

**Project Title:****Immobilization of Fission Iodine by Reaction with a Fullerene Containing Carbon Compound and Insoluble Natural Organic Matrix****May 15, 2003**

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- AFCI Research Area:** Separations
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\$ 65,000 (KIRSI-KRI Subcontract)

**Abstract:**

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 sorbition 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.

**Work Proposed For Academic Year 2003-2004:**

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) have been developed, along with procedures to test the sequestration of iodine from the vapor mixture. Iodine trapping experiments will continue. 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).

### Overview of Project Year 1

During the first two quarters of this program we have explored the analytical method available for characterization of iodine. We reproduced an analytical method proposed by Mishra et al., 2000. This method involves 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 solution, however, we did encounter some interference in the presence of natural organic matter (NOM). The method should still be useful for FCC material studies. We have 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 NaHSO<sub>3</sub>). The DPD colorimetric method has also been demonstrated to be useful for routine monitoring of iodine. We have employed the DPD method for batch reaction studies and for monitoring breakthrough in sequestration tests. An ion chromatography method has been employed for monitoring iodide and iodate during binding studies with natural organic matter. This approach should also be useful for FCC investigations as well. Iodine binding experiments with model organic compounds and several types of NOM were conducted during the first two quarters of the project and indicated the nature of NOM bound iodine. The pyrolysis investigations that were conducted during the first two quarters will serve as a basis for additional investigations of iodine binding in NOM and FCC materials.

### Review of Project Research Objectives and Goals

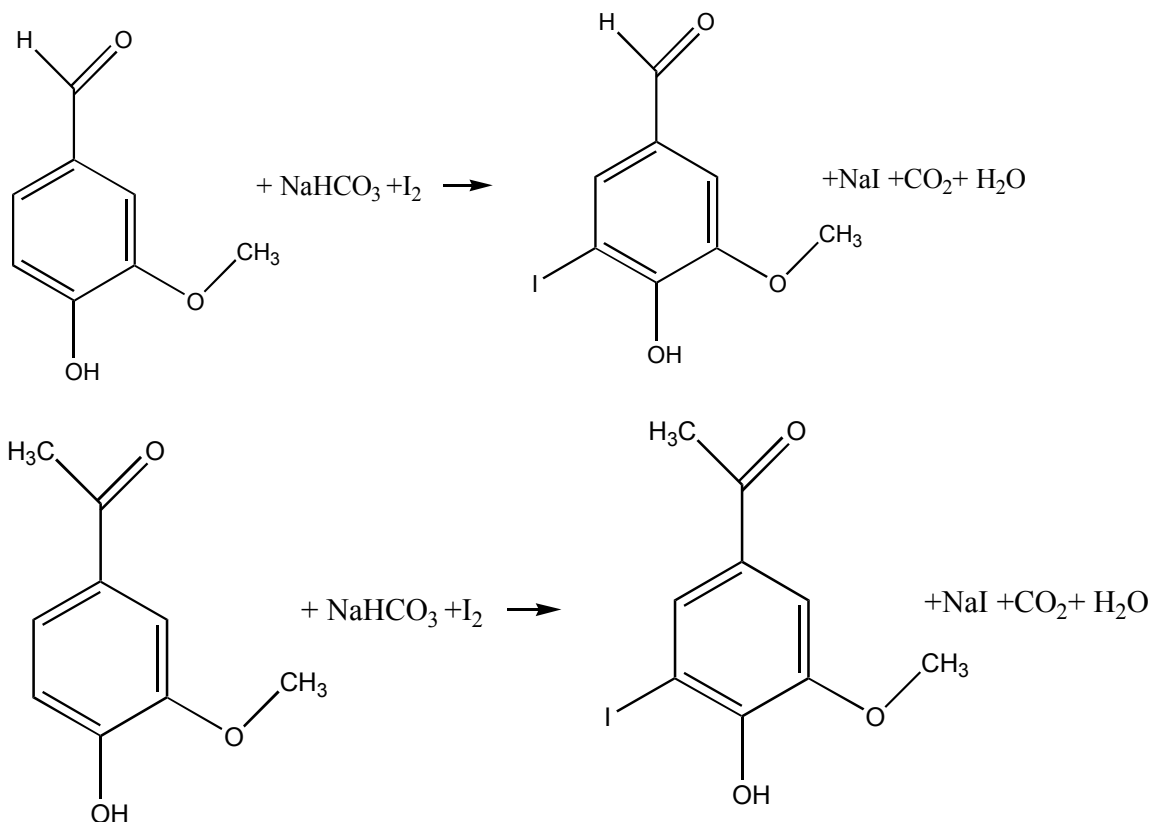
- Develop bench-scale experimental set-up and procedures for simulating PUREX head-end vapor phase; Develop experimental procedures for evaluating I sequestering methods using bench scale procedures.
- Develop FCC-bearing material as potential I sequestration matrix.
- Determine binding of iodine to 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.

### Review of Year 1 Accomplishments

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 (<sup>129</sup>I and <sup>127</sup>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<sub>2</sub> with phenols and humic substances. Bischel and Von Gunten (2000) investigated the reaction of iodide with various model phenols and  $\alpha$ -methylcarbonyl compounds during oxidative treatment of iodide containing waters with ozone, chlorine and chloramine. Oxidative reagents react rapidly with dissolved iodide converting it into hypoiodous (HIO) acid and hypoiodite (IO<sup>-</sup>), depending on the pH. Hypoiodous 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 hypoiodite. Other oxidants, including hypochlorite, can convert iodine to iodate (IO<sub>3</sub><sup>-</sup>) (Vel Leitner et al., 1998).

Model compound studies indicate that phenolic and  $\alpha$ -methyl carbonyl groups in natural organic matter (NOM) should be especially reactive toward active iodine (I<sub>2</sub> and IOH). The reaction of iodine with two phenolic compounds (vanillin and acetovanillone) is illustrated in Scheme 1. The reaction mechanism with phenols is reasonable well understood. The reaction is promoted by both H<sup>+</sup> and OH<sup>-</sup> ions. At low pH the

$\text{IOH}_2^+$  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. This reaction is promoted by electron releasing functional groups on the reacting phenol.



Reaction Scheme 1: Ring addition of iodine to phenolic compounds.

Reaction of iodine with  $\alpha$ -methylcarbonyl involves the initial conversion of the  $\alpha$ -methylcarbonyl to the enol, which then reacts with IOH. Enolization of the  $\alpha$ -methylcarbonyl is promoted by both  $\text{H}^+$  and  $\text{OH}^-$ . During the first 6 months of this study we demonstrate that Sphagnum Peat, 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  $\alpha$ -methyl group. This was preference was demonstrated by monitoring the reaction of iodine with acetovallinone, a phenolic ketone constituent of lignin that also possesses an  $\alpha$ -methyl containing acetyl group. Hydrolysis of the fully iodinated  $\alpha$ -methyl group results in the formation of iodoform. This sequence of reactions is illustrated in Scheme 2.

