

IMMOBILISATION OF FISSION IODINE BY REACTION WITH INSOLUBLE NATURAL ORGANIC MATTER

**Gregory T. Schmett¹, Ginger M. Kimble¹, Spencer M. Steinberg¹,
David W. Emerson¹; Gary S. Cerefice²**

¹Department of Chemistry, University of Nevada Las Vegas, Las Vegas, NV 80154

²Harry Reid Center for Environmental Studies, University of Nevada Las Vegas, Las Vegas, NV
89154

Abstract

Commercial nuclear power plants produce Iodine-129 (¹²⁹I) as a fission by-product. Iodine-129, along with other stable isotopes of iodine, is released during the reprocessing of nuclear fuel. Silver-impregnated activated carbon, activated carbon, cinnabar and chalcocite have been used in the past to remove iodide and iodine from waste streams. There is environmental and geological evidence that iodine can become associated with natural organic matter (NOM). For example, a number of previous studies have shown that iodine (including ¹²⁹I) can be strongly retained in organic-rich surface soils and humic material. This research explores the use of NOM (sphagnum peat) to sequester iodine from acid vapour and aqueous solution. NOM may be stable for geological storage or the sequestered iodine can be recovered to prepare target materials for transmutation. The nature of the sphagnum iodine association has been explored as well as method that can be used to concentrate and recover sequestered iodine from the peat moss.

Introduction

Iodine-129 (^{129}I) 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 vapour 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. Our objective 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 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.

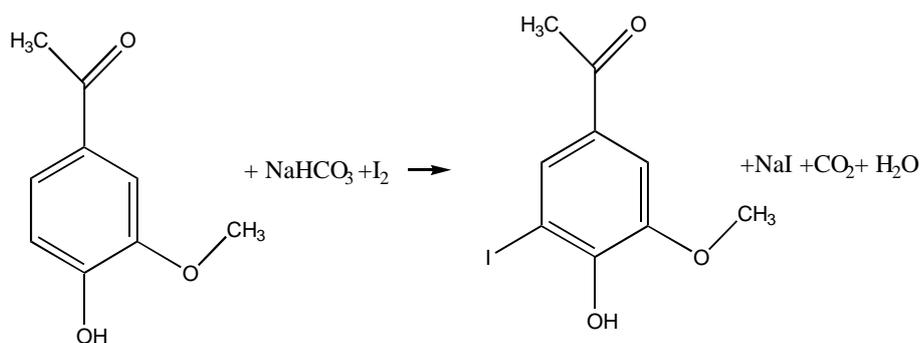
Radioactive iodine has the same environmental and geochemical properties as stable iodine, and in its predominant oxidation states of -1 and 5 (I⁻ and IO₃⁻), it is a highly soluble and mobile element that is likely to become rapidly dispersed in the environment (Whitehead, 1984). Whitehead (1973) noted 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. Volatile species, that are formed biologically, include iodomethane and iodoethane (Laternus et al., 2000; Amachi et al., 2000; Huo et al., 2000).

Our primary research objectives were to develop bench-scale experimental set-up and procedures for simulating PUREX head-end vapour phase and to develop experimental procedures for evaluating I sequestering methods using bench-scale procedures. In addition, we sought to examine the effect of reaction conditions on binding and elucidate the nature of the reaction products. 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 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).

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 acetyl 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 (methoxy and hydroxy groups). During the early stages of this study we examined the reaction of iodine (I_2) with model compounds that were selected because they possessed functional groups that would be found in sphagnum peat. In Figure 1, one such model reaction is illustrated.

Figure 1. **Substitution of iodine on the acetovanillone ring.**



Experiments with model compounds were performed at ambient temperature in aqueous pH buffered solution. For example, when an aliquot of iodine is added to a bicarbonate buffered solution of the model phenol, the iodine “colour” rapidly fades. The solution was acidified and extracted with diethylether. Trimethylsilyl (TMS) derivatives of the extracted compounds were separated and analyzed by GC/MS and iodinated compounds were confirmed by their mass spectra.

