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REPORT

**REVIEW OF
METHYL IODIDE BEHAVIOR
IN SYSTEMS CONTAINING
AIRBORNE RADIOIODINE**

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REVIEW OF METHYL IODIDE BEHAVIOR IN SYSTEMS CONTAINING
AIRBORNE RADIOIODINE

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A B S T R A C T

The scientific literature describing research and other data concerned with the formation, behavior and removal of gaseous methyl iodide in a reactor containment system following a fuel melt-down accident is reviewed. The amount of methyl iodide airborne under any set of circumstances is the result of several competing mechanisms of formation and decomposition. The mechanisms are not well defined and extrapolation of data taken under one set of conditions to other situations can seldom be justified. At gas temperatures under 100 C, the airborne methyl iodide is relatively stable and may at times become the predominant iodine species airborne.

Charcoal is the most generally favored adsorbent for removing organic iodides, yet the usual industrial charcoals are found to permit methyl iodide to bleed through with time, particularly under high humidity conditions. Various chemicals have been used to treat the charcoal to enhance its efficiency for removal and retention of methyl iodide. Investigation of impregnating materials continues.

Vapor phase reactions of methyl iodide with other compounds are being studied. The objective of these studies is to find reactions whose iodine-containing products can be collected on filters or scrubbed from containment atmospheres.

Although much research has been devoted in recent years to clarifying the mechanisms of formation and the behavior of methyl iodide there remain many unanswered questions and a good many apparent conflicts in reported observations.

REVIEW OF METHYL IODIDE BEHAVIOR IN SYSTEMS CONTAINING AIRBORNE RADIOIODINE

INTRODUCTION

The control of radioiodine release to the atmosphere is an important factor in siting nuclear reactors. Nuclear fuels produce considerable amounts of radioiodine and, under certain conditions, can release a portion of that inventory. Because iodine taken into the body is concentrated in the thyroid gland, the maximum permissible air concentration of ^{131}I for a 168-hour week is only 3×10^{-9} $\mu\text{c}/\text{cc}$. The maximum permissible body burden of ^{131}I is 0.7 μc .^[1] A considerable number of investigations have been undertaken covering many facets of iodine control. Keilholtz and Barton^[2] have published a comprehensive review of this work.

In the investigation of iodine, the possibility of other than molecular iodine forms has been mentioned. Since these forms could potentially penetrate the existing reactor iodine clean-up systems, investigations to identify these materials were undertaken. This report is an attempt to bring together much of the data available in the release and control of airborne methyl iodide, to aid in the understanding of this problem and reveal areas where additional investigation would be fruitful.

SUMMARY

Identification of Methyl Iodide in Systems Containing Radioiodine

Eggleton and Atkins were the first to identify low molecular alkyl iodides as one of two unreactive fractions found in molecular iodine vapors. Methyl iodide constituted $\sim 85\%$ of the alkyl iodide fraction -- the larger of the two fractions. Subsequent observations indicate that methyl iodide comprises some part of almost all systems containing airborne radioiodine.

Chemical Properties of Methyl Iodide

Iodides are the most reactive of the alkyl halides. Methyl iodide is a colorless liquid, very soluble in organic solvents but of limited solubility in water. Methyl iodide has a density of ~ 2.3 and a boiling point of 42.4°C . It can be formed in solution by substitution of the appropriate alcohol, chloride and bromide. Formation by direct substitution in the paraffin is difficult. Iron can

be a carrier in iodide substitutions. Methyl iodide reacts with alkali metals and their alcoholic hydroxides, silver fluoride, hydrazine and nascent hydrogen to form the paraffin and iodide. Methyl iodide decomposes on the absorption of many forms of energy -- heat, light and radiation.

Formation of Methyl Iodide in Systems Containing Airborne Radioactive Iodine

Several possible mechanisms for the formation of organic iodides have been postulated -- the vapor phase reaction between iodine and organic vapors, the adsorption of iodine vapors by organic materials and subsequent desorption of organic iodides, the direct substitution of more energetic, newly formed iodine atoms into organic vapors. No thorough, systematic study has been reported. The amount of methyl iodide released from overheated reactor fuel elements reported varies from a few thousandths to thirty per cent of the elemental iodine airborne. The amount of methyl iodide formed is affected by the atmosphere -- oxidizing or reducing -- but type of cladding is not significant.