Reaction of acetovallinone 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.

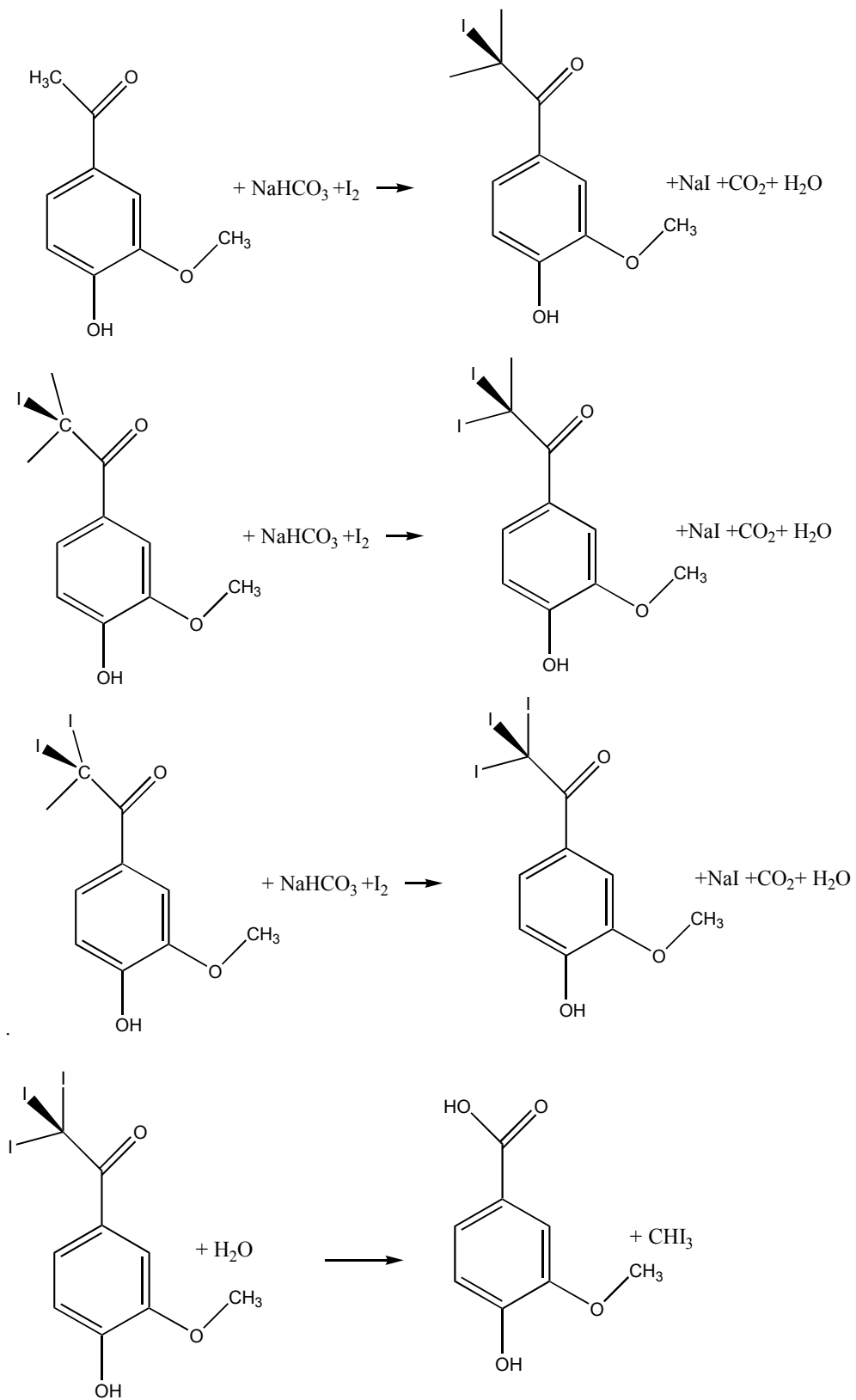
Schwehr and Santchi (2003) indicate that iodine is released from marine natural organic matter by alkaline hydrolysis at  $65^\circ\text{C}$ . We have conducted several hydrolysis studies with iodinated model compounds to test the stability of iodinated phenols toward alkaline hydrolysis. These experiments were conducted in 1-5 N

NaOH heated to 60 or 90C 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 have tested Cu metal as a catalyst/promoter and did not find notable acceleration this reaction. We will continue these studies over the next few months. As discussed below, we have observed that iodine can be released as methyl iodide under pyrolysis conditions, and this sort of procedure may serve as a facile method for concentration iodine from NOM.

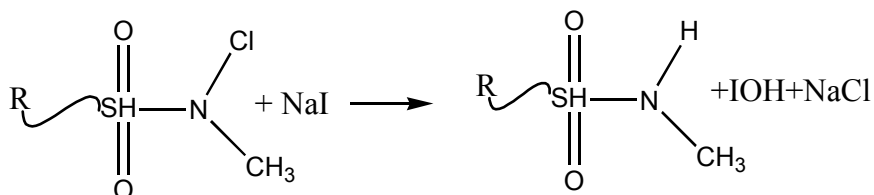
As noted above, reports in the literature, indicate that the binding of iodine by high molecular weight natural organic matter (NOM) is also promoted by microbial activity or by chloramination. Microbial activity may include, iodination of  $\alpha$ -methyl carbonyl groups results in the formation of triiodomethyl ketones which undergo hydrolysis to form iodoform and a carboxylic acid (haloform reaction). The hydrolysis step is however, considerably slower than the initial binding of active iodine and iodoform yields are generally only a small percentage of theoretical. At this time we do not find evidence to indicate that non-biological haloform reaction is significant with Sphagnum peat moss or lignin. The iodination of phenols (electrophilic aromatic substitution) is a rapid process under moderate conditions (pH 7-10), and many stable iodinated products have been isolated.

Natural organic matter (such as sphagnum moss, peat or brown coal) is an inexpensive and a renewable resource. NOM that is rich in lignin contains a myriad 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 tetramethylammonium hydroxide pyrolysis produce numerous aromatic products that can be related to lignin as a precursor (Hedges et al., 2000). Lignin is an abundant biopolymer that comprises approximately 30% of higher plants. The dissolution of spent nuclear fuels in concentrated nitric acid will produce iodine as  $I_2$  and HI in an off-gas. We propose to allow iodine released from fission products (in dissolution off-gas) to react with NOM, isolating it from the off-gas and from the fuel rod dissolution process. The off-gas can be condensed and mixed with an aqueous suspension of NOM and a buffering agent (e.g.  $CaCO_3$  or  $Ca(OH)_2$ ) that will increase the pH of the reaction medium to insure that most of the iodine will be in the form of the hypoiodite anion and iodide. The high pH of this medium and rapid reaction with phenolic functional groups will prevent the loss of volatile elemental iodine. Addition of chloramines to the off-gas should render all of the iodine reactive with the NOM (see discussion below). If  $CaCO_3$  is used as a buffering reagent, the high calcium concentration in the medium resulting from dissolution of  $CaCO_3$ , should minimize the dissolution of humic and fulvic acids from the NOM (Oste et al., 2002), and keep most of the bound iodine in an insoluble form. Trujillo et al., (1991) have immobilized peat biomass in polysulfone resin. This immobilized biomass was used to sequester heavy metals. A similar stabilization of the peat may work for iodine sequestration and prevent the release of soluble iodine species.

