10, the ionization of the phenolic hydroxy group enhances the reaction of IOH with the phenolate ion. This reaction is promoted by electron releasing functional groups on the reacting phenol.

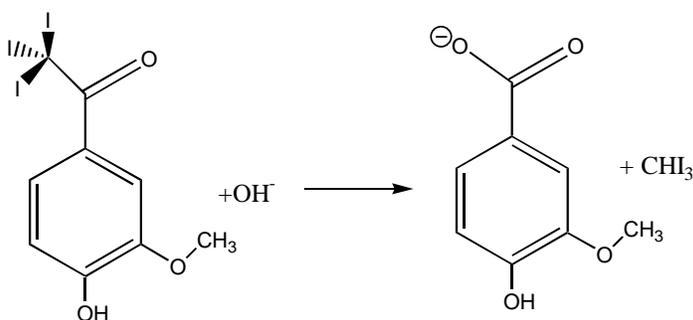


Reaction of iodine with α -methylcarbonyl involves the initial conversion of the α -methylcarbonyl to the enol, which then reacts with IOH. Enolization of the α -methylcarbonyl is promoted by both H^+ and OH^- .

During the first 6 months of this study we demonstrate that sphagnum peat, Kraft lignin and several model compounds react rapidly with active iodine species at moderate pH (8-10). Our results indicate that iodine is bound preferentially by the phenolic ring rather than at the methyl of the acetyl group. This preference was demonstrated by monitoring the reaction of iodine with acetovallinone, a phenolic ketone constituent of lignin that also possesses an α -carbonyl containing acetyl group. The sequential substitution of iodine on the methyl group is illustrated by the following reaction sequence.



Basic hydrolysis of the fully iodinated α -methyl group results in the formation of iodoform and a carboxylate group.



Experiments with model compounds were performed at ambient temperature in aqueous solution. 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 tetramethylammonium hydroxide (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. The solution was acidified and extracted with diethylether. The ether was removed by gentle heating under 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. Reaction of acetovanillinone with iodine produced only the ring iodinated product, which was confirmed by GC/MS analysis of reaction products. As discussed below, we were unable to detect any formation of iodoform during this reaction. In addition, reaction of iodine with other model compounds and NOM samples including, Sphagnum peat moss and soluble alkali lignin, did not produce any measurable iodoform.

Schwehr and Santchi (2003) indicate that iodine is released from marine natural organic matter by alkaline hydrolysis at 65°C . We have conducted several hydrolysis studies with iodinated model compounds to test the stability of iodinated phenols toward alkaline hydrolysis. These experiments were conducted in 1-5 N NaOH heated to 60 or 90°C for as much as 6 hours. These experiments indicated that phenolic iodides do not easily release iodide. Several reports in the literature have indicated that Cu(I) salts or metallic Cu promotes the release of iodine, from phenolic iodides. We tested Cu metal as a catalyst/promoter and did not find notable acceleration this reaction. We are presently are investigating hydrolysis of iodine from sphagnum peat.

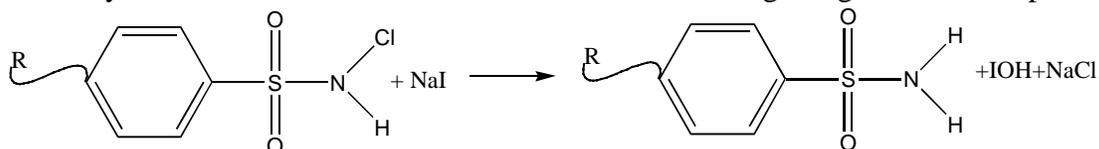
NOM Batch Studies:

Natural organic matter (such as sphagnum moss, peat or brown coal) is an inexpensive and a renewable resource. NOM sources such as sphagnum peat are rich in lignin. Lignin is an abundant biopolymer that comprises approximately 30% of higher plants. Lignin contains of phenolic groups and that react with iodine or hypoiodite. The phenolic nature of lignin and Sphagnum is well established. For example degradation studies using CuO

oxidation and TMAH chemopyrolysis produce numerous aromatic products that can be related to lignin as a precursor (Hedges et al., 2000).

Experiments with sphagnum peat moss, sphagnum peat and a commercially available alkaline lignin indicate that these materials all interact strongly with molecular iodine. Experiments that were conducted in aqueous suspensions (solutions) indicate rapid reaction with iodine. In addition, we demonstrated efficient sequestration of iodine from the vapor phase using an experimental apparatuses that were assembled during the first 6 months of this study. Using these devices we demonstrated that iodine could be removed from a saturated nitrogen vapor stream onto a small packed column of Sphagnum peat moss. These experimental results are discussed further below.

Some experiments have also been performed with an active chlorine donating resin (chloramines) that we propose can be used to promote the conversion of iodide to bound organo-iodine. The reaction of an active chlorine donating sulfonamide resin with NaI is illustrated by the following reaction, where R~ indicates that the functional group is bound by a resin matrix. IOH that is formed can then undergo ring addition to a phenol.



Using model compounds such as vanillin we have demonstrated rapid transformation of iodide to iodo-vanillin by a sulfonamide resin. In these experiments we monitored both the loss of iodide from solution and the appearance of iodovanillin. Iodovanillin was confirmed by GC/MS analysis. The results of one such experiment 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 sulfonamide resin with approximate 1 meq/gram (wet) of active chlorine.

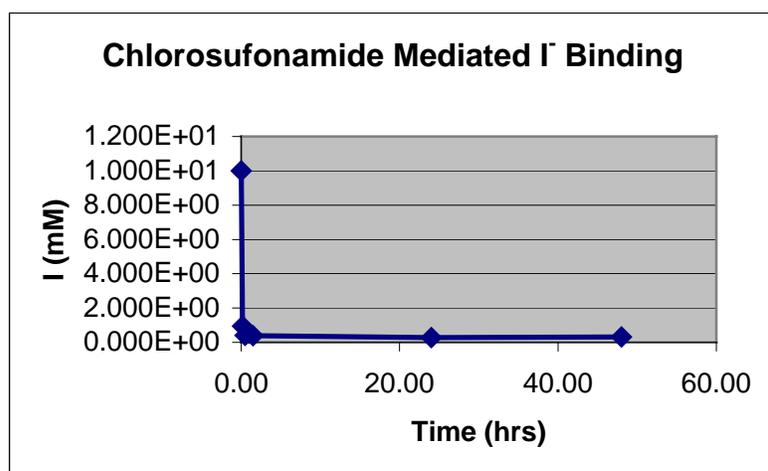


Figure 1: Binding of reaction of iodine with vanillin in the presence of a chlorosulfonamide resin.

If small amounts of volatile iodine species are generated during reaction with NOM, they could be trapped on activated charcoal or a Tenax™ and charcoal combination. Volatile alky iodides can also be trapped on a nucleophilic resin (-SeCH₂CH₃ or -SCH₃). This application is discussed further below. As noted above the production of volatiles, during iodine trapping does not appear to be quantitatively important at this time. However, we are continuing to study the potential for formation of volatile and semi-volatile iodinated products.

As will be discussed below, we have observed that under pyrolysis conditions (400-700oC) NOM bound iodine is released as methyl iodide. We are quantifying the extent of iodine release by this process and we are investigating the means of trapping methyl iodide released by pyrolysis.