Behavior of Methyl Iodide in Systems Containing Airborne Radioiodine

At temperatures below those required for decomposition, methyl iodide remains airborne for considerable periods and can be the predominant airborne species in time. Only 0.07 per cent of the airborne methyl iodide was found in the condensate after the temperature of a steam-air mixture was reduced from 75° to 30°C in a five hour period and 0.08 per cent deposited on the walls. In dry gases at 100°C, methyl iodide is adsorbed well by charcoal but charcoal loses its effectiveness at room temperature or in the presence of moisture. Chemical additives show promise in increasing the retention of charcoals for methyl iodide. The most promising additives reported to date are: potassium iodide (also appears to lower the ignition temperature of some charcoals), triethylene diamine and iodine (some workers disagree on its effectiveness). Only a small amount of the airborne methyl iodide is removed by its passage through water and the amount absorbed is lost rapidly. An acid-bromate solution at elevated temperature was found to be effective in removing airborne methyl iodide probably due to the vapor phase exchange with "nascent" bromine. Replacement of the active airborne iodide with chlorine or bromine requires high gas concentration of these corrosive materials. Hydrazine appears to react with airborne methyl iodide to form a filterable or soluble aerosol. Aqueous hydrazine sprays appear to be effective in removing airborne mixtures of methyl iodide and elemental iodine. Several means of distinguishing the various chemical forms of airborne iodine have been reported. The most commonly used is the "Maypack" -- a composite type sampler using a membrane filter to collect particles, silver screens

for elemental iodine and HI, charcoal impregnated filter paper for less reactive iodine vapor forms and charcoal granules. The distribution of methyl iodide between the charcoal impregnated filter paper and granules depends upon the contact time between the methyl iodide and charcoal and moisture absorbed upon the charcoal. Gas-liquid chromatography is proving to be a useful analytical and preparative instrument for methyl iodide. Retention times for many column conditions and stationary phases have been reported.

THE DISCOVERY AND IDENTIFICATION OF METHYL IODIDE IN SYSTEMS
CONTAINING AIRBORNE RADIOIODINE

The presence of non-elemental vapor forms of radioactive iodine in air containing predominantly molecular I_2 was suggested as early as 1951. The relatively low removal efficiency of caustic scrubbers for what was presumed to be elemental iodine was an early evidence of the presence of a non-reactive iodine compound.^[3] Morris, et al^[4], deduced the presence of an unidentified form (or range of compounds) from the deposition and sorption behavior of trace quantities of ^{132}I released in the PLUTO containment vessel. The compound(s) were subsequently fractionated into two groups by Eggleton and Atkins^[5], and one fraction was identified as the alkyl iodides, predominantly methyl iodide (~ 85 per cent). The other fraction remains to be identified.

Eggleton and Atkins^[5] fractionated and identified the iodine released upon heating dried, carrier free sodium iodide in a stream of iodine-free air. Elemental iodine released was removed by passing the vapors through a bed of copper mesh, and particles were removed by a high efficiency fiber glass filter. The remaining airborne iodine was either collected in a series of "bubblers" containing 0.02 M sulfuric acid or was condensed, after drying with magnesium perchlorate, in a trap at liquid oxygen temperature. The iodine in the 0.02 M sulfuric acid was found to be of two types: (A) compounds readily soluble in benzene but relatively insoluble in the aqueous solutions used, and (B) compounds equally soluble in benzene and aqueous solutions. Fraction A was found to be composed of the seven low molecular weight alkyl iodides by a combination of gas chromatographic and effusion techniques. Methyl iodide was the predominant compound comprising approximately 85 per cent of this fraction.

Perkins^[6] identified organic iodide as a significant portion of the radioiodine in fallout and plutonium processing plant effluents. In his survey of the chemical forms of airborne radioiodine over the Hanford Project, Perkins separated the elemental iodine and HI by deposition on silver-coated copper mesh, collected the particles on high efficiency filters and trapped the remaining airborne iodine forms in charcoal. The gaseous fraction constituted 10 - 90 per cent of the airborne radioiodine fallout of which only 10 per cent was elemental or HI. Less than 0.3 per cent of the airborne radioiodine released from chemical separation plants was in the particulate form with less than 1/3 of the gaseous radioiodine as elemental or HI.

