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Project Title:

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

(Task 15 for Third Year Renewal)

April 30, 2004

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- AFCI 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 two years of this program the use of Fullerene Containing Carbon (FCC) compounds and Natural Organic Matter (NOM) as potential sorbents for iodine release from the reprocessing of nuclear fuel was examined. This work also included the development of bench-scale testing capabilities at UNLV to allow the testing of the FCC and NOM materials in a simulated process off-gas environment. In the final year of the project we will complete studies of FCC and NOM and develop a method for conversion of recovered iodine into NaI. In addition, this work will also examine the development of a process to convert the iodine-loaded carbon matrices 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.

FY04 Requested Funds:	Student Research	\$71,804	(TRP Task 15)
	International Collaboration	\$65,000	(KIRSI)
FY04 Total Budget Request:		\$136,804	

Background and Rationale

Iodine-129 is an important fission product formed by both commercial nuclear power generation and nuclear weapons testing. Iodine-129 is released from the fuel rods during the decladding stage of the PUREX or UREX processes (Choppin and Morgenstern, 2000), primarily as HI and I₂. A significant fraction of the iodine is lost to the vapor phase where it may potentially become a fugitive emission, or it can be trapped using specialized filtration systems that may incorporate activated carbon. Szente et al. (1999) has discussed the use of cyclodextrines for trapping iodine from nuclear waste. Hoskines and Karanfil (2002) have discussed the use of silver-impregnated activated carbon for removal and sequestration of iodide from aqueous solutions. Balsley et al. (1996) have discussed iodide retention by cinnabar and chalcocite. Ideally the iodine released during nuclear fuel reprocessing should be isolated in a form that can be transmuted to a stable product using nuclear transmutation technology such as those proposed in the Advanced Accelerator Applications program. The objective of the research proposed here is to immobilize iodine in a form that can easily be converted to a suitable target for neutron-induced transmutation. We believe that iodine released during fuel reprocessing can temporarily be immobilized in a Fullerene Containing Carbon (FCC) compound or an inexpensive Natural Organic Matter (NOM) matrix prepared from natural peat. Further processing of the trapped iodine using simple desorption or combustion processes should be able to produce iodine in a form suitable for transmutation.

Radioactive iodine has the same environmental and geochemical properties as stable iodine, and in its predominant oxidation states of -1 and 5 (I⁻ and IO₃⁻), it is a highly soluble and mobile element that is likely to become rapidly dispersed in the environment (Whitehead, 1984). Whitehead (1973) noted that the sorption of iodide by soils was correlated to organic carbon content. Ticknor and Cho (1990) investigated the sorption of iodide and iodate by granitic fracture-filling minerals and reported little sorption of iodide however several minerals did adsorb iodate under a variety of conditions. Kaplan et al. (2000) reported the sorption of iodide by illite. Iodine is also a biologically reactive element. For example, numerous volatile, organic iodine species are formed by marine algae and by bacteria. These biological reactions are responsible for transferring iodine to the atmosphere and this process is an important leg of the geochemical iodine cycle. Volatile species, that are formed biologically, include iodomethane and iodoethane (Laternus et al., 2000; Amachi et al., 2000; Huo et al., 2000).

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).
- Develop methodology and host matrix for converting sequestered I to solid matrix for evaluation as transmutation target and/or disposal matrix.
- Examine recovery of iodine from sequestration matrices.
- Conversion of recovered iodine to NaI.

Technical Impact

The proposed work is intended to enable researchers to optimize (develop a simple, economical and safe method) the sequestration and subsequent immobilization of iodine from the off-gas stream of the PUREX (or equivalent solvent extraction) process. This work will examine a number of approaches, with a preliminary focus on FCC or NOM matrices. The stability of the association of iodine with FCC and NOM products will continue to be studied. The product distributions for the various matrices under various reaction conditions will be examined in order to maximize the binding of iodine to the insoluble fraction. The recovery of the iodine from the sequestration matrices will also be examined, along with the

conversion of the iodine to matrices more suitable for geological storage and/or use as transmutation targets.

Accomplishments

Initial experiments for FCC and NOM characterization were performed using an I₂ vapor generator. I₂ was to be passed through the FCC substrate and then the nature of the sequestration was studied. Iodine crystals are held at a constant temperature so as to generate a known concentration of iodine vapor. A stream of nitrogen gas was passed through the I₂ chamber. The iodine vapor stream of known concentration was directed through FCC and NOM test materials. The concentration of iodine in the gas stream from the generator was measured by allowing a known volume of gas to flow through a NaHSO₃ filled impinger where it can be measured using an iodide selective electrode. This experimental setup allowed for the addition of nitric acid fumes, so that the influence of this acid on iodine sorption was assessed. A second impinger placed after the sorbent trap can be used to measure breakthrough of iodine.

Fullerene-containing carbon material (FCC) was prepared at KRI and reacted with iodine. It was found that crystalline fullerenes phases are not effective for the iodine incorporation despite some interaction between crystalline C₆₀ that has been observed. At the same time, FCC, which is used as starting precursor for fullerene extraction, was characterized by high capacity for iodine sorption (higher than 450 mg iodine per gram FCC). This powder consists of three carbon forms: graphite, fullerenes and amorphous carbon, which associate with each other by uncharacterized bonds. In general, FCC material is amorphous (Fig. 1-a) and it retains nearly the same structure after doping with iodine (Fig. 1-b).

Experimental evidence suggested that sorption capacity for iodine correlates with fullerene content. The powder completely purified from fullerenes has at least 30% less capacity in comparison with powder containing about 3 wt.% fullerenes (mainly - C₆₀ and C₇₀). The preliminary data show that fullerene admixture also increases significantly the thermal stability of iodine-doped FCC materials.

Unexpected results were obtained from the study of FCC samples hot pressed at 800-1000°C, pressure 3500-4000 Mpa for 5 min. As a result of strong hot pressing iodine-doped sample was partly converted to graphite (as well as undoped FCC material), preserving iodine in its matrix. Detailed HRTEM analysis of hot pressed iodine-doped sample showed that iodine was fixed only in the amorphous areas (Fig. 2) while no iodine was found in the crystalline (graphite) parts.