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 have been conducted in aqueous suspensions (solutions) indicate rapid reaction with iodine. In addition, we have demonstrated efficient sequestration of iodine from the vapor phase using an experimental apparatus that were assembled during the first 6 months of this study. Using this apparatus we have demonstrated that iodine can be removed from a saturated nitrogen vapor stream onto a small packed column of Sphagnum peat moss. For example, 95% of reactive iodine was removed from a stream of iodine saturated nitrogen delivered at a flow rate of 40 mL per minute, by a column containing less than 5 grams of peat. We anticipated that for each iodine atom that has become associated with a phenolic ring, one iodide anion would be formed that we be readily released by a distilled water leach. A 24- hour distilled water leach of the entire trap contents released less than 0.1% of the anticipated amount of iodide. One possibility is that  $I^-$  is being oxidized to IOH in the organic matter trap, and that IOH is in turn bound by addition to phenolic rings. We are still investigating this observation.



Experiments with the iodine vapor generator are discussed further below. Preliminary experiments have also been performed, in batch reaction, with an active chlorine donating resin (N-Chlorosulfonamide) that we propose can be used to promote the conversion of iodide to bound organo-iodine (Emerson, et. al., 1997; Emerson et al., 1982; Emerson, Shea and Sorenson, 1978). 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.



Reaction Scheme 3: Transformation of iodide to iodine by N- chlorosulfonamide resin.

Using model compounds such as vanillin we have demonstrated rapid transformation of iodide to iodovanillin by a sulfonamide resin. In these experiments we have 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 (Figure 1). This experiment was conducted with 10.0 mM NaI and 13.0 mM vanillin in a NaHCO<sub>3</sub> buffered solution. The reaction was initiated by addition of 50 mg of a sulfonamide resin with approximate 1 meq/gram (wet) of active chlorine.

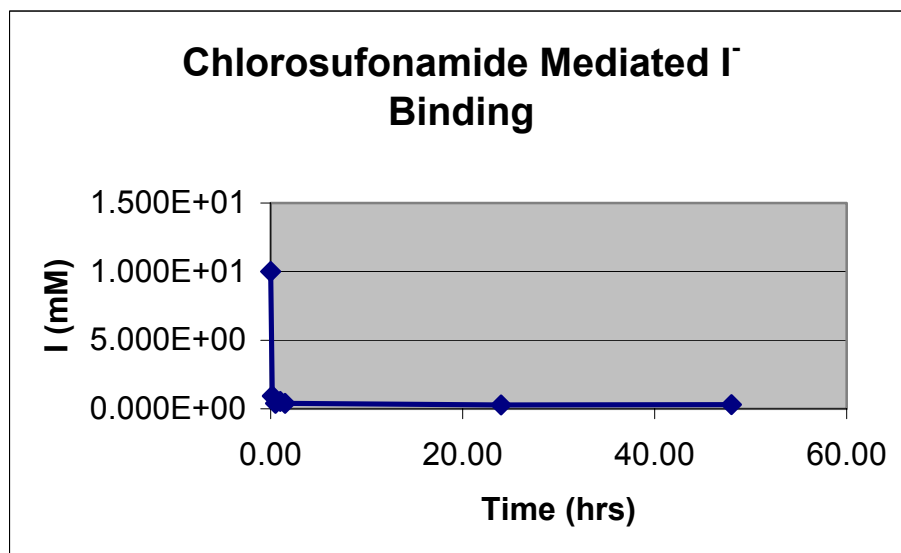


Figure 1: The concentration of free I<sup>-</sup> as a function of time in the presence of vanillin and an active chlorine donating resin.

After reaction, the iodinated NOM substrate could be further processed in order to concentrate the iodine. For example, alkaline oxidation of the sphagnum moss should leave behind iodine as an iodate salt in the residual ash. Similar processes have been used with kelp to produce iodine commercially. Organic substrates such as sphagnum could perhaps be directly subjected to processing using advanced accelerator techniques for transmutation of radioactive iodine. 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. However, as noted above the production of volatiles does not appear to be quantitatively

important at this time. We will continue to investigate this possible reaction. Volatile iodides can be thermally released from activated charcoal-Tenax™ trap and oxidized to CO<sub>2</sub> and iodate salts, although charcoal has been utilized for neutron activation analysis of iodine in natural samples (Quintana and Thyssen, 2000). As will be discussed below, we have observed that under pyrolysis conditions (400-700°C) Sphagnum and lignin bound iodine is released as methyl iodide. We believe that this process can serve as a basis for concentration radio-iodine from NOM sequestering agents and processing this iodine into a form suitable for accelerator processing.

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 moss suspension. Volatile compounds that partition into the vapor phase (head space) are sampled by solid phase micro extraction fibers (SPME). Using this technique with iodoform standards, we have demonstrate sub-ppm detection. Our head space analysis of iodine NOM reaction products failed to produce and evidence for the formation of iodoform. These results confirm that ring iodination is the dominant reaction under these conditions.

We have conducted various degradation experiments using pyrolysis GC/MS in order to elucidate the chemistry of iodinated lignin under thermal conditions. Chemo-pyrolysis with tetramethylammonium hydroxide (TMAH) has been established as a useful method for characterizing NOM. We have tested this approach in this study 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 methylation of the decomposition products. The products are then separated and characterized by GC/MS. Treatment of Sphagnum and alkali lignin produces 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. Our results suggest that at 350C 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 these reaction conditions.

We examined the TMAH chemo-pyrolysis products of lignin treated with iodine in a sodium bicarbonate buffer. The lignin is soluble in the buffer and reacts rapidly with iodine in solution. This lignin can was precipitated from this solution by acidification (to pH 2). The lignin was recovered by centrifugation and then dissolved in TMAH solution (25% in water). An aliquot of the solution is then analyzed by chemopyrolysis GC/MS. With iodine treated alkali lignin, we were not able to identify and iodinated phenolic compounds, however, the amount of semi-volatile phenolic compounds (that have been associated with lignin in NOM) that are released by the TMAH procedure decreased with increasing concentration of iodine. We interpret this result to indicate that the iodine is reacting with the bound phenolic precursors in the lignin. During chemo-pyrolysis these iodinated moieties are evidently destroyed perhaps as a result of homolytic C-I bond cleavage under the reaction conditions. While this technique did not indicate the nature of the bound iodine, the reaction was intriguing in that it may be a useful technique for recovery of bound iodine.

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. 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.