Experimental

All reagents used during this study were of analytical quality or better. Sphagnum peat was purchased from a local nursery and used as received. Iodate and iodide were detected and quantified using by electrochemically-suppressed anion conductivity. Ion chromatography was performed on a system comprised of a Dionex gradient pump, a Milton-Roy conductometric III detector, a Reodyne 9010 injector and an SRI Data system. A Novasep A-1 column was selected for routine separations. Separations were performed with a 0.005 M Na₂CO₃ buffer delivered at 1.0 mL/min. The ion chromatograph was calibrated with external standards that were prepared gravimetrically and then diluted to the appropriate concentration range. For some experiments iodine was detected using an ion sensitive electrode obtained from Cole-Parmer. The electrode underwent a four-point calibration daily with iodide standards that were prepared in the laboratory following the directions of the manufacturer.

Iodine was measured by either the DPD (N,N-diethyl-p-phenylene diamine) colorimetric method or by and adaptation of the method of Mishra et al. (2000). The DPD method is a colorimetric method and was implemented using a kit purchased from LaMotte. Measurements were made on a LaMotte Smart colorimeter. The method of Mishra et al., (2000) involves reaction of active iodine with N,N-dimethylaniline. A 0.5 mL aliquot of a 16 μM solution of N,N-dimethylaniline (in methanol) was added to the experimental solution. Care was taken to insure that NNDMA is in excess over the free iodine in solution. The NNDMA reacts nearly instantaneously with iodine to form p-iodo-N,N-dimethylaniline, which is extracted from the aqueous solution with hexane and measured by GC/MS. Free iodine remaining in solution is thus quantified by the amount of p-iodo-N,N-dimethylaniline formed.

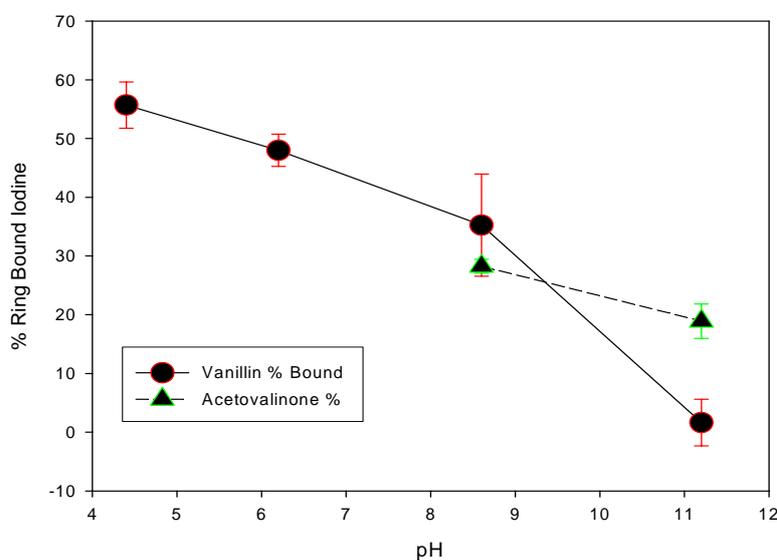
The GC/MS system consisted of a Varian 3400 gas chromatograph interfaced to a Varian Saturn III ion trap mass spectrometer. Pyrolysis experiments were performed on a CDS Pyroprobe 2000 equipped with a model 1500 pyrolysis interface. This instrument was connected to a Saturn III instrument similar to the above. Samples were pyrolyzed at 500°C, for 20 seconds, in a helium atmosphere. Methyl iodide, that was released during pyrolysis, was cryogenically focused by inserting a 10 cm loop of the capillary gas chromatography column in liquid nitrogen. At the completion of pyrolysis the liquid nitrogen was removed and the column temperature program was initiated. Column temperature was generally held constant at 40°C for 5 minutes and then ramped to 280°C at 10°C/minute.

Iodination experiments with model compounds (vanillin and acetovanillone) and kinetic experiments with Sphagnum peat were conducted at ambient temperature in buffered aqueous solutions. For experiments with model compounds the iodination products were characterised. Products (and remaining starting material) were extracted from aqueous solutions with diethyl ether. The ether was evaporated to dryness with a stream of dry N₂ and the residue was silylated with N, O-Bis(trimethylsilyl)trifluoroacetamide (BSTFA). The silylated derivatives were then analyzed by GC/MS. Compounds were identified using the NIST 2000 mass spectral library or by comparison to standard compounds.