Although FCC material demonstrated high loading capacity for iodine sorption it is necessary to take into account that FCC itself is not a final form for ¹²⁹I immobilization. For either for disposal in geological formation or iodine transmutation in nuclear reactors the FCC should be converted into more chemically and mechanically durable material. In case of transmutation it is necessary to provide, also, an acceptable «transparency» of final material to neutron fluxes. Therefore, we decided to consider two main groups of durable compounds: silicon carbides and carbon nitrides (of fullerene structure) as possible targets of FCC conversion. It was assumed that synthesis of Si_xC_y might be carried out at relatively low temperature as a result of chemical reaction between FCC and Si-organic chemicals. Successful synthesis of C_xN_y of fullerene-like structure using N-ion bombardment of carbon material was reported earlier. We propose that admixture of fullerenes in FCC will provide effect of “seeds” helping formation of C_xN_y of fullerene-like structure.

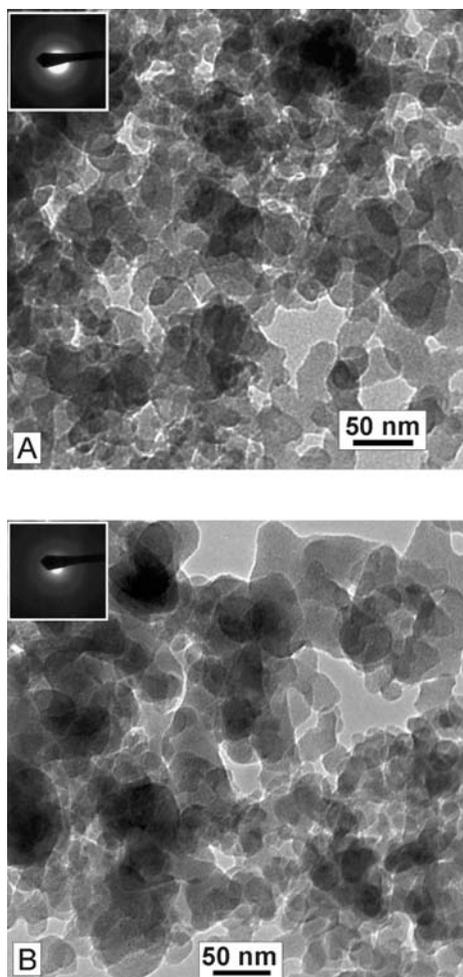


Figure 1: HRTEM images of fullerene-containing carbon (FCC) materials: a) initial; b) after iodine doping. Electron diffraction (inset in left up corner) shows amorphous structure of both materials.

The reversibility of the sorption of iodine on FCC and NOM was examined by performing a variety of experiments. We assessed the stability of the FCC and NOM to leaching with water and with solutions containing various reagents that can change the oxidation state of the iodine or displace iodide from anion exchange sites. The thermal stability of the iodine-FCC and iodine-NOM associations was examined by using pyrolysis mass spectrometry of FCC material exposed to the iodine vapor in simulated fuel rod processing experiments. We also did some studies to assess thermal stability of the iodine-FCC using Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC).

The iodine release from the dissolution of spent fuel was simulated using the experimental system shown in Figure 3. The off-gas stream flowed through a column containing the test matrix (NOM, activated carbon, FCC, etc.). Sorption and breakthrough of iodine on the test matrix was quantified and the speciation of iodine remaining in solution was measured using a specific ion electrode, a colorimetric assay and ion chromatography. Under these reaction conditions remaining soluble inorganic iodine should consist only of HIO , IO^- , IO_3^- and I^- .

Iodine sequestration in aqueous suspensions of NOM were analyzed by the adapting the method of Mishra et al. (2000). This method involves reaction of active iodine with N,N-dimethylaniline. The product p-iodo-N,N-dimethylaniline was quantified by GC/MS. Iodate (IO_3^-) and iodide were determined by ion chromatography or by specific ion electrode. We had planned to determine total iodine in solution and in

the NOM or FCC using (pyrolysis) ICP- MS. However, this instrument was not available during the first years of the project. This part of the study will be completed in the third year if the instrument becomes available.

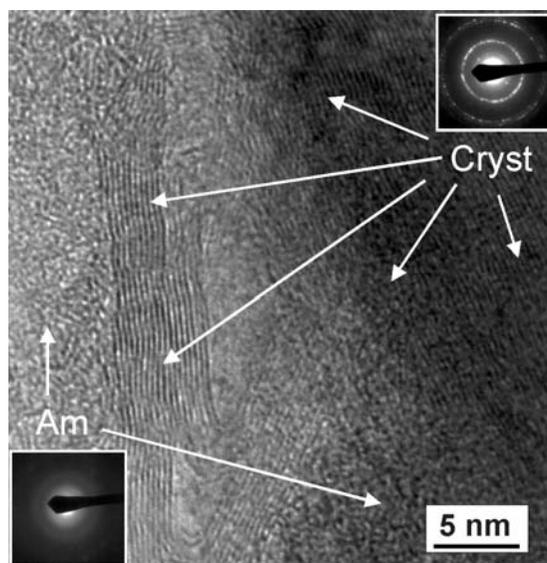


Figure 2: HRTEM image of iodine-doped FCC material hot pressed in air at 800-1000°C, pressure 3500-4000 Mpa, for 25 min. Amorphous area (Am - see electron diffraction inset in left down corner) preserved iodine during hot pressing while new formed crystalline graphite layers (Cryst – see electron diffraction inset in right up corner) are free of iodine.

During the first two years of this program we have demonstrated that nitric acid and NO_x fumes can change the speciation of iodine (I₂) during trapping experiments. Oxidation of iodine was apparent after examining the details of iodine recovery from Fuel Rod simulation experiments. Fuel rod simulation involved sparging iodine from a warm concentrated nitric acid solution. The experiments were conducted with and without added Cu (granular). The Cu metal decomposition in the strong acid created NO_x, which simulated conditions, observed during fuel rod decladding.

In the presence of strong nitric acid most of the trapped iodine was converted to iodate. Iodate is the thermodynamically stable form of iodine, is water-soluble and can be easily leached from various waste forms. Thus any method developed for immobilizing fugitive iodine must address methods for immobilizing this oxidation state.