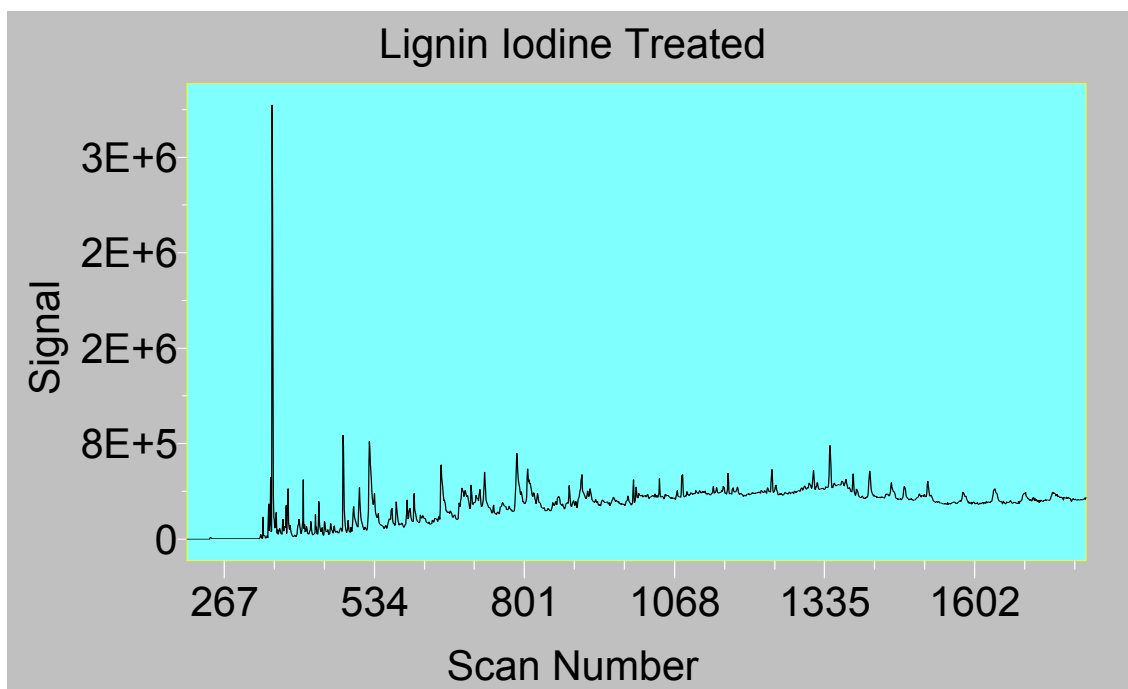


Figure 2a: Chromatogram of pyrolysis products of lignin that was allowed to react with iodine in aqueous solution.

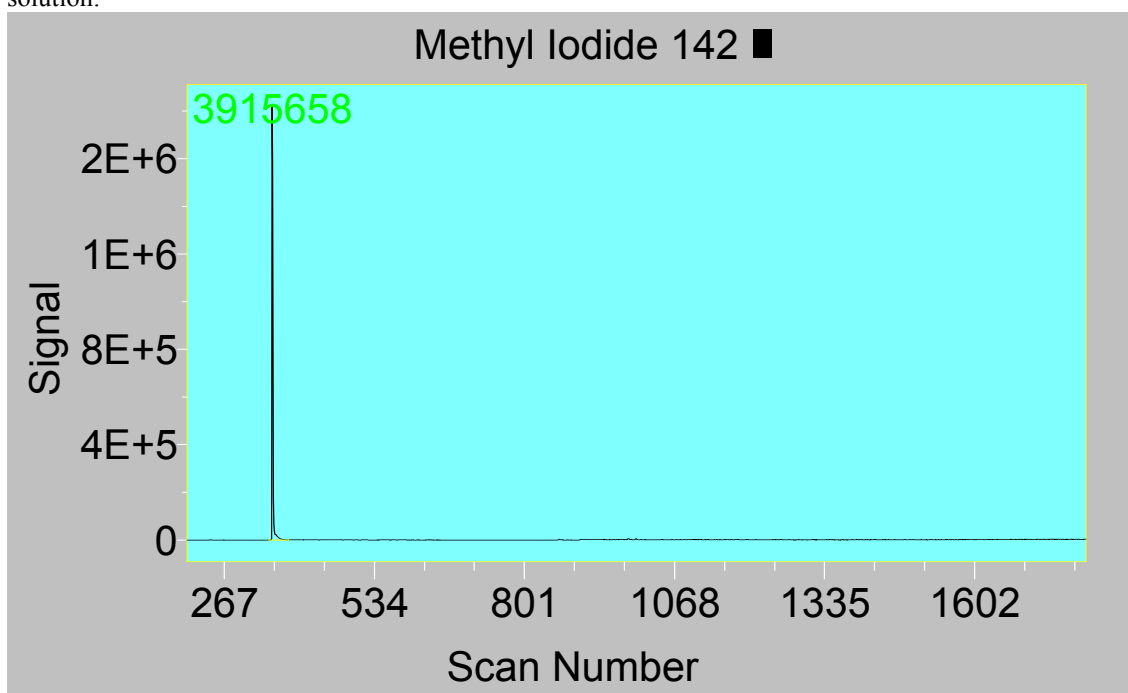


Figure 2b: Specific ion chromatogram (142 m/e) corresponding the molecular weight of methyl iodide. The integrated peak area is shown in the figure.

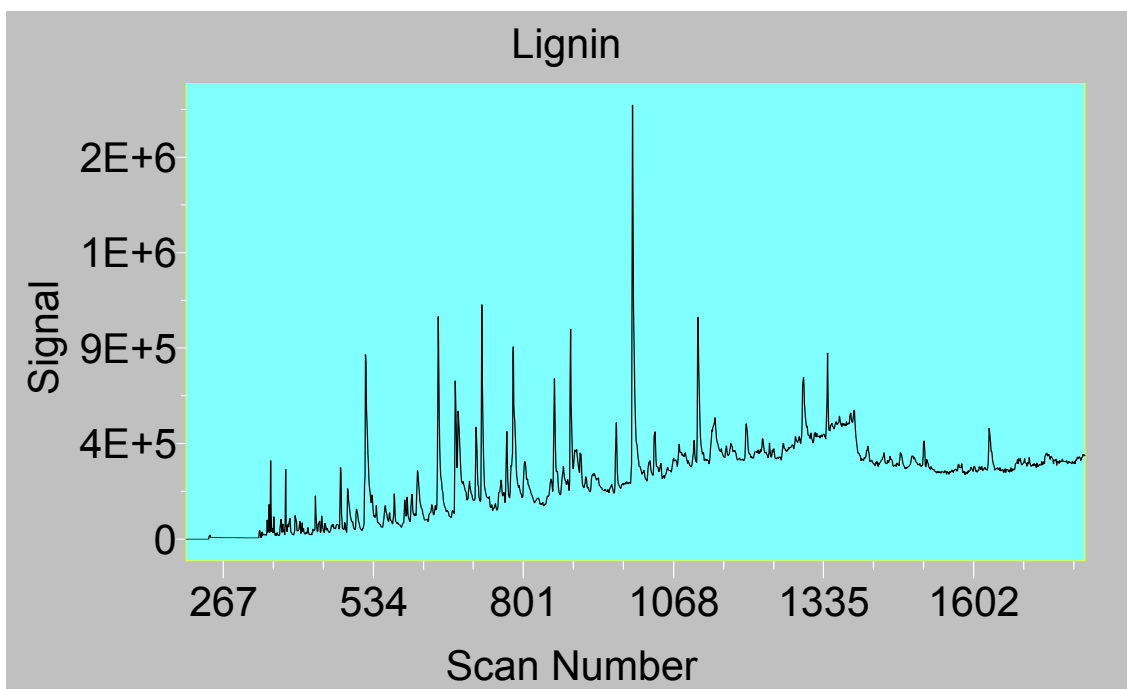


Figure 3a: Pyrogram of lignin that was not exposed to iodine treatment.