Results and Discussion

For iodine in the presence of excess vanillin, in aqueous solution, two reactions are possible. Iodine can substitute on the ring system or be reduced to iodide. For the latter reaction the vanillin is oxidized to vanillic acid. Vanillic acid can be detected by GC/MS as the TMS derivative. The results of a series of experiments are summarized in Figure 2. In all cases the reaction was complete within a few minutes so kinetics were difficult to study with the analytical equipment available. With acetovanillinone only ring iodination was detected. We did not find any evidence of reaction at the acetyl group. No other oxidation products of acetovanillinone were detected even though a substantial portion of the iodine was reduced to iodide. The oxidation product may not have been extractable.

Figure 2. Percent ring bound iodine as a function of pH. Vanillin and acetovanillinone were in excess.

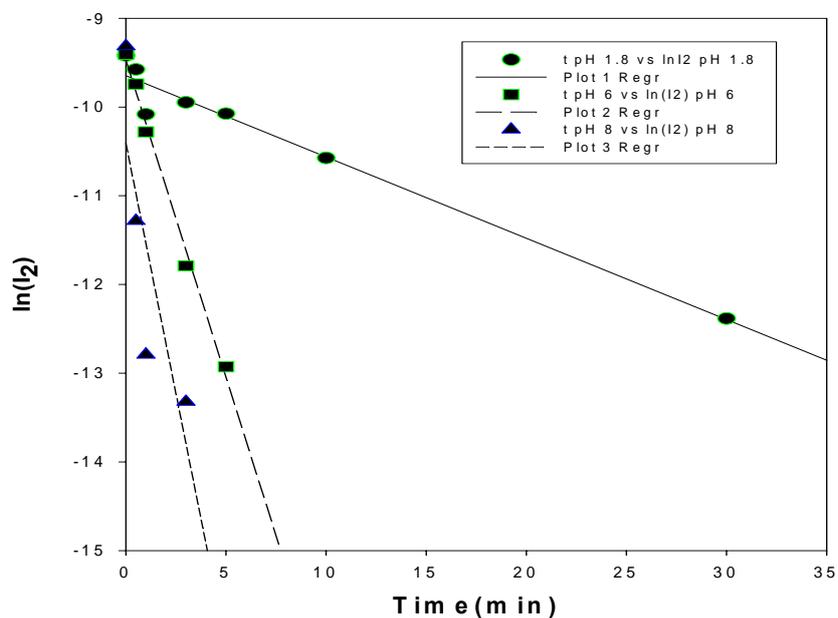


If all of the iodine in the model compound experiments reacted by ring addition, than 50% of the iodine atoms (at maximum) would be incorporated into vanillin or acetophenone. At low pH(4-6) our results are consistent with ring substitution being the dominant reaction. Reduction of iodine by vanillin resulted in the formation of vanillic acid which was detected by GC/MS.

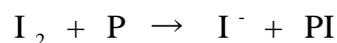
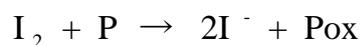
Experiments with sphagnum peat moss indicate that this material interacts strongly with molecular iodine. Experiments that were conducted in aqueous suspensions (solutions) indicate rapid reaction with iodine. In addition, we demonstrated efficient sequestration of iodine from the vapour phase using two experimental apparatuses that are discussed further below. Iodine sequestration in aqueous suspensions of NOM was analyzed by the adapting the method of Mishra et al. (2000).

The reaction of iodine (I_2) with a suspension of sphagnum peat (350 mg/10 mL of buffer) appears to follow pseudo first order kinetics (Figure 3). At pH 10 the reaction was too rapid to follow by this method.

Figure 3. First reaction of iodine with peat suspensions.



The loss of iodine and the appearance of iodide (Figure 4) can be modelled using the simple reaction scheme (P represents the reactive sphagnum and Pox has been oxidized by iodine).