The conversion of iodine to iodate was very apparent on FCC material. Although volatile iodide was trapped on FCC during the fuel rod dissolution simulation experiments, it was apparent that most of the trapped iodine was easily leached from the fuel rod as iodate. FCC is not a useful waste form for iodate, although it did temporarily remove some of the fugitive iodine from the simulated off-gas. It is likely that some of the iodine trapped on NOM was also converted to iodate during fuel rod dissolution simulations. Unfortunately quantification of iodate by ion chromatography can be somewhat difficult. Iodate elutes very rapidly from the column and emerges very close to the “water dip” in the ion chromatogram. This makes integration of small peaks difficult. In addition, the potential for co-eluting interference is very high for iodate because of the complexity of the NOM matrix, which made ion chromatograms difficult to interpret. We will try to address this problem by improving the chromatography or reducing iodate to iodide for analysis. We have experimented with indirect measurements of iodate that involve addition of excess iodide and high acidity. This converts iodate to I₃⁻ which can be quantified colorimetrically or by iodometric titration.

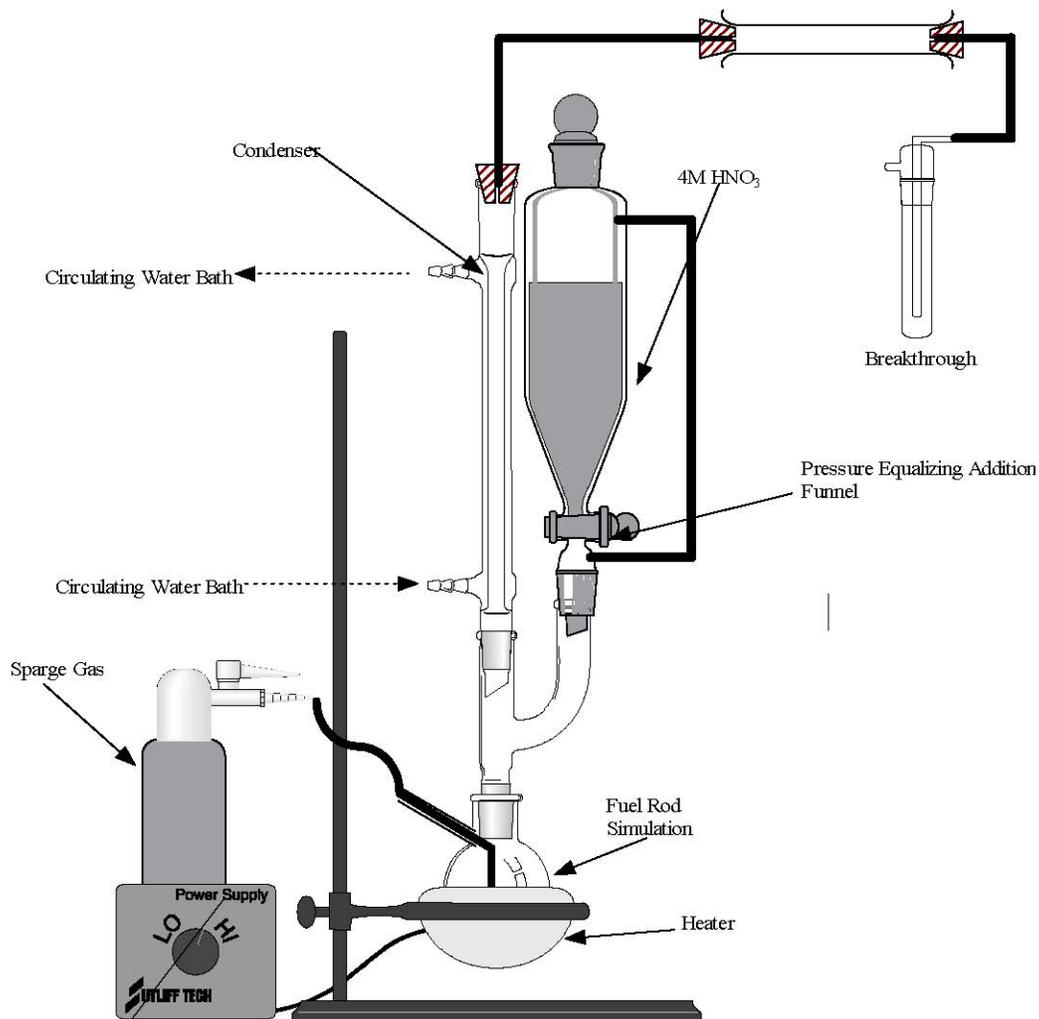


Figure 3: Simulation of Nuclear Fuel Dissolution

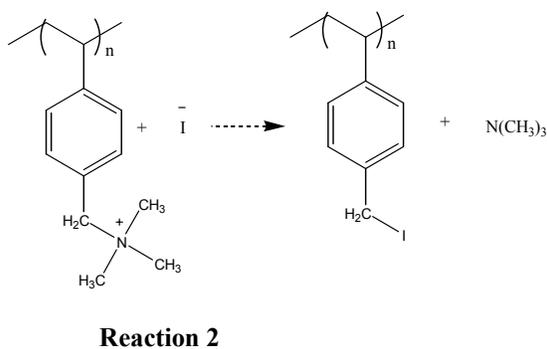
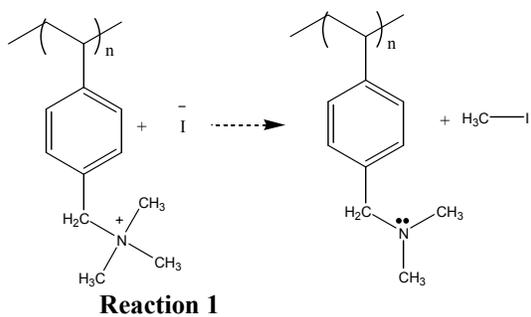
Iodate can be easily reduced to iodide by a number of inexpensive reducing agents. These agents include hydrazine and ascorbic acid. In addition, iodate formed on the NOM trapping media may eventually be reduced to iodide, once the trap is removed from the source of NO_x and strong acid. Batch experiments with iodine and several different forms of NOM (sphagnum, humic acid, tannic acid) indicated that at high pH the iodine was converted to iodide. During the final year of this study, we will continue experiments with NOM and examine the fate of iodate under batch reactions conditions in the presence of NOM. We believe that the rapid reaction of iodine (and iodate) with NOM can be exploited for the purposes of isolating iodide from the waste stream and eventually converting the iodine to a form suitable for transmutation (NaI).