Iodination of α -methyl carbonyl groups results in the formation of triiodomethyl ketones. These ketones hydrolyze to form iodoform and a carboxylic acid (haloform reaction). In order to test for the occurrence of iodoform formation we have reacted NOM and several model compounds with iodine under conditions that we be suitable for detecting volatile products. These experiments have been conducted in the batch mode, in septum sealed "head space vials". These vials have a capacity of 60 mL. The experiments were conducted in vials containing 25.0 mL of a bicarbonate buffered solution of iodine (30-50 ppm) and either a model compound, alkali lignin or a sphagnum peat suspension. We conducted experiments with peat/Ca(OH)₂ and have allowed the reaction to proceed for up to 14 hours. Volatile compounds that partition into the vapor phase (head space) were sampled by solid phase micro extraction fibers (SPME). Using this technique with iodoform standards, we have demonstrated sub-ppm detection limits. Our head space analysis of iodine NOM and model compound reaction products, in the presence of bicarbonate buffer, failed to produce and evidence for the formation for more than trace amounts of iodoform (ppt). In the case of the peat/Ca(OH)₂ reaction mixture, trace levels of methyl iodide, iodoethene, iodoethane, chloriodomethane bromiodomethane, diiodomethane and iodoform were apparent. These results are illustrated in Figure 2. In this figure we show both a total ion chromatogram or TIC (signal proportional to abundance) and a single ion chromatogram of the 127 peak, from a section of the chromatogram where some iodinated methane compounds elute. Iodinated compounds can often be identified by the predominance of a 127 (m/e) peak (corresponding to I⁺) in their mass spectrum. The TIC is a measure of the relative concentration of various organic compounds in a sample. In the TIC shown the signal is dominated by non-halogenated compounds. Toluene was the most abundant compound identified in this section of the chromatogram. From the relative peak heights in the upper TIC and lower specific ion chromatogram, it can be surmised that the contribution of volatile iodinated compounds the total volatile products is very low. The observation of only trace iodoform (not shown) confirms that ring iodination is the dominant reaction under these conditions. At this time we do not find evidence to indicate that the haloform reaction is significant with sphagnum peat moss or lignin.

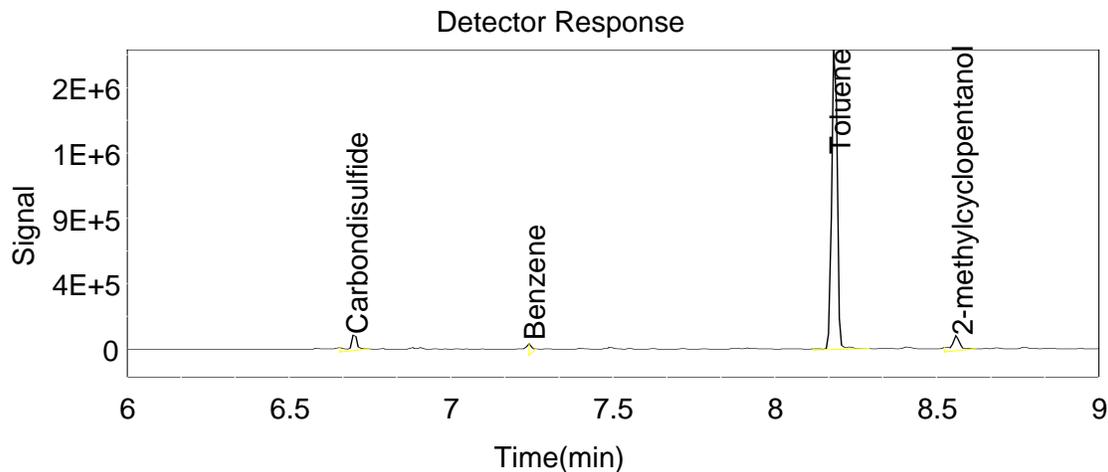


Figure 2: A total ion chromatogram for volatile compounds released from an iodinated suspension of Sphagnum peat and $\text{Ca}(\text{OH})_2$.

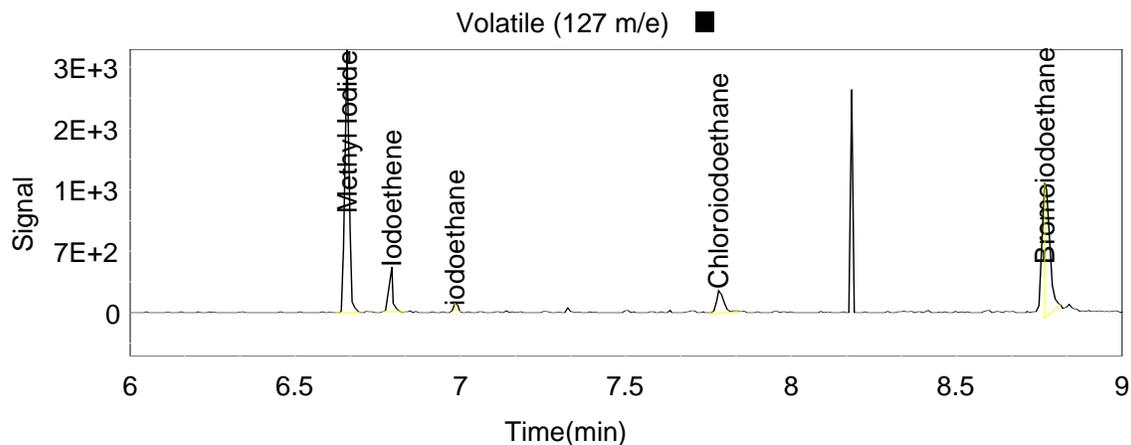


Figure 3: A specific ion chromatogram indicating the presence of various volatile iodinated compounds released from an iodinated suspension of Sphagnum peat and $\text{Ca}(\text{OH})_2$.

We have conducted several experiments to search for semi-volatile iodinated products from peat as well. After iodinating a 1.0 grams/ 30 mL suspension of peat/ $\text{Ca}(\text{OH})_2$ the reaction mixture was fractionated by the scheme shown in Figure 4.

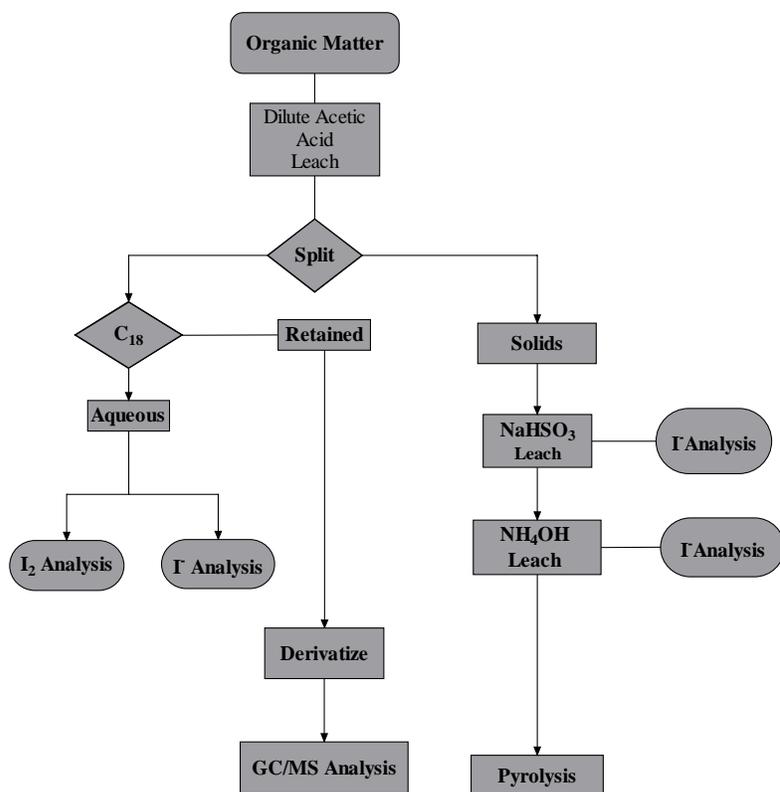


Figure 4: Fractionation of iodinated sphagnum peat for isolation of semi-volatile products.