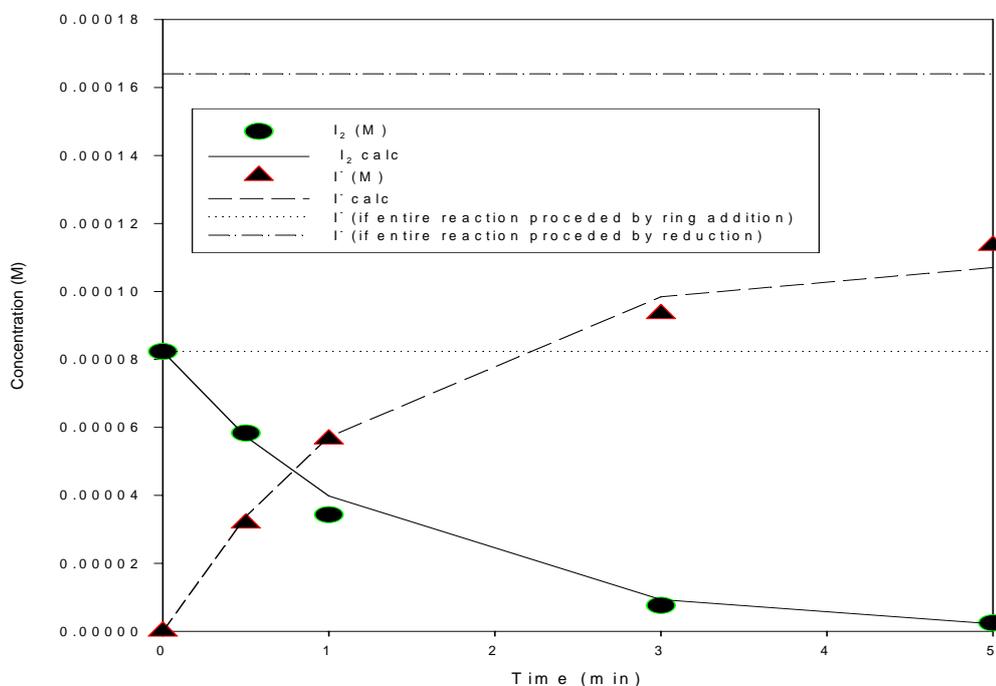
This reaction scheme can be modelled as two parallel first order equations (1 and 2).

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

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

The rate constant k_{red} and k_{sub} are pseudo first order rate constants for the reduction of iodine and incorporation into the organic matrix (ring substitution?). The system of equations (1 and 2) were numerically fit to the time series measurements of iodide and iodine using commercially available software.

Figure 4. Peat-iodine reaction time series at pH 6. The loss of I₂ and the appearance of I⁻ are shown along with model predictions using the “best fit” rate constants.



The reaction of iodine with sphagnum peat at pH 6 proceeds partially by reduction and partial by incorporation of iodine into the organic material. The top horizontal line represents the iodide concentrations for complete reduction. The bottom horizontal line represents the predicted iodide concentration for ring addition. The best-fit values for the rate constants at pH 6 and 8 are presented in Table 1.

Table 1. Best fit rate constants for equations 1 and 2.

pH	k _{red}	K _{sub}
6	0.25	0.48
8	0.95	2.91

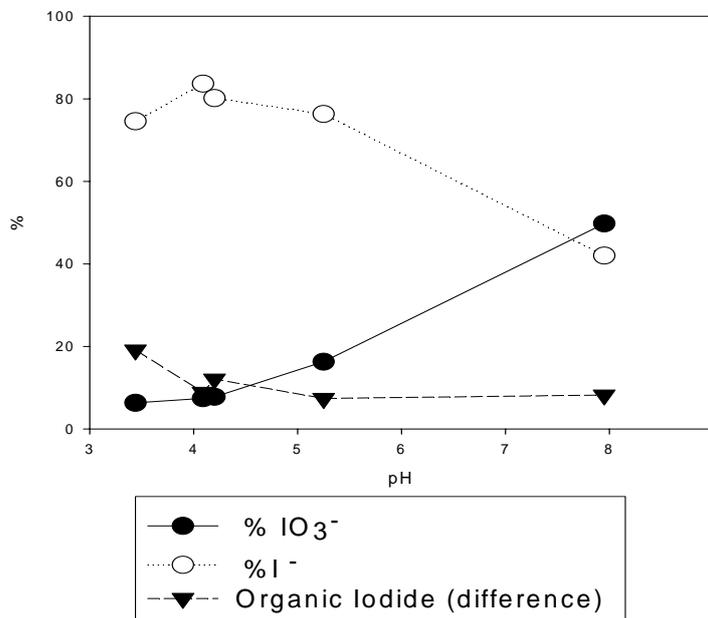
The fraction of iodine that reacts by addition can be calculated from the rate constants:

$$\% \text{Addition} = \frac{100 * k_{\text{sub}}}{k_{\text{sub}} + k_{\text{red}}} \quad (3)$$

From the “best fit” rate constants, about 65% of the iodine reacted by “ring substitution” at pH 6, and 75% at pH 8. Pyrolysis of iodine treated Sphagnum Peat at 500°C releases bound iodine as methyl iodine. The only volatile iodine product that was identified was methyl iodide. Methyl iodide was identified and confirmed by mass spectrometry and gas chromatography retention time.