Reduction of iodine to iodide (in vapor phase experiments) does prevent fugitive losses of iodine. However, iodide is still rather mobile and can be eluted from both FCC and NOM with water. The eluted iodide can be extracted (removed) from aqueous solutions with strongly basic ion exchange resins. Strongly basic ion exchange resins contain tetra-alkyl ammonium ion exchange sites. Hydrophobic anions have a high affinity for these sites. In fact, adsorbed iodide is not easily removed from commercially

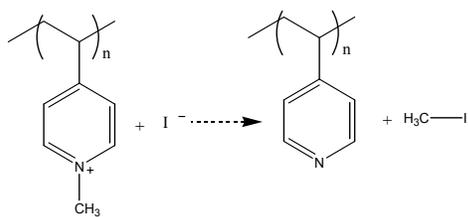
available anion exchange resins (Powell et al., 2002). Non-destructive iodide removal generally requires elution of the resin with a phenolate or perchlorate solution (Ito, 1999). Our own experiments with strongly basic anion exchange resin (AG-1) confirm that iodide is difficult to recover. Rinsing AG-1 with 2M HCl or 2M NaCl failed to displace iodide from these resins.

To recover iodine from these anion exchange resins one can take advantage of the strongly nucleophilic nature of iodide. Quaternary ammonium ions are known to be susceptible to nucleophilic displacement reactions. For example Tsai and Ding (2004) utilized the thermal decomposition of the iodide salts of alkyltrimethylammonium surfactants as a means of producing the alkyl dimethylamine that can be analyzed by GC/MS. The iodide salts of the surfactant were allowed to decompose at 300C during GC analysis. Hind et al., (1997) utilized a similar method for analysis of surfactants in Bayer process liquors. In the case of benzyl trimethyl ammonium cations, nucleophilic attack by iodide results in the formation of either benzyl iodide or methyl iodide.

We performed some preliminary experiments with two different anion exchange resins. The first resin was DOWEX 1 (AG-1 x8). This is a standard commercially anion exchange resin that is normally available commercially in the chloride form. The second resin that can possibly be used in this type of application is a methyl-pyridinium type resin. This resin was made from a commercially available polyvinyl-pyridine resin. Reacting methyl iodide with the polyvinyl-pyridine starting material formed the iodide salt of methyl-pyridinium. Vacuum dried (over NaOH) specimens of both resins were analyzed by pyrolysis GC/MS. The pyrolysis analysis was performed on a Varian Saturn III GC/MS equipped with a CDS Pyroprobe 2000. Several resin beads were packed into a small diameter quartz tube and held in place by quartz wool. The beads were generally heated to 300-500C for 20 seconds. The pyrolysis products are swept from the quartz tube onto the GC column with the helium carrier gas. One loop of the column was immersed in liquid nitrogen to focus (cryo) the off-gas onto the column. Heating experiments with the iodide form of the strongly basic AG-1 resin indicated that heating produced either methyl iodide (Reaction 1) or trimethyl amine (Reaction 2).



Heating experiments with the methyl pyridinium resin produced methyl iodide. The reaction we propose is shown in reaction 3. With mixed iodide and chloride salts of the methyl pyridinium resin both methyl iodide and methyl chloride were observed.



Reaction 3

Preliminary results with AG1-X8 indicate that reaction 2 occurs preferentially at 300 C while at 500 C methyl iodide production dominates. A series of pyrolysis experiments was performed on iodine saturated AG-1 X8. The ratio of methyl iodide to trimethyl amine was measured as a function of temperature. Samples (0.5-1 mg) were heated for 20 seconds and the pyrolysis gases analyzed by GC/MS. The ratios reported are the integrated ratios from the total ion chromatograms. These results are summarized in Figure 4, which illustrates that formation of methyl iodide dominates the resin decomposition at higher temperatures.

AG1-X8 Pyrolysis

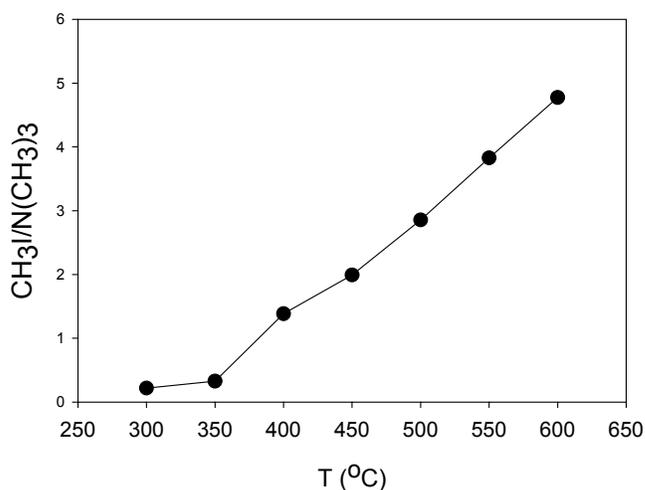


Figure 4: The ratio of methyl iodide and to trimethyl amine as a function of pyrolysis temperature

Methyl iodide formed during this process can be recovered for further processing. AG-1 resin was purchased in the chloride form. The resin was treated with excess 0.1 M NaI solution and then dried in a vacuum desiccator. Pyrolysis of the dried resin and produced methyl iodide, while pyrolysis of the starting material produced trimethyl amine and small amount of methyl chloride. As noted above the analogous reaction tetraalkyammonium iodide salts is known to proceed at lower temperatures. Therefore, one of the tasks involved in exploring this approach will be to determine a temperature suitable for high recovery of methyl iodide while minimizing the formation of other cracking products.

Preliminary experiments with methyl pyridinium resin in the iodide form produced methyl iodide upon heating. Preliminary experiments indicated a maximum production of methyl iodide at 450 °C (Figure 5).