The aqueous phase was separated from the insoluble peat by vacuum filtration. The peat was leached with 2 M acetic acid, and the pH of the eluant was adjusted to about 5. This extract/leachate was processed through an octadecyl silylated silica cartridge (C₁₈) in order to isolate semi-volatile compounds. Iodine measurements in the aqueous extract confirmed the loss of active iodine. The concentration of iodide produced in the aqueous extract, was consistent with the mechanism proposed where one iodine atom is incorporated into the NOM. We have begun experimenting with active chlorine donating resins as a means of converting this iodide to IOH. Preliminary results with this resin demonstrate rapid conversion of iodide to active iodine that reacted rapidly with a model compound.

The retained fraction was eluted from the C₁₈ cartridge with methanol and the methanol was removed by rotary evaporation. The residue was reacted with N,O-bis(trimethylsilyl) trifluoroacetamide (BSTFA) and analyzed by GC/MS. Although a number of compounds were identified in the extract, there was evidence of only trace quantities of iodinated products (iodoform).

Reducing (and nucleophilic) agents such as hydroxylamine or sulfite or strong alkali may release covalently bound iodine forming iodide which would be considerable more mobile in the environment and very susceptible to leaching from an FCC- ceramic composite. Early results from treatment of the NOM with both NaHSO₃ and NH₄OH for

24 hours at room temperature indicate that covalently bound iodine is not released easily at ambient laboratory temperatures by either strong alkali or nucleophilic reagents. Several workers have reported that iodine bound in insoluble organic matter can be measured after alkaline oxidation. We will continue our studies and include some of these methods. The approach utilized will be similar to the methods summarized in Copper et al., 1998, Olesky-Frenzedl et al., 2000.

Iodine Sequestration from the Vapor Phase:

We developed and characterized bench scale experimental apparatuses and methodologies to simulate iodine entrainment in the vapor phase released from the head end of the PUREX process (the strong acid (nitric) dissolution of spent nuclear fuel) FCC, NOM and various other materials (activated charcoal, commercially available nonotubes) were tested with these devices for their ability to sorb iodine from an acidic vapor phase. We have examined the thermal stability of iodine doped FCC-bearing materials that were prepared under laboratory conditions by KRI-KIRSI. We also explored the stability of FCC and NOM toward several leaching procedures.

We constructed an I₂ generator for use in testing of iodine sequestration (Figure 5).

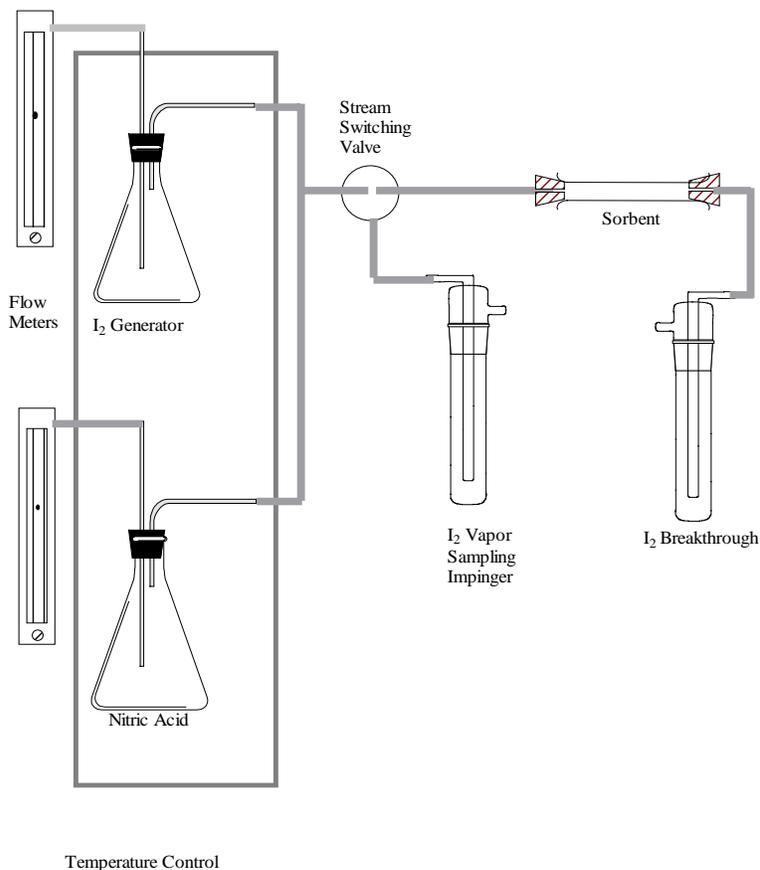


Figure 5: Iodine Vapor Generator

Using this experimental set up, we tested various materials for the iodine sequestration potential (adsorption capacity). Iodine sequestration by sphagnum peat was tested in the presence of various inorganic bases. Heating iodine crystals to 50°C, and passing a metered stream of N₂ over the crystals generated iodine vapor. The iodine vapor was diluted to 50% with a stream of N₂ that was passed through an impinger filled with concentrated nitric acid (16 M) and saturated with nitric acid vapor. All of our experiments were run under these conditions. Flow rates were varied to study the effect of flow rate on iodine breakthrough. This stream was directed through a column that was packed with a mixture of sphagnum peat and the various inorganic bases (Ca(OH)₂, Na₂CO₃, NaHCO₃). Iodine breakthrough was monitored by passing the effluent through a glass impinger filled with NaHSO₃, which reduces the iodine to iodide, which can be measured using the iodide sensitive electrode. The results from these experiments are summarized in Figure 6.

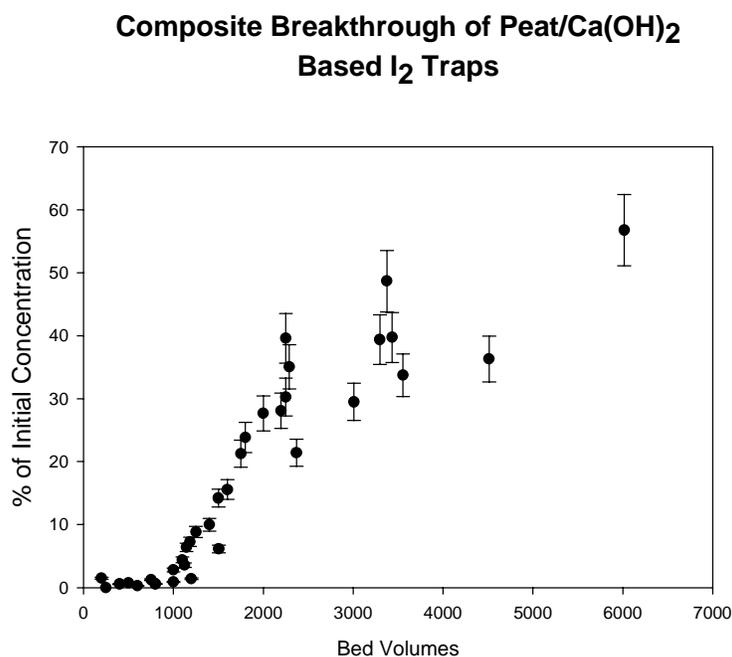


Figure 6: Breakthrough volumes of NOM/Ca(OH)₂ iodine traps.