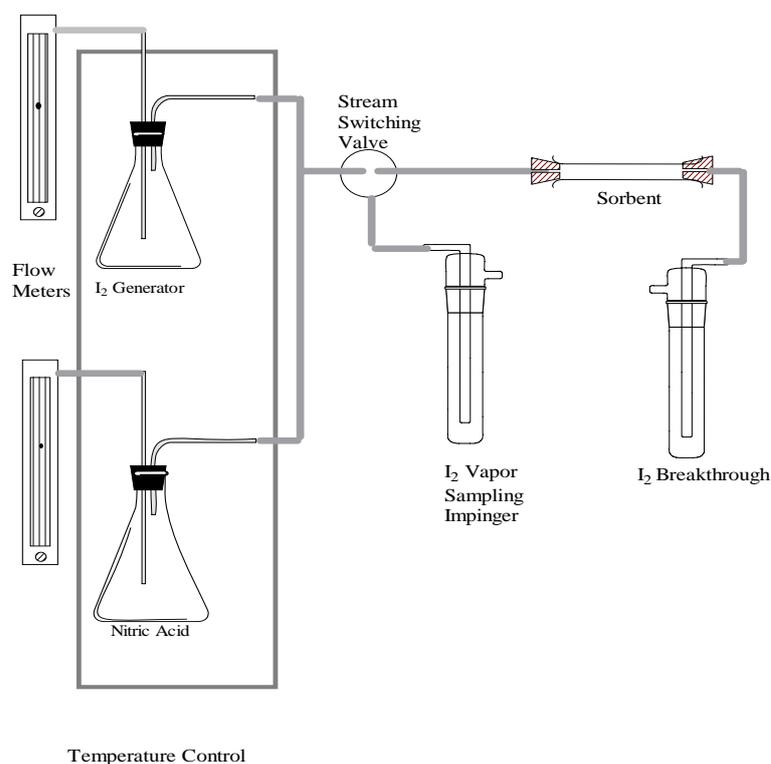
Our investigations indicate nitric acid and NOx fumes (encountered during fuel rod dissolution) can oxidize I₂ to IO₃⁻. Oxidation of iodine was apparent after examining the details of iodine recovery from Fuel Rod simulation experiments. Fuel rod simulation involved sparging iodine from a warm concentrated nitric acid solution. The experiments were conducted with and without added Cu (granular). The Cu metal decomposition in the strong acid created NOx, which simulated conditions, observed during fuel rod decladding. It is likely that some of the iodine trapped on NOM was converted to iodate during fuel rod dissolution simulations. Because it is clear from experiments that simulate the dissolution of fuel rods that some iodine is converted to iodate, we have also investigated the reaction of iodate with sphagnum peat. Twelve hour heating experiments were conducted over a pH range (~3.5-9). These experiments were conducted with 350 mg of sphagnum peat in 10 mL of 57 μM iodate. The results are presented in Figure 5. It is clear from these results that much of the iodate is reduced to iodide. In addition, a significant amount of the iodine was incorporated into the peat (5-10%).

Figure 5. **Reduction and binding (organic iodine) of iodate by Sphagnum peat. Suspensions were heated for 12 hours at 60°C.**