THE CHEMISTRY OF METHYL IODIDE^[7,8,9]

As a group, the alkyl halides are ethereal, sweet smelling liquids. They are scarcely soluble in water but dissolve readily in organic solvents. The halogen atoms are bonded covalently with the carbon atoms, and therefore do not react instantaneously with silver nitrate as do the metallic halides. Of this group, the iodides are the most reactive.

Methyl iodide is a colorless liquid at room temperature. It has a solubility of 1.8 g/100 g in water and is infinitely soluble in alcohol and ether. Its principal use is as a methylating agent. Methyl iodide forms a crystalline hydrate of the composition $2\text{CH}_3\text{I} \cdot \text{H}_2\text{O}$ (melting point -4°C) and a compound with methyl alcohol, $3\text{CH}_3\text{I} \cdot \text{CH}_3\text{OH}$, which boils at 40°C without decomposition. Some of the pertinent physical properties are listed in Table I.

TABLE I
PHYSICAL PROPERTIES OF METHYL IODIDE

Methyl iodide (iodomethane) CH_3I
 Formula Weight: 141.97 Specific Gravity: 2.27 20/4
 F.P.: 66.45°C B.P.: $42.50/760\text{ mm}$
 Density: 2.3346 0/0 2.25102 20/4
 Heat of comb. (Cp): 194.7 cal.

Temperature $^\circ\text{C}$	Vapor Pressure mm
-55	5
-45.8	10
-35.6	20
-24.2	40
-16.9	60
- 7.0	100
8.0	200
23.5	400
42.4	700

Formation

Methyl iodide can be considered the iodine ester of methyl alcohol corresponding to the metallic iodide. Haloid esters of the alcohols are generally most conveniently prepared by the reaction between the alcohol and halogen acid. In order for the reaction to go to completion, either the water produced must be removed, or there must be a great excess of the halogen acid. Iodine does not directly substitute into the paraffin owing probably to the reversibility of the

reaction, e.g.:

In the presence of substances capable of uniting with or decomposing HI (such as HIO), substitution frequently takes place:

A mixture of methyl or ethyl alcohol, sulfuric acid and alkali iodide react readily in aqueous solutions to yield the corresponding alkyl iodide. Phosphorus iodide (PI_3) also reacts with alcohol to form the alkyl iodide and phosphorus acid. Alkyl iodides can also be formed by the replacement of chlorine or bromine in boiling alcoholic solutions of alkali iodide or by reaction with AlI_3 or CaI_2 :

The higher alkyl iodides can also be formed by the reducing action of hydriodic acid upon polyhydric alcohols. The products are sec.-alkyl iodides when possible:

The unsaturated aliphatic hydrocarbons, olefins and acetylenes will unite with hydrogen halides. Hydriodic acid reacts especially readily.

Reactions

Under appropriate conditions, the alkyl halides will react with certain metals. With the alkali metals and copper, the halogen is removed and the two alkyl groups combine to produce a hydrocarbon. Alcoholic sodium or potassium hydroxide can cause the removal of the halogen acid with production of unsaturated hydrocarbons. In the reaction, the halogen takes with it the hydrogen of the least hydrogenated, adjacent carbon atom. Such decomposition sometimes occurs on the application of heat and is favored by the presence of anhydrous chlorides.

Reduction of alkyl halides to paraffins can be effected by: (a) nascent

hydrogen, (b) molecular hydrogen in the presence of a catalyst (platinum, palladium, nickel, palladium-calcium carbonate), and (c) by metals generally in the presence of acetic acid, alcohol or water. The zinc-copper couple is effective, giving methane or ethane mixed only with a little hydrogen.

With AgF, methyl and ethyl iodides yield the gaseous compounds methyl and ethyl fluoride. Methyl iodide also reacts with hydrazine to produce hydriodic acid and the alkyl hydrazine.^[45] The substituted nitrogen in mono methyl hydrazine is much more reactive than the unsubstituted nitrogens and tends to react to form asymmetrical dimethyl hydrazine.