**Comparison of CaCO_3 , Ca(OH)_2 , NaHCO_3 and Na_2CO_3
30% by Weight, 70% Sphagnum**

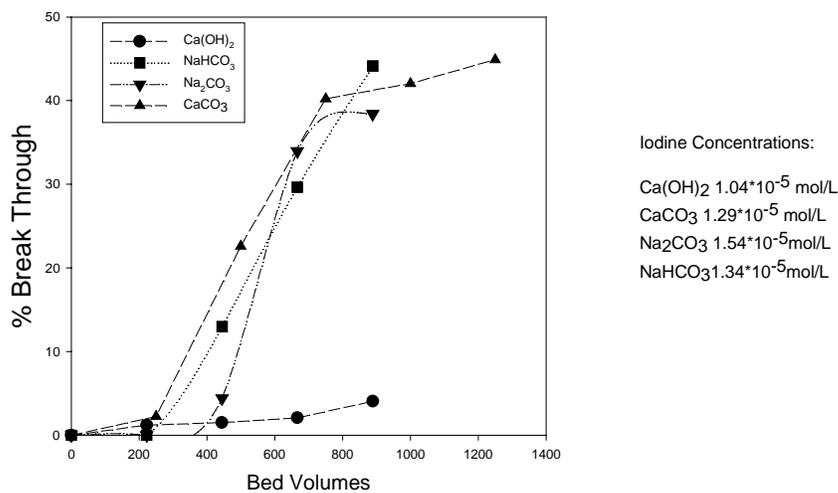


Figure 7: Comparison of various inorganic bases.

These experiments indicate that Ca(OH)_2 peat combination was the best for iodine sequestration. After breakthrough (vapor concentration =5% of initial) the packed columns were leached with either water or a KI solution. The peat/ Ca(OH)_2 combination did not release iodine to the leach solution. To our surprise very little iodide (or iodate) was released by the water leach. We anticipated that for each iodine molecule reaction with the peat only one iodine atom would become covalently linked to the peat matrix. Our expectation was that each iodine molecule would form one equivalent of iodide and that this iodide would be easy to remove from the peat. Our results indicate that that the second iodide is not easily liberated with distilled water. However, as noted above the iodide could be recovered with dilute acetic acids. We characterized a number of the water leachates by ion-chromatography. Ion chromatography revealed only trace amount of iodate in the leachate indicating that disproportionation of iodine in the presence of the strong base was not the dominant reaction.

During the first year of this study we examined iodine breakthrough on several carbon substrates in addition to the peat samples. We investigated breakthrough with a commercially available activated carbon (Alltech SK-2). This is a type 2 activated carbon frequently used for air quality studies. In addition we did some experiments with a commercially available fullerene preparation. This material is available from Aldrich Chemical Company and has been characterized as carbon nanotubes. Several samples of FCC were received from our KRI collaborators. Iodine sorption experiments with activated carbon, carbon nano-tubes and FCC were performed using the iodine generator.

Vapor containing I_2/HNO_3 was passed through the packed columns and the breakthrough volumes were measured. Examples of experimental results are shown in Figure 8-10.

We conducted several experiments using a commercially available Fullerene (carbon nanotubes) preparation. The breakthrough volume (1000 bed volumes) observed with this material was similar to the NOM results. This is illustrated in the figure 8. Iodine trapping on this material was demonstrated to be easily reversible (thermal or KI leach).

We developed a simple qualitative test for sorption reversibility using KI starch test strips. After conducting a breakthrough experiment the trap was removed from the vapor generator and a moistened KI –starch test strip was placed in each end of the trap. The trap was sealed with Teflon coated plugs for 10-24 hours. Iodine released from the trapping matrix causes the test strip to darken. This simple test indicated rapid iodine desorption from the Aldrich nano-tubes.

Comparison of Nano-Tubes (Aldrich) and Peat

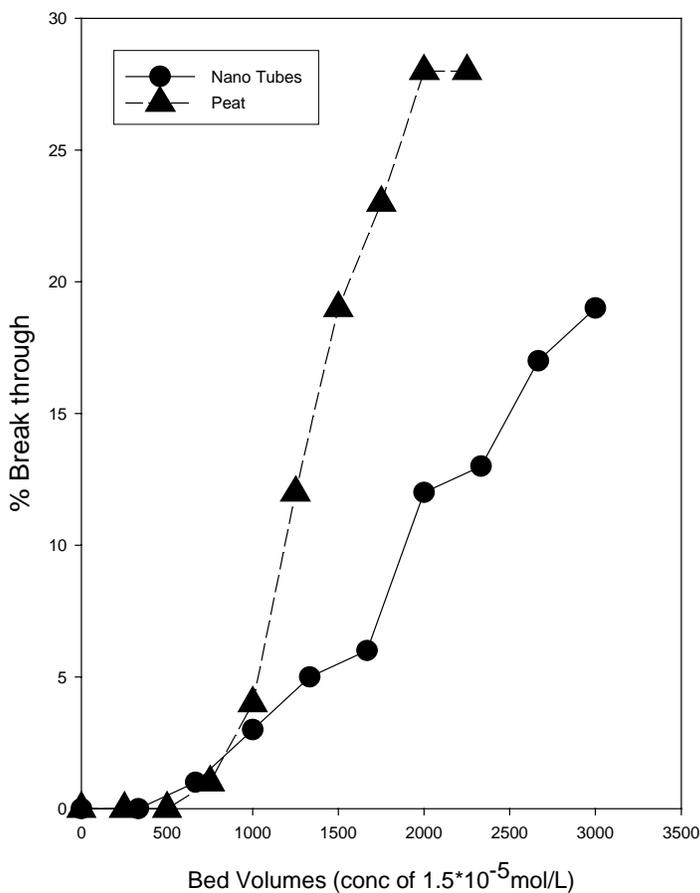


Figure 8: Comparison of iodine breakthrough on sphagnum peat and Aldrich nano-tubes.

FCC material received from KRI was crushed with a mortar and pestle and packed into glass columns for testing. The amount of column packing used was limited by the large pressure drop for these traps and by relatively large breakthrough volumes. As can be seen in Figure 9, breakthrough was observed after 12,000 to 14,000 bed volumes. These results were not highly dependent on flow rate. Qualitative testing with the KI strips indicated that iodine sorption was reversible. As will be discussed below iodine adsorbed by FCC could be released either thermally or by KI leaching.