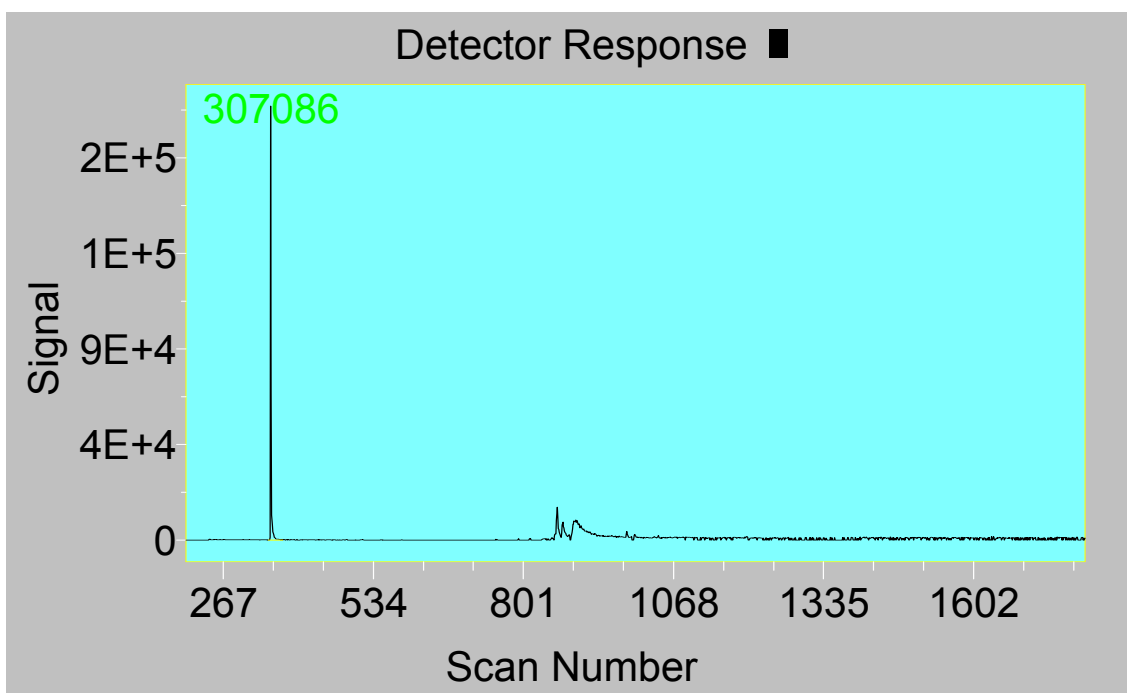
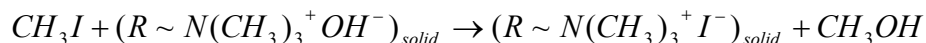


Figure 3b. Single ion chromatogram that indicates the presence of methyl iodide in untreated lignin.

In comparison, the chromatogram of pyrolysis products for untreated lignin had numerous peaks corresponding to phenolic compounds (Figure 3a). 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 3b). Biological iodine is evidently being detected by this method.

Very low levels of ethyl iodide and propyl iodide were also observed as well during this procedure. Pyrolysis leaves most of the starting material as an organic residue. Methyl iodide produced during this

process can be easily condensed from the vapor phase for further processing. We propose the following possibility. Methyl iodide, which has a low aqueous solubility can nevertheless be easily be hydrolyzed to methanol and sodium iodide. 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:



### Reaction Scheme 3

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 resins 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.

### Research Approach/ Scientific Investigation Plan for Project Year 2 (TRP FY03)

We are proposing to continue the detailed characterization of the reactions of active iodine with FCC and NOM for the purpose of developing technology for trapping radioactive iodine released from processed nuclear fuel. The FCC compounds will be developed and produced by the KRI-KIRSI team, and will be studied at both locations. The KRI-KIRSI team will study impacts of process parameters on sorption of I<sub>2</sub>, and will examine the material properties (such as how I attaches to the FCC compounds, etc.). The UNLV team will examine the FCC material, along with NOM and other potential sequestering agents, under simulated process conditions. The KRI-KIRSI team will also examine the conversion of the iodine-loaded FCC compound to a stabilized matrix (similar to a ceramic), for potential use as a disposal form, transportation phase, or potential target material. Both teams will examine recovery of the iodine from the sequestering matrices.

We have constructed an I<sub>2</sub> generator for use in testing of iodine sequestration (Figure 4). Test runs of this system have successfully demonstrated iodine sequestration by Sphagnum Peat. Iodine vapor was generated by heating iodine crystals to 50C and passed a metered stream of N<sub>2</sub> over the crystals. This stream was directed through a column that was packed with a mixture of Sphagnum and Ca(OH)<sub>2</sub>. Initial experiments for FCC characterization will also be performed using this iodine generator. I<sub>2</sub> will be passed through the FCC substrate and then the nature of the sequestration will be studied. Iodine crystals will be held and a constant temperature so as to generate a known concentration of iodine vapor. A stream of nitrogen gas will be passed through the I<sub>2</sub> chamber. This gas stream will be diluted with I<sub>2</sub> free nitrogen. The iodine vapor stream of known concentration will be directed through test materials. The concentration of iodine in the gas stream from the generator will be measured by allowing a know volume of gas to flow through a NaOH filled impinger where it can be measured using the DPD (N,N-diethyl-p-phenylenediamine) method. A second impinger placed after the sorbent trap can be used to measure breakthrough of iodine. *We have also monitored iodine breakthrough using a sodium bisulfite filled impinger which reduces iodine to non-volatile iodide. Iodide can be detected using ion chromatography or the ion specific electrode.* This experimental setup will allow the addition of other reagents such as water or nitric acid fumes, so that the influence of these compounds on iodine sorption can be assessed. The effect of nitric acid is presently being investigated with NOM. Because of delays encountered with the Khlopin project we will do some experiments with a commercially available fullerene preparation. This material is available from Aldrich Chemical Company and has been characterized as carbon nanotubes. A small amount of this material has been ordered for testing.