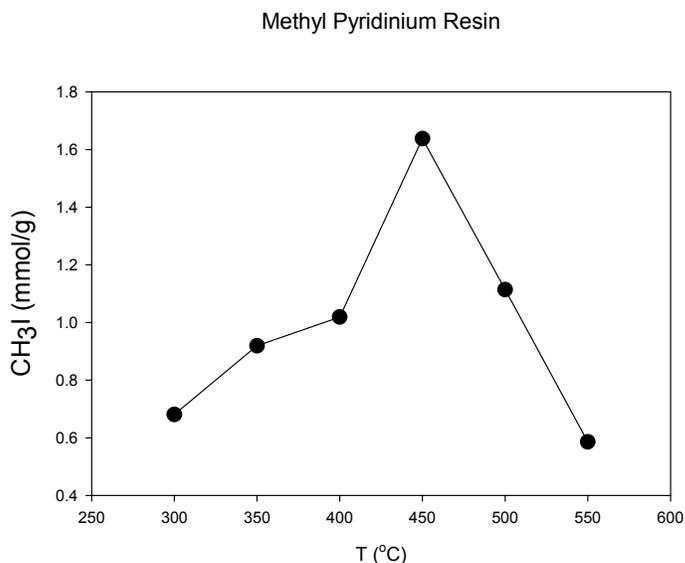


Figure 5: Methyl iodide produced from pyrolysis of methylpyridinium iodide resin.

We anticipate the methyl iodide produced by heating of the anion exchange resin can be concentrated cryogenically or by adsorption on carbon, or carbon molecular sieve. Preparative GC can also purify the pyrolysis product. If a non-destructive thermal conductivity detector was used with the preparative GC, the amount of methyl iodide recovered from a resin can be quantified. This information could be valuable for subsequent conversion of the methyl iodide into a form suitable for transmutation.

Chromatographically purified methyl iodide can be isolated by trapping the compound cryogenically or by adsorption. We propose that pyrolysis of resins (and NOM) can be performed using a tube furnace directly interfaced with a preparative “packed column” GC. The pyrolysate off gases can be directed into the GC and the methyl iodide isolated as it emerges from the column. Methyl iodide can then be converted into a target material for transmutation.

In parallel, the KRI team worked on developing more stable forms for the storage or disposal of the iodine. Two matrices were examined: silicon carbide (Si_xC_y) and a fullerene-like carbon nitride (C_xN_y). To form the silicon carbide matrix, cold pressed granules of iodine-doped FCC were rinsed in water-ethanol solution of tetraethoxysilane (TEOS), $\text{Si}(\text{OC}_2\text{H}_5)_4$, with the following proportions: 130 ml TEOS, 60 ml ethanol and 290 ml distilled water. Then FCC granules were dried at 60°C for 6-8 hours and calcined in air at temperature: 230; 300 and 360°C for 1 min in order to provide formation of Si_xC_y phase. For each calcination temperature the loss of iodine during leach test has been studied (Table 1).

Also, the correlation between release of iodine during leach test (at 90°C for 7 days in distilled water) and amount of new formed Si_xC_y phase in FCC samples after calcination at 360°C have been investigated. Different FCC samples with the following weight ratios $\text{Si}_x\text{C}_y/\text{initial sample}$: 0.09; 0.12; 0.16; 0.19; 0.24 were used. For each samples the iodine release was less 0.04 mg/g or less than 0.02 wt.% of the initial iodine content. Results of XRD analysis of iodine doped FCC after conversion into Si_xC_y material did not allow us to identify the crystalline structure of new formed Si-carbide. Although we could expect formation of amorphous Si-carbide phase, it was assumed that only insignificant part of FCC reacted with Si-organic. Even this partial conversion of FCC into Si_xC_y material caused essential increase of mechanical durability of FCC granules. During future experiments it will be necessary to identify optimal conditions for more effective conversion of iodine doped FCC into Si_xC_y material avoiding iodine loss

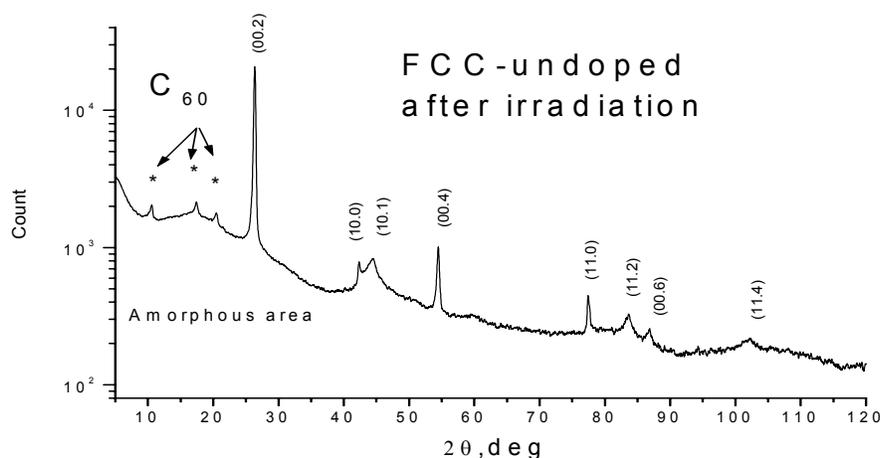


Figure 6: XRD patterns of undoped FCC after gamma-irradiation for 1.24×10^8 Rad. Reflections of crystalline phases: **graphite** and C_{60} are marked. Structure of amorphous part and C_{60} is based on benzene-like rings

Iodine-loaded FCC compounds may potentially be converted into a fullerene-like C_xN_y compound by N-ion bombardment. This requires special equipment, which is not available so far. In order to produce N-ions we decided to initiate nitrogen ionization by strong gamma-irradiation. Cold pressed granules and initial powders of FCC (iodine-doped and undoped FCC) were placed in glass capsules filled with nitrogen of high purity. Then these capsules were hermetically sealed up and irradiated by ^{60}Co -gun for 2.5 months to achieve dose 1.24×10^8 Rad. All FCC samples contained approximately 6 wt.% of bulk fullerenes. Iodine content in doped samples was 680 mg/g. The results of precise XRD analysis shows that under nitrogen atmosphere the irradiation of undoped FCC caused increase of amorphous part (Fig 6). In the same time irradiation did not affect C_{60} phase as well as general structure of amorphous part, which are based on benzene-like carbon rings. Irradiated iodine doped FCC was characterized by essential differences in comparison with undoped FCC. General structure of this material was based on carbyne chains and the chaoite crystalline phase was identified instead C_{60} . Also, irradiated iodine doped FCC contained at least 10 times higher graphite phase than irradiated undoped FCC. We did not observe qualitatively the release of iodine from FCC matrix after irradiation. However, it requires an additional confirmation from future experiments.