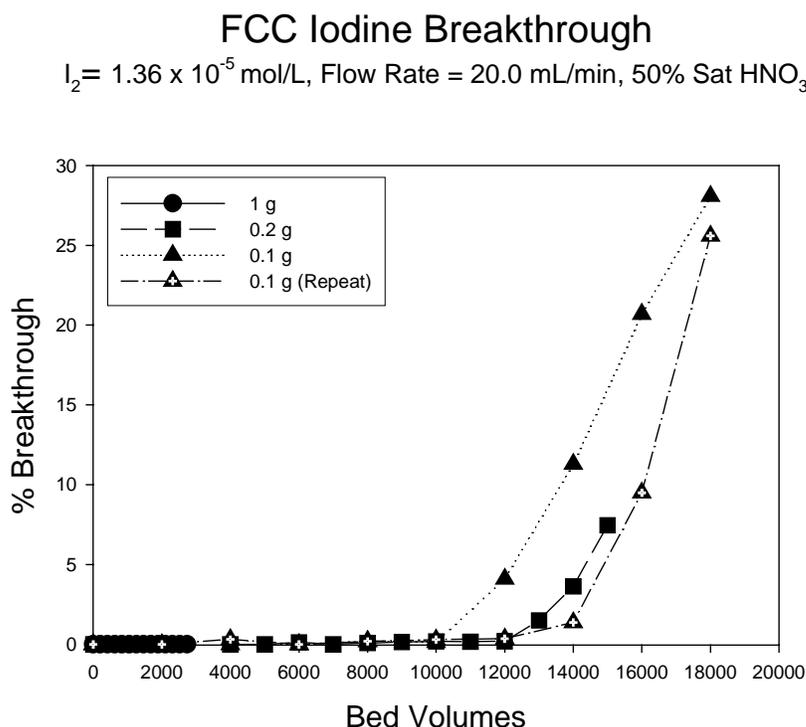


Figure 9: FCC iodine breakthrough.

Because it was apparent that iodine could be removed from FCC, we decided to test used material for iodine sequestration. The results of this experiment are illustrated in Figure 10. The breakthrough volume for used FCC was 50% lower. The lower breakthrough corresponded to a loss in surface area that will be discussed further below.

Comparison of Recycled and Fresh FCC

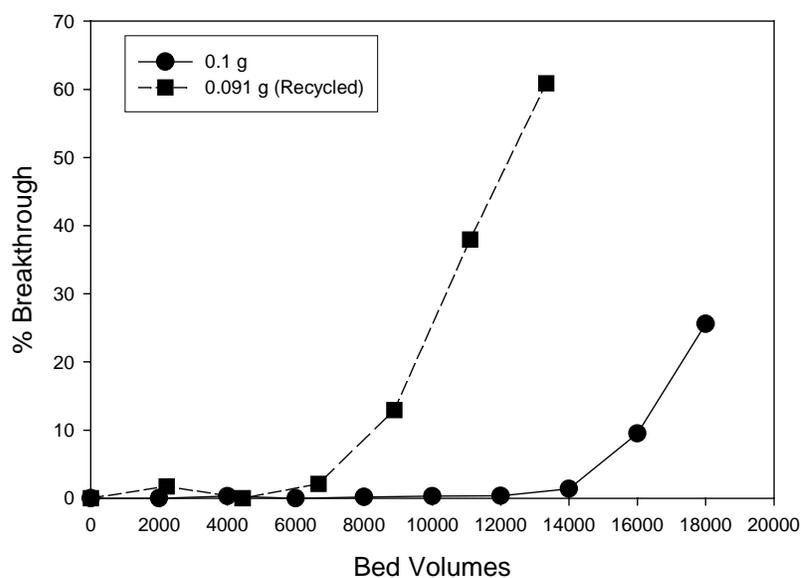


Figure 10: Comparison of “fresh” and “used” FCC.

Iodine breakthrough experiments were conducted with activated carbon substrate (Alltech SK-2) for a comparison with NOM and FCC. Activated carbon is presently used for industrial iodine sequestration in the industrial workplace. With as little as 0.1 g of the activated carbon, no iodine breakthrough was observed with N_2 flowing at 20 mL/min (1.5×10^{-5} mol/L vapor concentration). This result is consistent with the high surface area observed for the activated charcoal (discussed below). Qualitative testing of the exposed charcoal with KI strips also indicated that sorption of iodine on activated carbon appears to be physical in nature and readily reversible.

We decided to investigate the sorption efficiency of a combination the activated carbon and NOM. Our thoughts were that the activated carbon would represent an immediate efficient barrier to iodine vapor, while the organic matter (with $Ca(OH)_2$) would represent an ultimate sink for any iodine released from the activated charcoal during storage. Initial experiments with this combination (20% activated carbon by weight) are promising and indicate a large increase in break-through volume over NOM alone. The increase in breakthrough was so dramatic that only 0.02 grams of material were used in the trap. No breakthrough was observed with larger quantities of charcoal-NOM. Two replicate trials are shown in Figure 11. Breakthrough volume was dramatically increased for NOM alone. The variance between the two experiments is likely explained by the small quantity of material used. We are examining the reversibility of the sorption process as a function of storage time to determine if iodine trapped by the charcoal is eventually transferred to the NOM.

**Carbon (20%)/Peat Combination
0.02 grams**

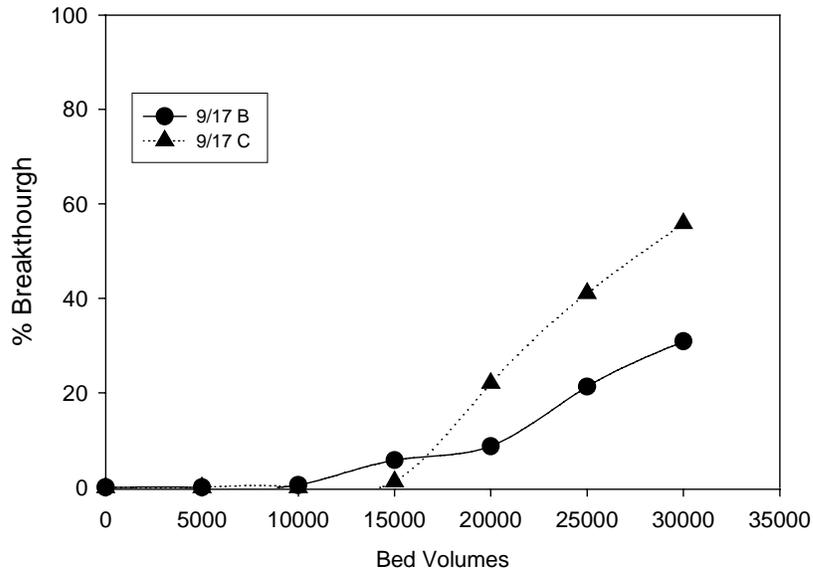


Figure 11: Break through experiment with Activated carbon/NOM combination.