In addition an experimental apparatus for simulating nuclear fuel dissolution has been constructed to simulate iodine sequestration under more realistic conditions. This experimental apparatus is shown in Figure 5. This experimental system has not yet been tested as we are still awaiting several additional parts. Material with a known concentration of iodine will be placed into a round bottom flask that will be used as a reaction chamber. Nitric acid (i.e. 4M) will be added with a pressure equalizing addition funnel. The

mixture will be heated to a known temperature either with a heating mantle or a circulating temperature bath. The condenser will be used to control the loss of water from the system and to prevent flooding of the sampler. A carrier gas will be used if necessary, to strip iodine from the reaction chamber. Both of these devices will allow us to assess the breakthrough of iodine with various sorbents, and the effect of water and various oxides of nitrogen on sorption.

We propose to examine the reversibility of the sorption of iodine on FCC by performing a variety of experiments. We propose to assess the stability of the FCC to leaching with simulated groundwater and with solutions containing various reagents that can change the oxidation state of the iodine. For example, reaction with sorbed  $I_2$  with reducing agents such as hydroxylamine or sulfite may form iodide which would be considerable more mobile in the environment and very susceptible to leaching from an FCC-ceramic composite. On the other hand, if the objective of the program is to concentrate the iodine for transmutation a simple leaching method for recovery from the FCC will be prerequisite. We believe that the release of  $CH_3I$  during pyrolysis may be a useful means of release NOM trapped iodine for concentration and transformation (after hydrolysis) to  $NaI$ .

We also propose to measure the thermal stability of the iodine-FCC association. This will be done by pyrolysis mass spectrometry of FCC material exposed to the iodine vapor in simulated fuel rod processing experiments. Pyrolysis will be performed using a temperature programmable pyrolyzer that can be interfaced to either a GC/MS for characterization of organic iodide compounds or to an ICP-AES or ICP-MS for measurement of iodine. The pyrolyzer and ICP instrument have been obtained and are awaiting installations. This instrumental approach will enable us to measure the decomposition temperature of the iodine-fullerene association and to characterize the products of decomposition. This information will be useful for assessing geological stability of FCC-iodine associations and for devising a method for recovery of iodine from FCC for transmutation. We anticipate doing additional studies to assess thermal stability of the iodine-FCC using Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). Using these methods we may be able to associate iodine loss with thermally induced physical and chemical transformations of the FCC sorbent.

For initial studies with NOM we propose the following approach. The off-gas from nuclear fuel dissolution would be condensed using a cooled trap or directed through an NOM packed column, where the acidic condensate would be mixed  $CaCO_3$  and NOM. A suitable oxidizing agent will be added to convert all of the iodine to  $HIO$ . As noted before, we have begun experimenting with active chlorine donating resins as a means of converting iodide to iodine. Preliminary results with this resin demonstrate rapid conversion of iodide to active iodine that reacted rapidly with a model compound. Other buffering agents will be examined in order to determine the role of pH in the conversion process. The solid and aqueous fractions will be centrifuged and separated for further characterization. Iodine bound in insoluble organic matter will be measured after alkaline oxidation. The approach utilized will be similar to the methods summarized in Copper et al., 1998, Olesky-Frenzedl et al., 2000 or Gu et al., 1997.

The potential production of volatile iodine species have and will continue to be addressed by several approaches. The reaction system will be sparged with an inert gas and volatile species will be recovered on Tenax-activated charcoal. A commercial dynamic headspace concentrator will be used for this purpose. Volatile iodides will be thermally released from charcoal and analyzed by GC/MS. As noted above, solid phase micro extraction has also been utilized to monitor the production of volatile iodine species. These studies indicate that volatile iodine species are not formed in significant quantities.

Absorbable organic iodide species will be measured after solid phase extraction (SPE) of aqueous phase with  $C_{18}$  silica. Low molecular weight organic compounds retained by  $C_{18}$  will be analyzed by GC/MS. Iodine associated with humic and fulvic acids will be recovered by resin extraction of the acidified aqueous solution. These materials will be analyzed by pyrolysis GC/MS or by pyrolysis ICP. Alternatively, after alkaline destruction of the organic matter, this associated iodine will be measured using ion chromatography or by ICP-MS.

The speciation of iodine remaining in solution will be measured as follows. Under these reaction conditions remaining soluble inorganic iodine should consist only of  $HIO$ ,  $IO^-$ ,  $IO_3^-$  and  $I^-$ . Iodine/iodide

and iodate can be analyzed by the method of Mishra et al., 2000. This method involves 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. Iodate ( $\text{IO}_3^-$ ) will be determined by difference or by ion chromatography. Specific ion electrodes can be used to determine iodide in order to corroborate other analytical results. Total iodine in solution will also be measured using ICP-MS. ICP-AES will be utilized for sample screening and as a corroborative method of analysis. This approach is summarized in the Figure 3. We will also attempt to utilize the NOM for vapor phase sequestration of iodine using the experimental approaches outlined in Figures 4 or 5.