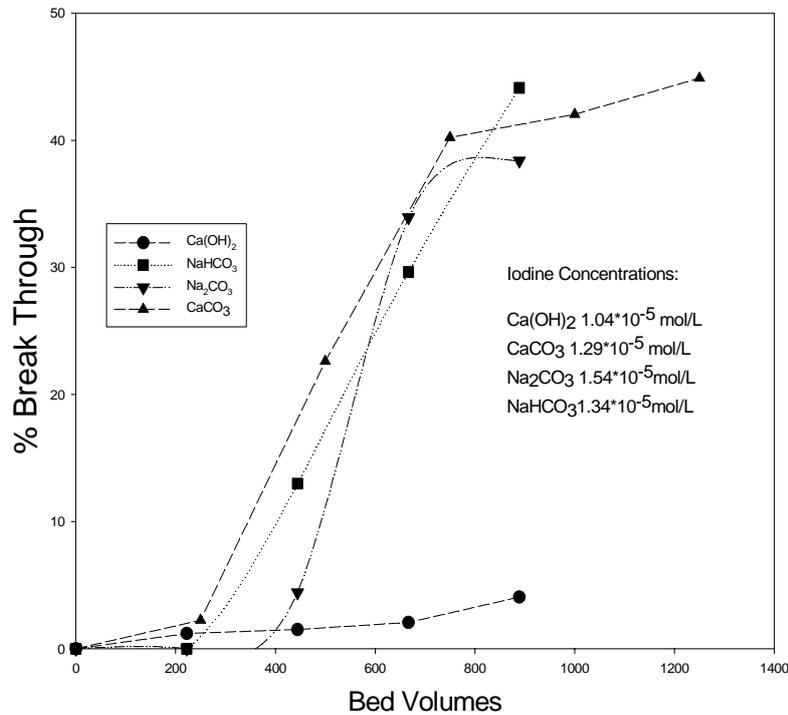
We constructed an I₂ generator for testing the sequestration of iodine from the vapour phase. Iodine that escapes the test sorbent is trapped as iodide in bisulfite filled bubblers (Figure 6).

Figure 6. Iodine vapour generator



Iodine crystals and concentrated nitric acid were heated to 50°C in separate impingers, and a metered stream of N₂ was passed over each to generate iodine vapour and nitric acid vapour. This stream was directed through a packed column containing peat and an inorganic base. The breakthrough of iodine as monitored by measuring the iodide concentration in bisulfite filled impingers (specific ion electrode). The breakthrough of iodine vapour ($\sim 10^{-6}$ mol/L) through columns packed with sphagnum peat and various inorganic bases (30% by weight) is shown in Figure 7. The columns generally contained 0.5 g of material and had bed volumes of 0.8 mL. The flow rates were generally 20 mL/min however we did not observe significant changes in breakthrough with flow rates (10-30 mL/min). It is clear that Ca(OH)₂ was the best choice of base. We have demonstrated the reproducibility of breakthrough volumes by examining four experiments with 30% Ca(OH)₂. For all experiments breakthrough (5%) occurred at about ~ 1100 B. The rise time after break-through does show some variation. The addition of a small percentage (20%) of activated carbon to the peat/Ca(OH)₂ trapping material increased breakthrough volumes by an order of magnitude. Activated carbon has a high affinity for iodine, however iodine is easily desorbed from activated charcoal. We believe that iodine released in the presence of peat should react and either be reduced or bound to the peat matrix. Variation in Ca(OH)₂ was tested. Ca(OH)₂ at 10% and 60% was less effective than 30%.

Figure 7. Breakthrough volumes of iodine vapour (in the presence of nitric acid vapours) on NOM/InorganicBase filled traps. Traps were ~0.5 grams of material with a base content of 30%.



We simulated fuel rod dissolution using the device illustrated in Figure 8. Nitric acid is added to 4-6 mg of an aqueous iodine solution. The solution is then heated and sparged with nitrogen through a NOM trap, breakthrough is monitored as described above. With a trap consisting of 0.01 grams of 70:30 sphagnum peat/Ca(OH)₂. Iodine (6 mg) was added to 55mL of 60% concentrated nitric acid. Sparging was started immediately. The amount of iodine remaining in the simulator was determined colourimetrically. The percent of the iodine removed from the system that escaped the trap was recorded as a function of sparging time. The results are presented as a graph of percent iodine against sparging time and trap bed volumes (Figure 9). No breakthrough was observed up to 20,000 bed volumes. Higher trapping efficiency could be obtained with a larger trap. The 0.01 grams of material was used to facilitate flow rate adjustments and allowed breakthrough to be observed in less than two hours.