Table 1: Correlation between FCC calcination temperature and iodine release after static leach test at $90^\circ C$ for 7 days in distilled water.

Calcination temperature, $^\circ C$	Iodine loss	
	in mg/g	in wt.% of initial content
230	0.28	0.08
300	less 0.04	less 0.02
360	less 0.04	less 0.02

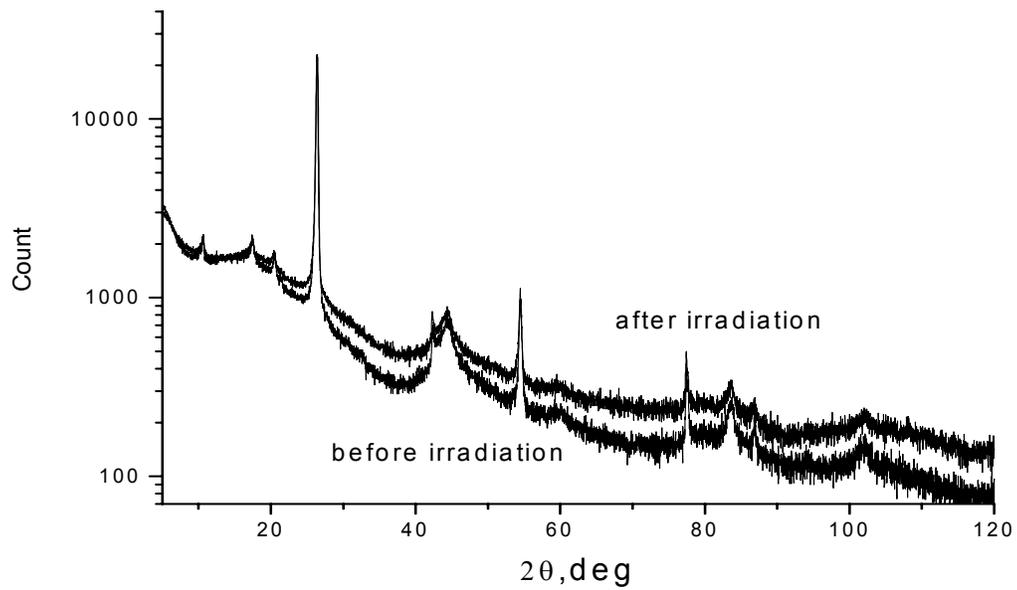


Figure 7: Comparison between XRD spectra of undoped FCC before and after gamma-irradiation. There is no principal difference excepts increase of amorphous part after irradiation.

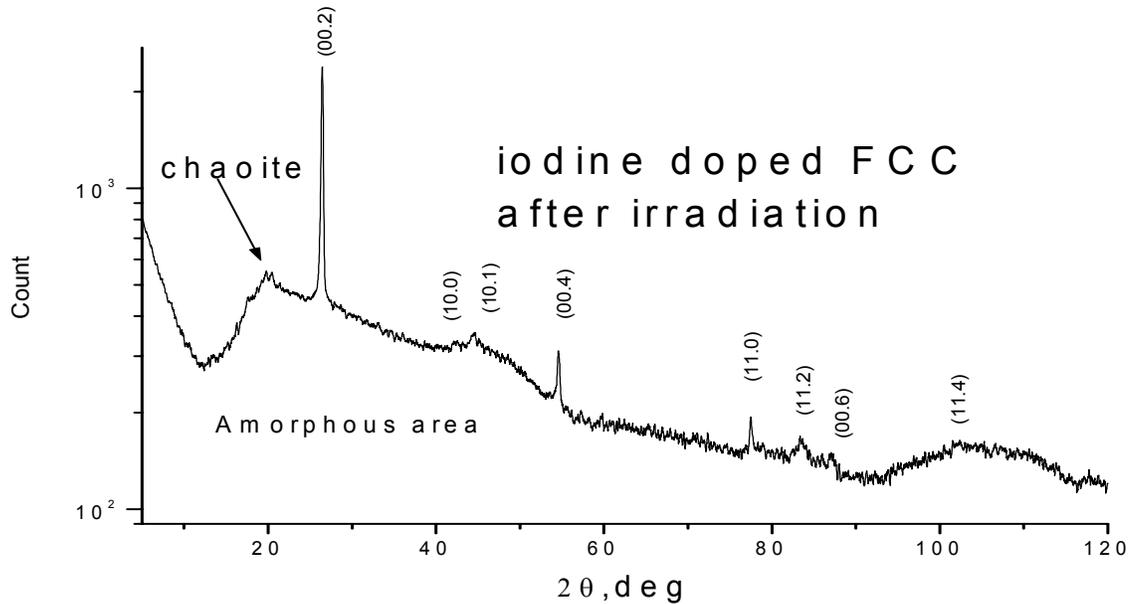


Figure 8: XRD patterns of iodine doped FCC after gamma-irradiation for 1.24×10^8 Rad. Reflections of crystalline phases: graphite and chaoite are marked. Structure of amorphous part and chaoite is based on carbyne chains.

The use of XRD analysis did not allow us identifying formation of C_xN_y phase of fullerene structure in the matrix of FCC material after irradiation under nitrogen atmosphere. We would assume that there are two possible reasons: overlapping of XRD patterns of C_{60} and C_xN_y ; or insignificant formation (even absence) of C_xN_y phase. In order to understand this in detail we plan carrying out experiments on longer irradiation and applying HRTEM method for study of irradiated FCC samples.

Research Approach/Scientific Investigation Plan

We are proposing a 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 UNLV team will examine the FCC material, along with NOM and other potential sequestering agents, under simulated process conditions. The KRI-KIRSI team will continue the development of 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.