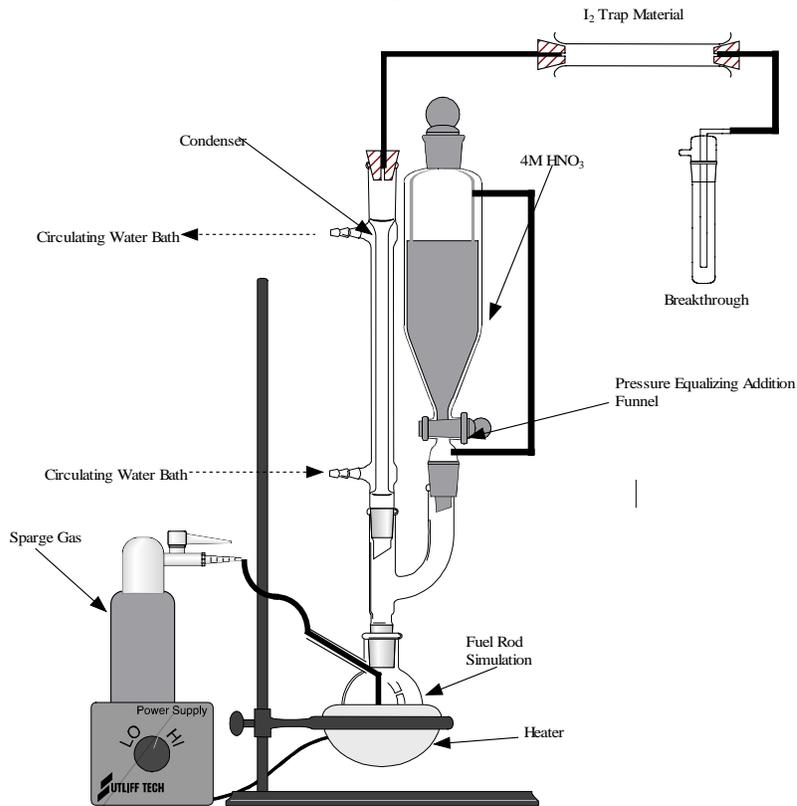


Figure 12: Apparatus for simulation of Nuclear Fuel Dissolution

An experimental apparatus for simulating nuclear fuel dissolution was constructed to simulate iodine sequestration under more “realistic” conditions. This experimental apparatus is shown in Figure 12. At this time several experiments with NOM/Ca(OH)₂ and FCC have been completed. Known quantities of iodine were placed into a round bottom flask that will be used as a reaction chamber. Nitric acid (i.e. 4M-16 M) was added with a pressure equalizing addition funnel. The mixture was heated to a 45°C with a heating mantle. The condenser controlled the loss of water from the system and prevented flooding of the sampler. A N₂ carrier gas (20 mL/min) is used to strip iodine from the reaction chamber. The results of several of these experiments have been summarized in Table 1. The results indicate that both FCC and NOM trap iodine under these conditions, although NOM trapping was easily reversible.

Table 1: Nuclear Fuel Dissolution Simulation Results.

Date	Material	Mass (g)	Time	Initial I ₂ (mg)	Trap (mg)	Impinger (mg)	% Trapped
09/26/2003	NOM/CaOH ₂	0.4	120	3	2.59	nd	--
09/30/2003	NOM/CaOH ₂	0.4	150	3	2.3	0.37	13.9
10/03/2003	NOM/CaOH ₂	0.4	150	3	1.76	0.96	35.3
10/07/2003	FCC #1	0.02	150	2.41	0.68	1.45	68.1
10/10/2003	FCC #1	0.07	150	3	2.66	0.14	5.0
10/15/2003	FCC #1	0.07	150	3	2.01	0.46	18.6

Experiments were conducted over 120 or 150 minutes with 2-3 mg of iodine placed into the round bottom flask with 8 M nitric acid. Percent trapped refers to the fraction of iodine trapped on the NOM or FCC. FCC experiments were conducted with very small amounts of material so that breakthrough could be observed under these experimental conditions. FCC traps tended to have significant backpressure, which complicated these experiments. For example the 10/07/03 experiment was conducted with only 0.02 grams of FCC. Breakthrough could be reduced with scale up of the traps although backpressure may become problematic.

We examined the reversibility of the sorption of iodine to FCC, carbon nano-tubes and activated carbon by performing a variety of qualitative and quantitative experiments. Qualitatively, FCC, carbon nano-tube or charcoal traps were removed from the apparatus and moistened KI paper was placed in the ends. The traps were then sealed with Teflon coated plugs and stored overnight. Darkening of the KI paper was indicative of iodine release. FCC, carbon nano-tubes and charcoal traps all darken the KI paper indicating that sorbed iodine was being released. Under most conditions, the NOM did not notably darken the KI paper indicating iodine binding was not easily reversible. The results of these experiments were corroborated by KI leaches. KI leaching involves forcing 10 mL of a 0.1 M KI solution through the exposed trap. The iodine in the effluent was then quantified using the DPD method. KI leaching removed a significant fraction of the iodine from charcoal, FCC and the nano-tubes. This observation indicates that iodine is sorbed as molecular iodine and that this sorption was readily reversible.

The potential for iodine sorption by commercially available activated carbon was similar to the FCC material. Both types of carbon sorbed iodine reversibly. We have assessed the stability of the iodine to leaching with 0.1 M KI solution. The KI solution promotes aqueous solubility of iodine by formation of the I_3^- ion. Ultimately we will also simulate leaching with synthetic groundwater. The results from various 0.1 M KI leaches are summarized in Table 2. Iodine trapping was performed on both experimental apparatuses. The average iodine content was 2×10^{-5} mol/trap ($\pm 2 \times 10^{-5}$). The iodine trap was leached with 10 mL of a 0.1 M KI solution. The solution was generally delivered to the trap over approximately one hour using a syringe pump. The effluent was collected as iodine measured using the DPD method. The fraction of recoverable iodine was significantly higher with the FCC material than with the NOM. We believe that this results from chemical reaction of the iodine with the NOM. There does seem to be some trend of lower recoveries with NOM with increasing time between trapping and leaching. A small fraction of the iodine may be trapped as the iodate/iodide disproportionation product by the strongly alkaline $Ca(OH)_2$ in the trap. Because this disproportionation process is reversible and the “iodine” trapped in this form may slowly react over time with the NOM. We are still exploring this effect.

Table 2: KI-I₂ Leaching Results

Experimental Apparatus	Substrate	Leachate	Percent Recovered
Iodine Generator	FCC #1	0.1M KI	62.3
Iodine Generator	FCC #1	0.1M KI	73.6
Iodine Generator	FCC #1	0.1M KI	100
Iodine Generator	Activated Carbon SK-2	0.1M KI	77.15
Iodine Generator	Peat/ $Ca(OH)_2$ /Act. C	0.1M KI	36.8
Iodine Generator	Peat/ $Ca(OH)_2$ /Act. C	0.1M KI (24 hrs)	18.24
Fuel Rod Dissolution	Peat/ $Ca(OH)_2$	0.1M KI (20 days)	8.88
Fuel Rod Dissolution	FCC #1	0.1M KI (15days)	91.2
Fuel Rod Dissolution	FCC #1	0.1M KI (12 days)	92.0
Fuel Rod Dissolution	FCC #1	0.1M KI (7 days)	93.0
Fuel Rod Dissolution	Peat/ $Ca(OH)_2$	0.1M KI (16 days)	10.4
Fuel Rod Dissolution	Peat/ $Ca(OH)_2$	0.1M KI (13 days)	12.5

We also measured the thermal stability of the iodine-FCC association. This was done by pyrolysis mass spectrometry of FCC material exposed to the iodine. Pyrolysis was performed using a temperature programmable pyrolyzer (CDS- Pyroprobe 2000) that was interfaced to a Varian Saturn III GC/MS for characterization of organic iodide compounds. The FCC material did appear to produce some methyl iodine under pyrolysis conditions, but a massive molecular iodine peak was also observed in the chromatogram again attesting to the association of iodine with FCC being primarily physical. We are still planning experiments with a pyrolysis interfaced to an ICP-AES for measurement of iodine. Although the both the pyrolysis instrument and ICP have been delivered, the instruments are not yet operational.

Results obtained with combined thermal gravimetric analysis (TGA) and differential scanning calorimetry corroborated this result. TGA/DSC was performed on NETZCH model TASC 414/3A. Sample temperature was increased at 20°C/min in a N₂ stream while weight loss was monitored. TGA/DSC measurements of an iodine loaded sample prepared at KRI indicated that most of the sorbed material was desorbed at temperatures of (90-110C) under TGA conditions (N₂ stream). Thermal release of iodine from FCC was also observed, under different conditions, by our KRI collaborators.