Summary and Conclusions

Sphagnum Peat reacts with iodine (I_2 , IOH and IO_3^-) by reduction and formation of covalent organo-iodine products. The combination of peat with $Ca(OH)_2$ can remove iodine from acidic vapour streams that are encountered during UREX and PUREX. Although breakthrough volumes are not as large as other materials (charcoal and modified charcoals), peat is less expensive. Iodine can be partially recovered from peat as methyl iodide using pyrolysis.

Figure 8. Fuel Rod dissolution simulation device

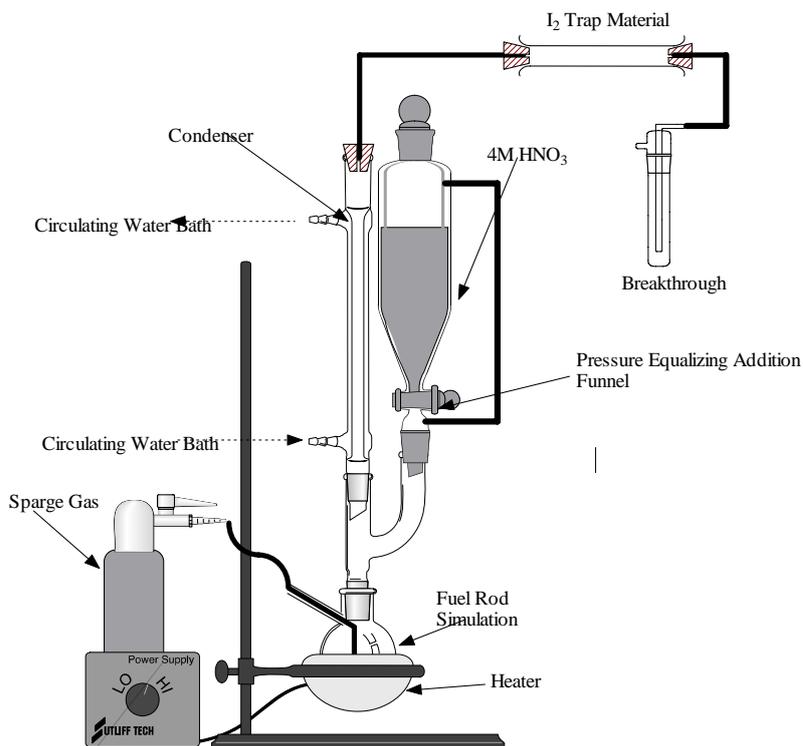
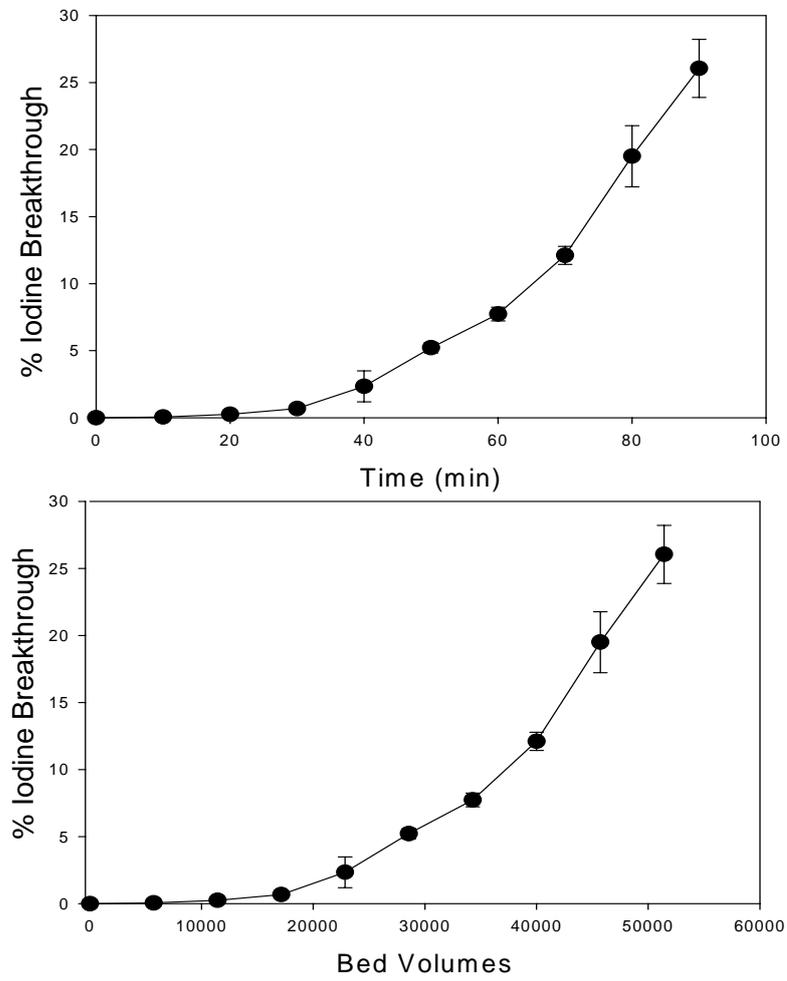