Analysis of iodine stability in FCC and NOM indicated that in the oxidative environment of the Purex process iodine was extensively converted to iodate. This conversion has important implications for the long-term performance/suitability of FCC and NOM. Methods for immobilization or transmutation of iodine must address the issue of multiple oxidation states. Our studies with NOM have indicated that bound iodine recovered from the nuclear fuel can be converted to methyl iodide upon pyrolysis. Furthermore, iodate that is created during trapping can be reduced by NOM to iodide, which can be recovered on anion exchange resin. Pyrolysis of several types of anion exchange resins release methyl iodide. We believe that methyl iodide can be easily purified and converted quantitatively to NaI. During the final phase of this project to convert iodide to methyl iodide for purification and we propose to test a procedure for conversion methyl iodide to NaI.

There are several possibilities we will explore for converting recovered methyl iodide to NaI. One possible method by which methyl iodide could be converted to NaI (a potential transmutation product) is to adsorb methyl iodide onto a resin having an ethylselenyl ($CH_3CH_2-Se\sim$, $EtSe\sim$) functional group that should react readily with the $EtSe\sim$ group to form $P\sim Se(Et)(Me)^+I^-$. Previously we reported a simple experiment to test this possibility. This experiment was carried out by placing 0.3 g of the resin in a bottle, introducing either 20 or 40 μ L of MeI, capping the bottle with a septum cap, and sampling the head space for MeI after a period of time. No solvent was used in these experiments. Preliminary results indicated that 58% of the MeI was removed by the resin. Direct pyrolysis of the resin produced both MeI and EtI as anticipated (Umemura et al., *Bull. Chem. Soc. Jpn.* **1990**, 63, 2593-2600) showing that $P\sim Se(Et)(Me)^+I^-$ was formed. This finding is important because if it becomes necessary to trap iodine from $Me^{129}I$, it can likely be done using this type of resin. Another candidate resin that we will test is a resin $P\sim SMe$ that will trap $Me^{129}I$ to form $P\sim S(Me)_2^+ ^{129}I^-$. It should then be possible to treat this sulfonium salt, $P\sim S(Me)_2^+ ^{129}I^-$, with sodium hydroxide to form $P\sim SMe$, methanol, and sodium iodide thus regenerating the trapping agent $P\sim SMe$ and producing a water solution of $Na^{129}I$, and volatile methanol. This process would in essence be a titration of the methyl iodide product to produce sodium iodide. In principle direct titration of methyl iodide could also be used. But in view of the volatility of methyl iodide, the proposed resin based trapping method should be more effective.

Another possible method of converting methyl iodide to sodium iodide involves reduction with sodium metal. After trapping methyl iodide from the preparative GC (cryogenically or by adsorption) the Wurtz reaction should be able to produce NaI. The Wurtz reaction is a conceptually simple process in which alkyl halides react with sodium metal to form an alkane product and NaI. In the case of methyl iodide the reaction should result in the formation of sodium iodide and ethane as a volatile and harmless byproduct.

With the measurement, by the preparative GC, of the quantity of methyl iodide recovered, it should be possible to add a stoichiometric quantity of sodium to the recovered methyl iodide. Excess sodium could be

converted to sodium iodide by addition of reagent grade methyl iodide. This would trap the radiogenic iodide in a stable NaI carrier. The sodium iodide should be easily eluted from the column with water, and the water removed by evaporation leaving the NaI solid residue. Other metals such as Zn, Pb and Li also react with methyl iodide (de Sa et al., 2003, Osborne et al, 1989; Meszaros, 1967). Zinc is stable in air and forms a highly water soluble iodide salt. Zinc iodide formed on the surface of zinc metal can be dissolved in water and converted to NaI by cation exchange chromatography. Granular zinc could easily be packed into a trapping column to react with methyl iodide exiting the preparative GC.

Preliminary measurements with pyrolysis GC MS have demonstrated that methyl iodide is easily released from NOM at 500 °C. For ion exchange resins such as AG-1 release begins at 300 °C but rates increase with temperature (up to 600 °C was examined). At higher temperature the quantity of cracking products from NOM and from AG-1 increases. Some of these cracking products could potentially interfere with NaI formation, thus we propose that methyl iodide produced by pyrolysis be chromatographically purified. We propose to carry out the purification with preparative gas chromatography. Pyrolysis yield will be monitored by quantifying the recovered iodine in the pyrolysis product and by examining the residual iodine in the pyrolysate. The residual iodine in the pyrolysate will be examined by photo-electron spectroscopy. In addition, the pyrolysate will be leached to determine if soluble iodide species were formed.

The researchers at KRI will continue work on the development of a more durable storage/disposal form. FCC samples, along with samples of activated carbon and other matrices, will be converted into CxNy materials by irradiation in a nitrogen environment. FCC samples will also be converted to a SixCy matrix. These matrices, fabricated from both iodine loaded and unloaded precursor material, will be examined by XRD and other techniques to determine solid-state chemistry and the nature of the iodine inclusions. Loaded samples will also be evaluated through leaching/dissolution experiments to determine the durability of the matrix.

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 communicated 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 3:

- **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 Program.
- **Monthly and Quarterly Progress Reports:** Brief reports indicating progress will be provided every month and quarter in support of the DOE APCI reporting requirements.
- **Final Report:** Written report detailing experiments performed, data collected, results, and conclusions.

References:

- Amachi, S; Muramatsu, Y.; Kamagata, Y., Radioanalytical determination of biogenic volatile iodine emitted from aqueous environmental samples. *J. Radioanalytical and Nuclear Chemistry* 2000, 246 (2) 337-341.
- Balsley, S.; Brady, P.; Krumhansl, J.; Anderson, H., Iodide retention by metal sulfides: cinnabar and chalcocite. *Environ. Sci. Technol.* 1996, 30, 3025-3027.
- Berdinsky, A.S.; Sheytsov, Y.V.; Okotrub, A. V.; Lee, J. H.; Gridchin, V. A.; Chadderton, L. T.; Yanovsky, Y. G.. Study on Resistance of Iodine-Intercalated Fullerene Films. *Korus* 1999, 667-671.
- Bichsel, Y; Von Gunten, U., Oxidation of iodide and hypiodous acid in the disinfection of natural waters. *Environ. Sci. Technol.* 1999, 33, 4040-4045.
- Bichsel, Y.; Von Gunten, U.; Hypiodous acid: Kietetics of the buffer catalyzed disproportionation. *Wat. Res.* 34 (12) 3197-3203.
- Choppin, G. R.; Morgenstern, A., Radionuclide separations in radioactive waste disposal. *J. Radioanalytical and Nuclear Chemistry*, 2000, 243(1) 45-51.
- Cooper, L. W.; Beasley, T. M.; Zhao, X. L.; Soto, C.; Vinogrova, K. L.; Dunton, K. H., Iodine-129 and plutonium isotopes in arctic kelp as historical indicators of transport of nuclear fuel-reprocessing wastes from mid-to-high latitudes in the Atlantic ocean. *Marine Biology* 1998, 131, 391-399.
- Francois, R. (1987) The influence of humic substances on the geochemistry of iodine in nearshore and hemipelagic marine sediments. *Geochim. Cosmochim. Acta* 51, 2417-2427.
- Geckeler, K.E.; Samal, S. Synthesis and properties of fullerenes, a review. *Polymer International* 48, 1999.743-757.
- Hedges, J. I.; Eglinton, G.; Hatcher, P.; Krichman, D. L.; Aronosti, C.; Derenne, S.; Evershed, R.P.; Kögel-Knabner, I.; de Leeuw, J. W.; Littke, R.; Michaelis, W.; Rullkötter, J., The molecularly-uncharacterized component of nonliving organic matter in natural environments. *Organic Geochemistry* 2000, 31, 945-958.
- Heumann, K. G.; Rädlinger, G.; Erbes, M.; Heiber, I.; Obst, U.; Filip, Z.; Claus, H., Ageing of dissolved halogenated humic substances and the microbiological influence on this process. *Acta Hydrochim. Hydrobiol.* 2000, 28, 193-201.
- Hou, X.; Yan, X.; Chai, C., Chemical species of iodine in some seaweeds II. Iodine bound macromolecules. *J. Radioanalytical and Nuclear Chemistry* 2000, 245 (3) 461-467.
- Hoskins, J. S.; Karanfel, T.; Serkiz, S., Removal and sequestration of iodide using silver-impregnated activated carbon. *Environ. Sci. Technol.* 2002, ASAP Publication on Web.
- Ito, K. (1999) Semi-micro ion chromatography of iodide in seawater. *J. Chrom. A* 830, 211-217.
- Kaplan, D. I., Serne, R. J.; Parker, K.E.; Kutnyakov, I.V. (2000) Iodide Sorption to Subsurface Sediments and Illitic Minerals. *Environ. Sci. Technology*.
- Laternus, F.; Giese, B.; Wiencke, C.; Adams, F. C., Low-molecular-weight organoiodine and organobromine compounds released by polar macroalgae- The influence of abiotic factors. *Fresenius J. Anal. Chem.* 2000, 368, 297-302.

Limonov, M. F.; Kitaev, Y.E.; Chugreev, A.; Smirnov, V.P. Grushko, Y. S.; Kolesnik, S. G.; Kolesnik, S.N. Phonons and electric-phonon interaction in halogen-fullerene compounds. *Physical Review B*, 1998, 75867594.

Oktay, S.D.; Santschi, P. H.; Moran, J. E.; Sharma, P., ¹²⁹I and ¹²⁷I transport in the Mississippi river. *Environ. Sci. Technol.* 2001, 35, 4470-4476.

Oleksy-Frenzel, J.; Wischnack, S.; Jekel, M., Application of ion-chromatography for the determination of the organic-group parameters AOCl, AOBr, AOI in water, *Fresenius J. Anal. Chem.* 2000, 366, 89-94.

Oste, L. A.; Temminghoff, E. J. M.; Van Reimsdijk, W. H., Solid-solution partitioning of organic matter in soils as influenced by an increase in pH or Ca concentration. *Environ. Sci. Technol.* 2002, 36, 208-214.

Powell, K. R.; Kaplan, D. I., Fondeur, F. (2002) Resin Longivity Studies. WSRC-TR-2002-00091 (<http://sti.srs.gov/tr2002091.html>)

Quintana, E. E., Thyssen, S. M., Determination of ¹²⁹I in conifer samples around nuclear facilities in Argentina. *J. Radioanalytical and Nuclear Chemistry* 2000, 245 (3), 545-550.

Rädlinger, G.; Heumann, K. G.; Transformations of iodide in natural and wastewater systems by fixation on humic substances. *Environ. Sci. Technol.* 2000, 34, 3932-3936.

Sheppard, M.I.; Thibault, D. H. (1992) Chemical behavior of iodine in organic and mineral soils. *Applied Geochemistry* 7, 265-272.

Ticknor, K. V.; Cho, Y.H. (1990) Interaction of iodide and iodate with granitic fracture filling minerals. *J. Radioanal. Nuclear Chem.* 140, 75-90.

Trujillo, E. M.; Jeffers, T. H.; Ferguson, C.; Stevenson, H.Q., Mathematically modeling the removal of heavy metals from a wastewater using immobilized biomass. *Environ. Sci. Technol.* 1991, 25, 1559-1565.

Truesdale, V. (1997) Kinetics of disproportionation of hypoiodous acid at high pH, with an extrapolation to rainwater. *J. Chem. Soc., Faraday, Trans.* 93(10), 1909-1914.

VanMiddlesworth, L.; Handld, J.; Johns, P., Iodine-129 in thyroid glands: A sensitive biological marker of fission product exposure. *J. Radioanalytical and Nuclear Chemistry* 2000, 245 (2), 447-453.

Vel Leitner, N. K.; Vessella, J.; Dore, M.; Legube, B., Chlorination and formation of organoiodinated compounds: The important role of ammonia. *Environ. Sci. Technol.* 1998, 32, 1680-1685.

Warner, J.; Casey, W.; Dahlgreen, R. A., Interactions of I₂(aq) with substituted phenols and humic substances. *Environ. Sci. Technol.* 2000, 34, 3180-3185.

Whitehead, D. C. (1973) The Sorption of Iodide by Soils as influenced by equilibrium conditions and soil properties. *J. Sci. Fd. Agric.* 24, 547-556.

Whitehead, D. C. (1984) The distribution and transformations of iodine in the environment. *Env. Internat.* 10, 321-339.