We have measured the surface area of the carbon sorbents using the Brunaur Emmet and Teller (BET)N₂ adsorption method. This automated method measures surface area by estimating the amount of nitrogen required for monolayer coverage of the sample under cryogenic conditions. The monolayer is estimated by assuming that sorption is described by the BET sorption isotherm. The results of these analyses are presented in Table 3.

Samples were analyzed on two different instruments (Micromeritics Gemini 2250 and Micromeritics ASAP 2010). There are several differences in sample processing between the two instruments. In the case of the Gemini 2250 samples are heated in a nitrogen stream in order to remove volatile compounds (primarily water) from the surface that is being investigated. Two different heating temperatures were investigated with the Gemini instrument (120 °C and 200°C). The ASAP 2010 utilizes a heated vacuum treatment to prepare samples for nitrogen adsorption measurements. A 24 hours treatment was employed for both systems.

Table 3: Experimental Surface Areas

Gemini 2250 Instrument	Bake Temp C	Surface Area m²/g
Activated Carbon	200	857.55
FCC#1	120	182.54
FCC #1 recycled	120	13.93
FCC #4	120	45.074
FCC #1	200	182.2
FCC #4	200	166.21
Aldrich Nano	200	8.08
Peat/Ca(OH) ₂	200	3.45

ASAP 2010 Instrument	Bake Temp C	Surface Area m²/g
Activated Carbon	200	955.1
FCC #1	200	207.4
FCC#4	200	40.58

Surface area measurements indicate that the activated carbon sample had at least 5 times the surface area as the FCC material. FCC material that had not been exposed to iodine had a surface area of 182 m²/g (Gemini) and 207 m²/g (ASAP) after out-gassing at

200°C. FCC that was preloaded with iodine at KRI (sample #4) had a considerable lower surface area on both instruments. It was apparent that vacuum treatment removed iodine from the sample. Even with vacuum treatment the “iodine treated” FCC had significantly diminished surface area. As noted above, FCC that was recycled from a previous breakthrough test also had greatly diminished surface area. Thus, despite the “reversibility” of iodine sorption some of the surface area is lost possibly due to blocked pores. The Aldrich fullerene sample had significantly lower surface area than FCC or the activated carbon. These correlates with the much lower break through volume. The surface area of the peat was only 3.5 m²/g which corresponds to the relatively low break though volume. However, iodine adsorption from the peat was irreversible under these conditions.

Pyrolysis Studies:

In order to demonstrate the presence of iodine in the treated organic matter, we have pyrolyzed (400-700C) 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 13a. 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 13b. Pyrolysis leaves most of the starting material as an organic residue.

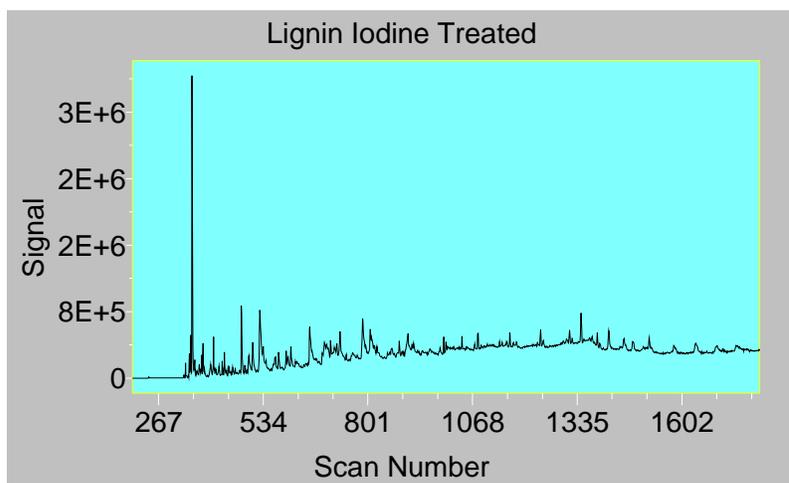


Figure 13a: Chromatogram of pyrolysis products of lignin that was allowed to react with iodine in aqueous solution.

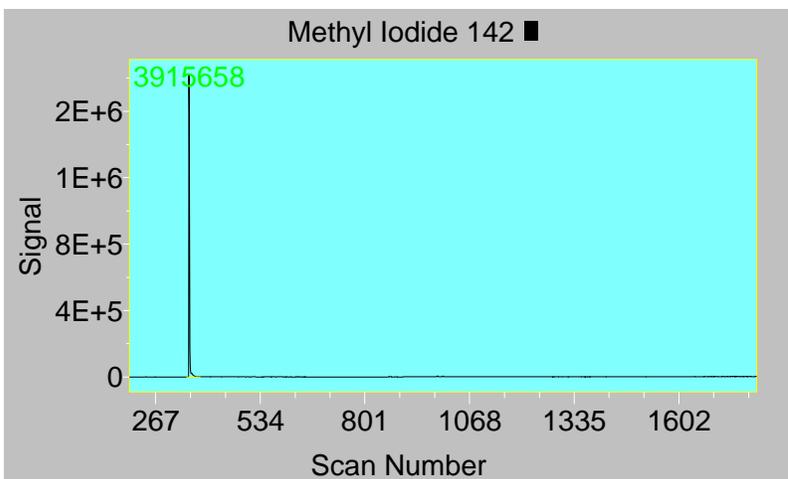


Figure 13b: Specific ion chromatogram (142 m/e) corresponding the molecular weight of methyl iodide. The integrated peak area is shown in the figure.

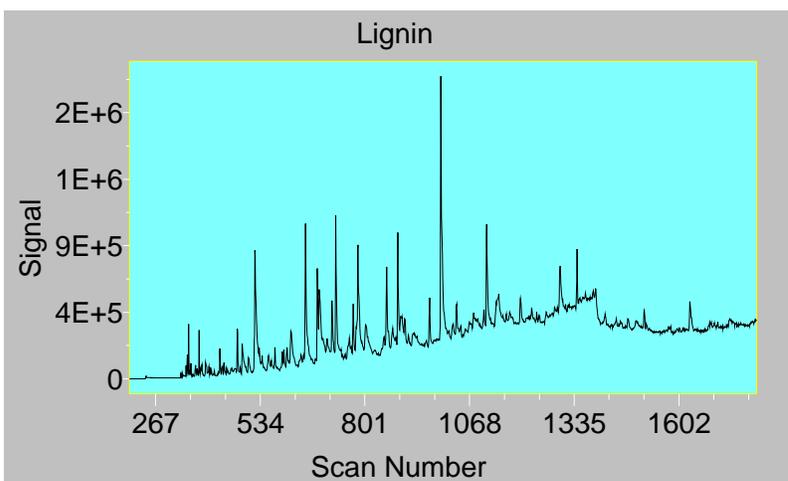


Figure 14a: Pyrogram of lignin that was not exposed to iodine treatment.