Iron is an excellent carrier for chlorine, bromine, and iodine in substitutions. The action is due to the formation and decomposition of ferric halides. Alkyl iodides can also be formed by the partial conversion of chlorides and bromines by heating with sodium iodide in acetone or higher ketones in which the sodium salt produced is insoluble. Alkyl iodide is obtained from magnesium alkyl chloride or bromide by the action of iodine:

Stability of Methyl Iodide

Alkyl iodides are chemically the most unstable of the alkyl-halides and decompose upon the absorption of many forms of energy. Methyl iodide is sensitive to light^[7, 10], heat^[11,12,20], and radiation.^[14,15,16,17,18,19] On exposure to light, alkyl iodides soon discolor by the liberation of iodine.^[7] Martin^[10] reports molecular elimination occurs when methyl iodide in the gas phase absorbs 1850 Å radiation with the production of hydrogen and/or hydrogen iodide.

Thermal Stability

Collins, et al,^[11] state methyl iodide thermally decomposes at 300-400 C. Parker and Farreli^[12] report partial decomposition during exchange reactions at 90 - 150 C, using microgram quantities of methyl iodide. The exchange reaction proceeded for 12 hours. Collins, Taylor and Yuille^[13] report from 2.5 to 85 per cent decomposition of methyl iodide during passage through temperature gradient deposition tubes. Methyl iodide in a steam atmosphere was passed through a 3 mm diameter silica tube at the rate of 250 cm³/min. The tube was wrapped in a 2.5 cm OD spiral. Linear temperature gradient through the tube averaged ~ 1.5 °C/cm. With the cool end of the tube at 120 C and a 5 second contact above 400 C, the decomposition of methyl iodide was:

Maximum Temperature of Tube, °C	500	600	700	800
Per Cent Decomposition of CH ₃ I	2.5	35	67	85

Collins, et al,^[11] investigated various methods of methyl iodide thermal decomposition as potential removal processes. Methyl iodide was not effectively decomposed (< 0.1 per cent) on a heated bed of silver plated copper mesh, presumably because of the limited residence time (~ 0.2 sec). A 1" OD $\times$ 4" deep bed of alumina at 300 C was ~ 80 per cent effective. The thermal decomposition of methyl iodide could be catalyzed by Hopcalite (manganese dioxide and copper oxide). Using a stream temperature at 100 C and the bed temperature at 300 C the following results shown in Table II were obtained.

TABLE II

DECOMPOSITION OF METHYL IODIDE ON HEATED HOPCALITE
CATALYST

(Linear Velocity Gas, 140 ft/min)			
Wt. CH ₃ I Loaded mg	Gas Composition	Duration Run (hours)	% CH ₃ I Decomp.
7.5	95% CO ₂ + 5% CO	1	40
12		1	75
54		1	60
64		3-1/3	95
170		2	30
10	47% CO ₂ + 47% Air + 6% CO	3-1/2	99.9
720		1	99.8

Unfortunately, the process is susceptible to carbon monoxide reduction, moisture, and is slow at room temperature.

Collins and Hillary^[20] report that > 99% of the methyl iodide heated to 700 C was decomposed. A mixture of Zircaloy powder and 25 g of uranium dioxide containing 0.1 mg CH₃I were heated to that temperature in a silica capsule and released into flowing steam. The steam leaving the silica tube was cooled to ~ 200 C by a spray of hot water. The remaining moisture was condensed and the gases passed through a water bubbler and demister before collection of the active iodine in a "Maypack". Only 0.9 per cent of the airborne iodine was found to be organic iodides.

Radiation Stability

Several authors have indicated the radiation instability of methyl iodide. Croft and Hanrahan^[17] measured the I_2 produced by the gamma radiation of a methyl iodide-cyclohexane mixture. More recently workers at Brookhaven National Laboratory^[18,19] radiated methyl iodide in air at a dose rate of 3.48×10^5 rads/hr. An average half life of 26 minutes was observed with ~ 90 per cent methyl iodide decomposition after an absorption of $\sim 5.5 \times 10^5$ rads. Methyl iodide concentrations ranging from 1.56×10^{-8} to 2.42×10^{-7} M in air were used.