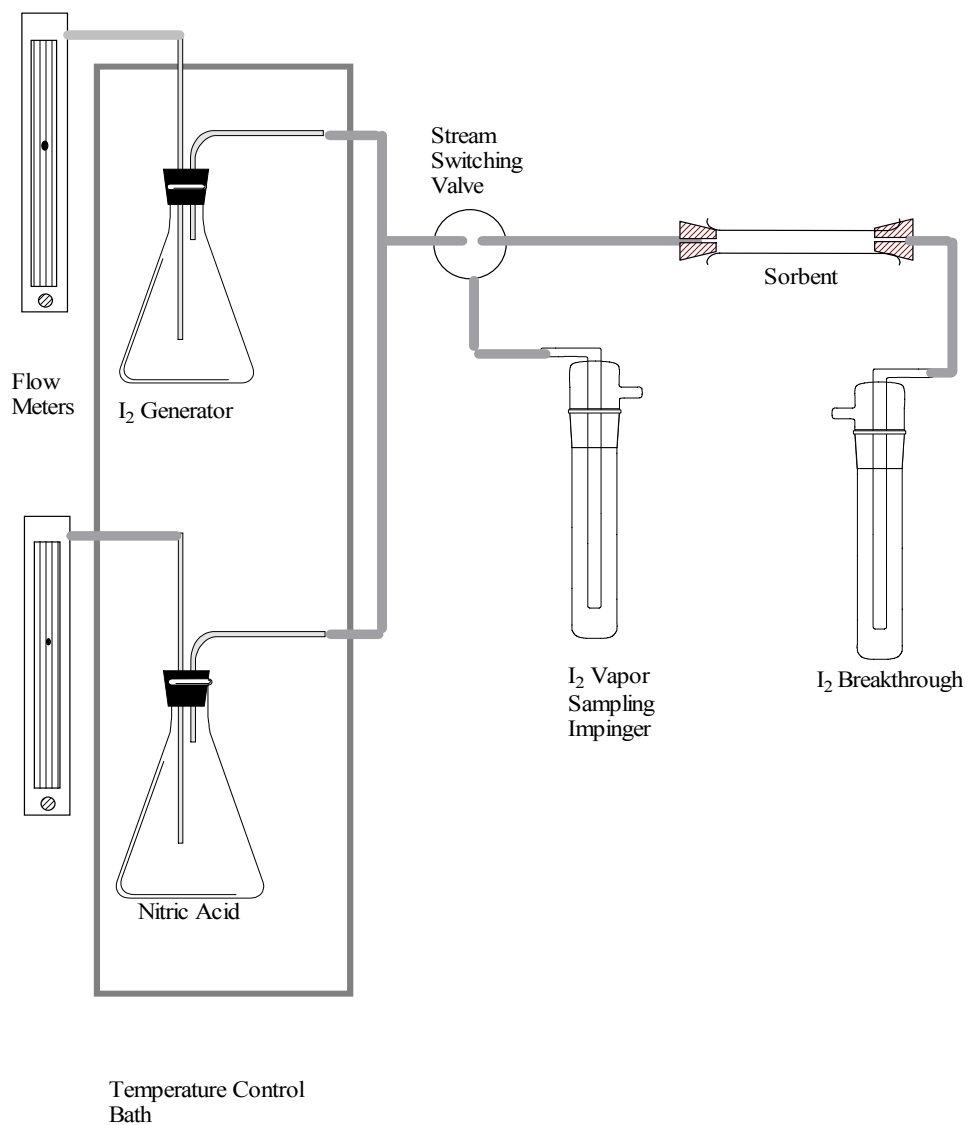


Figure 4: Iodine Vapor Generator

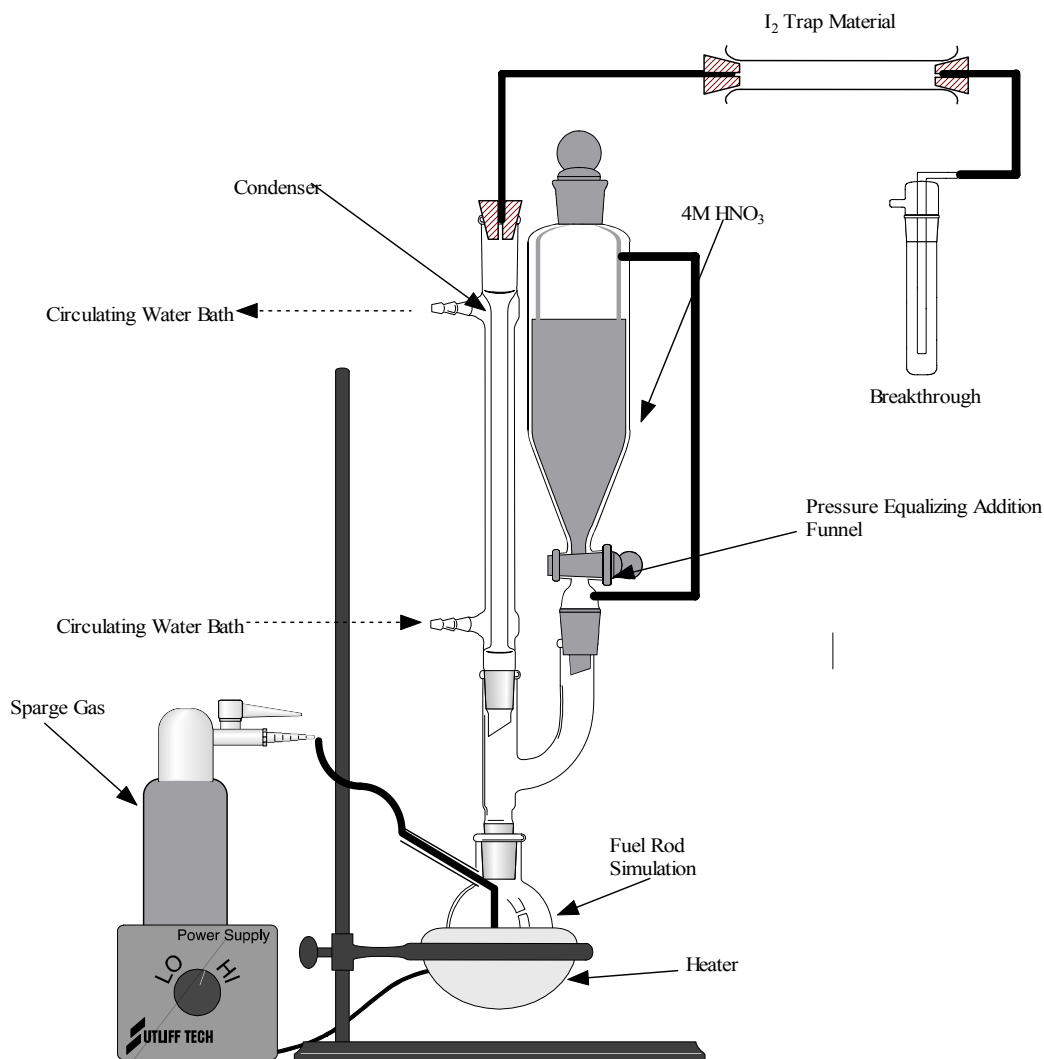


Figure 5: Simulation of Nuclear Fuel Dissolution

The execution of the project will involve using FCC prepared by the Khlopin Radiation Institute and NOM for preparation of vapor phase iodine trans. The chemical stability and form of the bound iodine will be inferred by various chemical and thermal experiments. In the case of NOM, the effect of pH, temperature on the reaction kinetics and the product distribution will be studied in depth. Once reaction conditions have been established refinements in the procedure such as pre-extraction of the NOM to remove soluble components and encapsulation of the NOM will be explored. In the final phases of the program conversion of the bound iodine (FCC or NOM) to a suitable transmutation target will be studied. This will likely involve an oxidation procedure as described above.

The materials prepared by the Khlopin Radiation Institute consist of a fine powder with many particles less than 50 nm in diameter (B. Burakov, personal communication). This powder can be compressed into pellets that should be able to “sorb” iodine from the vapor phase. With the small particle size the permeability of a packed sampling tube may be very low and render sampling difficult. Another possibility would be to coat the FCC powder onto the walls of an annular denuder. Annular denuders are constructed with several concentric tubes mounted within an outer tube. Coating of the FCC material may require addition of a binding agent. Gas-flow is forced through the annular spaces between the tubes of the coated denuder. Denuders are available commercially for air and stack-gas sampling. We will attempt to adapt a commercially available model to this application. In this way high flow rates can be maintained while effective surface area is exposed to the gas stream. A third possibility is to utilize the FCC material

in a fluidized bed reactor. This possibility will be explored if packed sampling tubes and denuders prove unworkable.