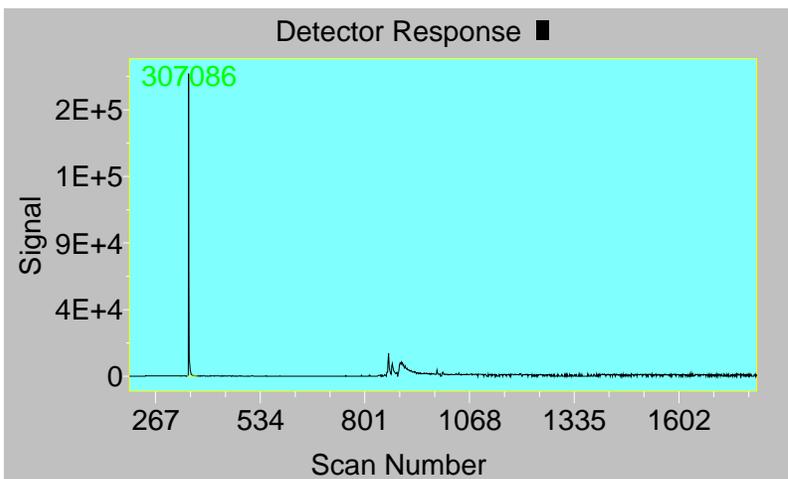


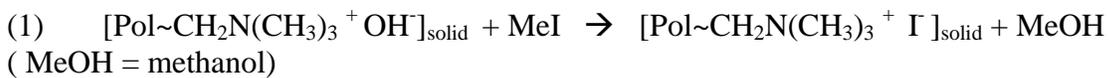
Figure 14b. This single ion chromatogram indicates the presence of methyl iodide in untreated lignin.

In comparison, the chromatogram of pyrolysis products for untreated lignin had numerous peaks corresponding to phenolic compounds (Figure 14a). 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 14b).

We have conducted various degradation experiments using pyrolysis GC/MS in order to elucidate the chemistry of iodinated lignin under thermal conditions. Chemopyrolysis with TMAH has been established as a useful method for characterizing NOM. We have tested this approach as a means of examining the effect of iodine on NOM structure. This technique involved heating organic matter in the presence of TMAH to 350°C. This process results in base promoted thermal decomposition and esterification (methyl ester) of the decomposition products. The products are then separated and characterized by GC/MS. Treatment of Sphagnum and alkali lignin produced methylated phenols and carboxylic acids. We had hoped that iodinated phenols would survive this process and could be identified by GC/MS. This was not observed. Experiments with TMAH chemo-pyrolysis of iodinated model compounds indicate that this procedure results in near quantitative removal of iodine from the model compounds. Our results indicated that at 350° C that iodine is lost from the ring structures by homolytic C-I bond cleavage. The aromatic radical produced apparently may abstract a hydrogen atom from a donor compound in the reaction matrix. For example, iodovanillin produced vanillin under TMAH chemo-pyrolysis reaction conditions.

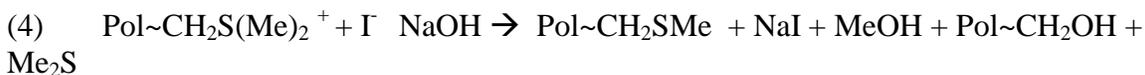
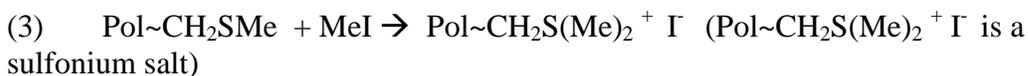
Using peat that had been exposed to iodine in the vapor generator we have investigated the fraction of bound iodine that can be released as methyl iodide by pyrolysis at 500 °C. Our results indicate 30-70% release of bound iodine as methyl iodide during pyrolysis. Pyrolysis temperatures in the range of 500 –700 °C gave similar results. Repetitive pyrolysis analysis with one sample indicates that 41 ± 11 % of the bound iodine was released by pyrolysis. The results of this analytical method are somewhat erratic, but this is consistent with the nature of pyrolysis analytical methods where, in general, samples less than 1.0 mg are used. With several samples we have removed the $\text{Ca}(\text{OH})_2$ before pyrolysis analysis, on the notion that methyl iodide may be reacting with the strong base upon formation. The $\text{Ca}(\text{OH})_2$ was rinsed from the peat sample using 2.0 molar acetic acid. This treatment did not result in consistently higher methyl iodine production. In fact methyl iodide production was more erratic after the rinsing. We will continue to investigate methyl iodide production during pyrolysis. Our plans are to scale up the pyrolysis procedure so that 0.5 to 1.0 grams of sample are processed.

Methyl iodide produced during pyrolysis process can be easily condensed from the vapor phase for further processing. Three approaches for sequestering methyl iodide have been screened on a qualitative level thus far. The first was to try to trap the MeI by use of a commercially available macroporous, strong base quaternary ammonium hydroxide in the hope that the reaction (1) might occur.



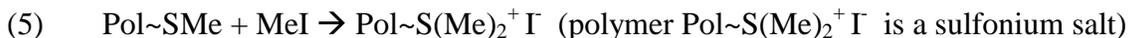
The reaction proceeds but the iodide ion is difficult to elute (Powell et al., 2002). One method, using chloride and perchlorate as the eluting anions worked but they would introduce possibly objectionable compounds into the eluant. MeOH is volatile and should not be a serious problem.

A second approach was to use a commercially available resin GT-73 (Rohm and Haas) that has little affinity for iodide ion and has a sulfhydryl functional group (Pol~CH₂SH). This resin has little affinity for iodide ions. The potentially useful reactions are (2-4).



In this case all of the products that elute are volatile except NaI. A disadvantage is that Pol~CH₂OH is not recyclable. Methyl sulfide (Me₂S) is malodorous, much like the aroma downwind of paper plants using the Kraft process. We have proceeded as far as reaction (2) and are awaiting measurement of the iodide ion in the effluent.

It may be possible to circumvent the side reaction that occurs in reaction (4) which produces Pol~CH₂OH. One of us and others (Emerson et al., 1978; Emerson et al., 1981, Farrall et al, 1976; Fréchet et al., 1979) has succeeded in making insoluble network polymers having either selenium or sulfur directly attached to an aromatic ring in the poly(styrene-co-divinylbenzene) polymer (backbone-C₆H₄-SH) and (backbone-C₆H₄-SeH) . The alkylated versions of these polymers are readily prepared as are the sulfonium or selenonium salts(Pope et al., 1902; Kobayashi et al., 1986; Umemura et al., 1990). The sulfonium or selenonium salts of these types of polymers should react as shown in equations (5 & 6)



Equations 5 and 6 may constitute a recyclable system, in which Pol~SMe captures MeI to make Pol~S(Me)₂⁺I⁻. Sodium hydroxide breaks down Pol~S(Me)₂⁺I⁻ into MeOH and NaI and regenerates Pol~SMe.

In a collection of polymer samples we found Pol~SeEt (Et = C₂H₅- ethyl). It was exposed to MeI at room temperature and the resulting product was pyrolyzed to produce

a mixture of EtI and MeI (equations 7 & 8) thus showing that Pol~SeEt captures MeI. Pol~SMe should behave similarly.

This approach seems worth further study.



Conclusions:

Both FCC and NOM can be used for sorption of iodine from the vapor phase. Iodine sorbed by FCC is readily desorbed either thermally or by KI rinsing. Iodine sorption by NOM is for the most part irreversible, however, the iodine can at least be partially recovered after pyrolysis as methyl iodide. Although the capacity (per gram) for iodine, of NOM (sphagnum peat) is lower than for FCC or activated carbon the cost for this material is negligible. We are exploring the effect of augmenting NOM with activated carbon on the capacity of the material to sequester iodine.

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