Figure 9. Fuel Rod Simulator Iodine Breakthrough for 0.01 grams of 70:30 Sphagnum/ $\text{Ca}(\text{OH})_2$ and a flow rate of 20 mL/min.



REFERENCES

- [1] S. Amachi, Y. Muramatsu, Y. Kamagata, "Radioanalytical determination of biogenic volatile iodine emitted from aqueous environmental samples." *Journal of Radioanalytical and Nuclear Chemistry* 2000, 246 (2) 337-341.
- [2] S. Balsley, P. Brady, J. Krumhansl, H. Anderson, "Iodide retention by metal sulfides: cinnabar and chalcocite." *Environ. Sci. Technol.* 1996, 30, 3025-3027.
- [3] Y. Bichsel, U. Von Gunten, "Oxidation of iodide and hypiodous acid in the disinfection of natural waters". *Environ. Sci. Technol.* 1999, 33, 4040-4045.
- [4] G.R. Choppin, A. Morgenstern, "Radionuclide separations in radioactive waste disposal." *J. Radioanalytical and Nuclear Chemistry*, 2000, 243(1) 45-51.
- [5] J. Hedges, G. Eglinton, P. Hatcher, D. Krichman, C. Aronosti, S. Derenne, R. Evershed, I. Kögel-Knabner, J. de Leeuw, R. Littke, W. Michaelis, J. Rullkötter, "The molecularly-uncharacterized component of nonliving organic matter in natural environments." *Organic Geochemistry* 2000, 31, 945-958.
- [6] K. Heumann, G. Rädlinger, M. Erbes, I. Heiber, U. Obst, Z. Filip, Z. H. Claus, "Ageing of dissolved halogenated humic substances and the microbiological influence on this process." *Acta Hydrochim. Hydrobiol.* 2000, 28, 193-201.
- [7] X. Hou, X. Yan, C. Chai, "Chemical species of iodine in some seaweeds II. Iodine bound macromolecules." *J. Radioanalytical and Nuclear Chemistry* 2000, 245 (3) 461-467.
- [8] 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.
- [9] Kaplan, D. I., Serne, R. J.; Parker, K.E.; Kutnyakov, I.V. Iodide Sorption to Subsurface Sediments and Illitic Minerals. *Environ. Sci. Technol.* 2000, 34(3); 399-405.
- [10] Laturnus, 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.
- [11] Mishra, S.; Singh, V.; Jain, A.; Verma, K.K. Determination of iodide by derivatization to 4-iodo-N,N-dimethylaniline and gas chromatography mass spectrometry. *Analyst* 2000, 125, 459-464.
- [12] 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.
- [13] 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.

- [14] Ticknor, K.V.; Cho, Y.H. Interaction of iodide and iodate with granitic fracture filling minerals. *J. Radioanal. Nuclear Chem.* 1990, *140*, 75-90.
- [15] Vel Leitner, N.K.; Vessella, J.; Dore, M.; Legube, B., Chlorination and formation of organiodinated compounds: The important role of ammonia. *Environ. Sci. Technol.* 1998, *32*, 1680-1685.
- [16] Warner, J.; Casey, W.; Dahlgreen, R. A., Interactions of I₂(aq) with substituted phenols and humic substances. *Environ. Sci. Technol.* 2000, *34*, 3180-3185.
- [17] Whitehead, D.C. The Sorption of Iodide by Soils as influenced by equilibrium conditions and soil properties. *J. Sci. Food. Agric.* 1973, *24*, 547-556.
- [18] Whitehead, D.C. The distribution and transformations of iodine in the environment. *Env. Internat.* 1984, *10*, 321-339.