**Proposed Experimental Fractionation Scheme**

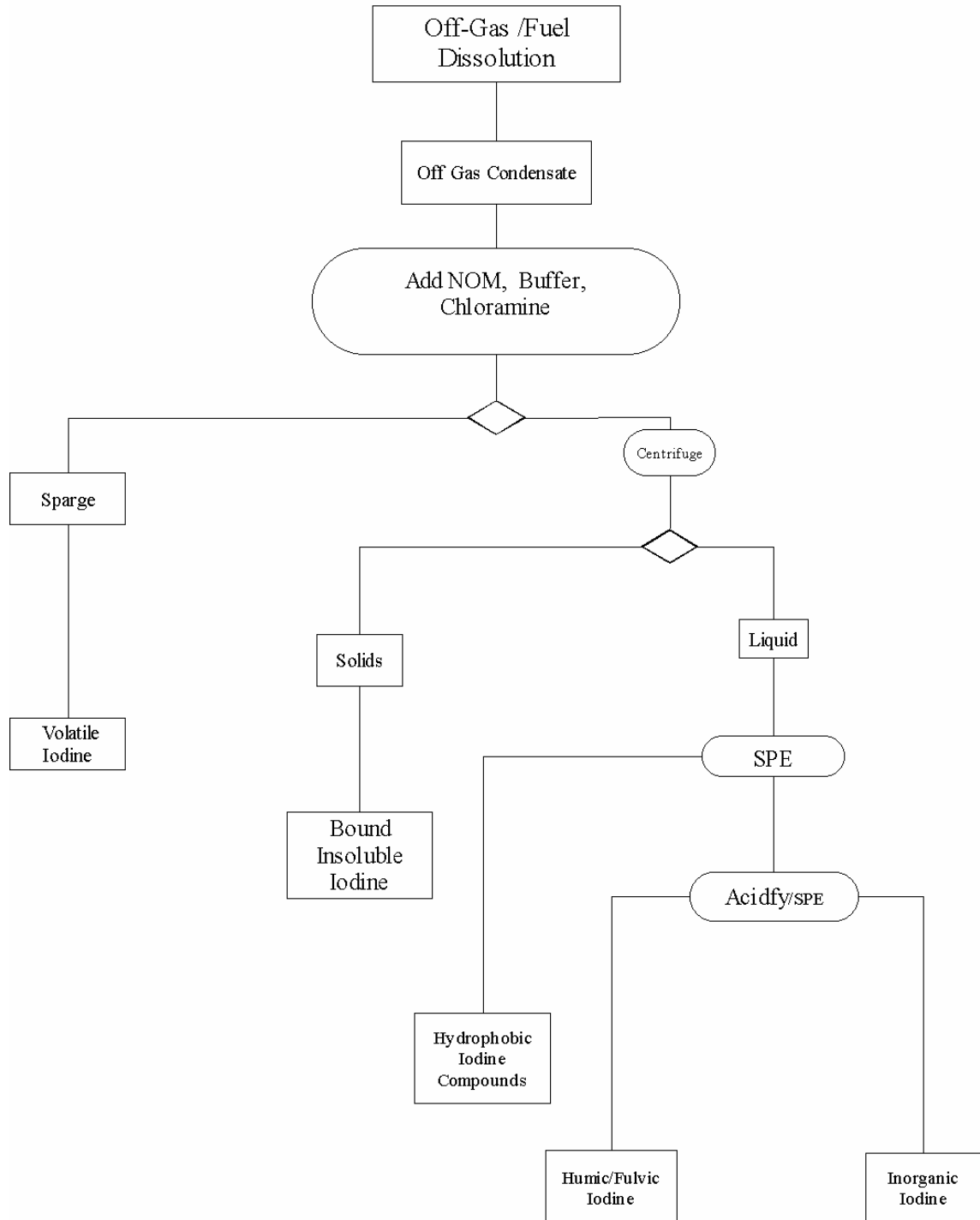


Figure 6: Proposed Fractionation

**Capabilities at UNLV and KRI-KIRSI:**

The majority of the equipment required to develop the sequestration matrices and characterize the reactions of iodine and these matrices is currently available at the UNLV and KRI-KIRSI facilities. These capabilities include gas chromatography, gas chromatography-mass spectrometry, ion-chromatography, ICP-MS (at UNLV); and XRD, SEM, EMPA, and experimental set-ups for MCC-1 protocol leach tests (at KRI).

A pyrolysis interface for use with the GC/MS *has been* acquired to support this work (this interface can also be used with the ICP-AES and ICP-MS systems). The bench-scale experimental set-up to simulate Iodine release in the PUREX off-gas stream *has been* constructed using commercially available laboratory glassware, gas pressure regulators, flow regulators, and heaters. *Two circulating temperature baths and several heating mantles with a temperature controller have been obtained to execute these experiments.* Various disposable supplies such as solid phase extraction cartridges and filters will be needed for the project.

An ICP-AES system capable of direct measurement of iodine (i.e. the Spectro CIROS CCD ICP-OES model FCE 12) *has recently been acquired for the project and* will greatly increase the measurement capability of the UNLV team, allowing direct measurement of the off-gas vapor (with proper connections), and will provide another reliable technique for iodine measurements in the pyrolyzed sequestration matrices, and will be useful in examining solutions obtained from both leach test and iodine recovery experiments.

**Projected Timeline with Milestones and Deliverables:**

This research program has been divided into several major tasks, which will be executed over a two- year period with the aid of a graduate assistant. Results will be communication through written quarterly reports. The projected schedules for the UNLV and KRI components are broken down for this program and shown below.

*Deliverables for Year 2:*

- **Collaboration with DOE:** Regular communication with DOE collaborator to assess progress, discuss problems, and allow for refocusing if necessary to address shifts in direction by the National Project.
- **Quarterly Progress Reports:** Brief reports indicating progress will be provided every quarter in support of the DOE AAA quarterly meetings.
- **Final Report:** Written reports detailing experiments performed, data collected and results to date.

**UNLV Work Timeline**

**Time Line Year 1**

Task	SEP	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP
Literature Search	▨											
Procurement and Preparation of Test NOM		▨										
Analytical Methods Testing			▨									
Set up Experimental Apparatus				▨								
Iodine Binding Experiments (pH)						▨						
Iodine Binding Experiments (Temperature)							▨					
Quarterly Reports			🏠			🏠			🏠			🏠

**Time Line Year 2**

Task	SEP	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP
Iodine Binding Experiments (pH)	▨											
Iodine Binding Experiments (Temperature)	▨											
Oxidation of Bound Iodine		▨										
Conversion to Transmutation Target							▨					
Quarterly Reports			🏠			🏠			🏠			🏠
Write Final Report										▨		

**KRI-KIRSI Timeline**

ID	Task Name	2002					2003												2004										
		Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	
1	Laboratory Prep. for FCC fabrication	█																											
2	Synthesis of FCC			█																									
3	Examination of FCC loading for I					█																							
4	Synthesis of Immobilization forms (I-doped FCC & ceramic-like matrix)						█																						
5	Optimization of Immobilization forms (I-doped FCC & ceramic-like matrix)								█																				
6	Examination of Immobilization forms																		█										

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