Exchange Reactions

McKay^[21] investigated the exchange of sodium iodide and alkyl iodides in alcohol and acetone. He concluded that the exchange does not take place in the absence of a dissociating solvent - carbon tetrachloride, carbon disulfide and ether were not effective. Methyl iodide is the only alkyl iodide exchanging at room temperature. At 100 C, the methyl iodide-iodine exchange is complete in <15 minutes. Ethyl, propyl, isopropyl, butyl and isoamyl all exchange at 100 C and are nearly complete in 15 minutes. Organic separation is effected by the addition of water.

Diffey, Rumary, Smith and Stinchcombe^[22] used the

reaction in 10 per cent water - 90 per cent n-propanol to produce up to a few tenths of milligram of tagged methyl iodide. Reaction time was 1/2 hour. The methyl iodide was extracted in benzene and water washed prior to purification in a gas chromatograph.

Parker and Farelli^[12] studied the production of high specific activity methyl iodide by exchange with sodium iodide in 95 per cent alcohol. High specific activity, carrier free, sodium iodide was contacted with microgram quantities of methyl iodide. Phase separation was effected by the addition of an equal volume of water and the methyl iodide extracted into n-hexane. The methyl iodide was separated by sparging the mixture with air or helium and passing the vapors into a cold trap at -78 C. Residual water and n-hexane are removed here and the methyl iodide condensed at -210 C (liquid nitrogen). Gas chromatography confirmed 99.9 per cent purity. Largest preparation to date has been 250 mc $^{131}I + 6$ mg CH_3I .

At a concentration of 0.25 mg methyl iodide per ml of alcohol 50 per cent exchange was effected in 12 hours at room temperature. At $\frac{1}{10}$ this concentration (0.025 mg $\text{CH}_3\text{I}/\text{cc}$ alcohol) under the same conditions, 3 days were required for 50 per cent exchange. Increasing the temperature to 95 and 150 C, increased the exchange rate but some decomposition was noted.

Atkins and Arkell^[24] conducted a thorough study of techniques for the preparation of tagged methyl iodide. They found the methyl iodide-sodium iodide exchange most suitable for their purposes. Aliquots of methyl iodide and sodium iodide at the required concentration were contacted at various temperatures. Periodic samples were removed to determine the rate of exchange and per cent exchanged compared to time for each of four methyl iodide concentrations: 10^{-1} , 10^{-2} , 10^{-3} and 10^{-4}M . Exchange half periods of 1 second using 0.1 M NaI and CH_3I at 100 C to hundreds of hours for 10^{-4}M NaI + CH_3I at 20 C have been found. Changes of pH between 4 and 10 do not affect exchange.

THE FORMATION OF METHYL IODIDE IN SYSTEMS CONTAINING AIRBORNE RADIOIODINE

Mechanism of Formation

The mechanisms responsible for the presence of methyl iodide in nuclear systems are not clearly defined. Different mechanisms appear operative at different phases in reactor accidents. Any methyl iodide present in or near the fuel during meltdown will be destroyed by the heat and radiation (see previous section). The radiation alone in highly irradiated fuels may be sufficiently high to preclude the existence in the fuel of any significant amounts.

The formation of methyl iodide by an active iodine vapor phase reaction has not been clearly demonstrated. Several have shown an increase of methyl iodide or "penetrating" iodine in the presence of organic vapor^[8,9] and whether the reaction is a vapor phase reaction or a deposition of an organic film with iodine absorption -- methyl iodide desorption has not been conclusively demonstrated. Methyl iodide formation could not be induced by radiation alone in a mixture of iodine vapor and methane.^[8]

Methyl iodide can be formed, however, by the reaction between newly formed iodine atoms and methane^[28] and by the reaction of absorbed or deposited iodine and organic materials upon surfaces.^[20] Morris, et al^[4], in explaining the varying behavior of iodine in a reactor shell suggested other iodine forms are

produced from trace impurities in the air. Browning and Adams^[23] contacted iodine and organic vapor for short lengths of time at room temperature with no detectable change in iodine forms. Conversion of 5 - 20 per cent of the elemental iodine vapor were obtained by increasing contact time.^[12]

Browning, et al^[12] contacted two types of organic vapors for 15 and 60 minute periods with iodine - dioctyl phthalate and the vapor from a mixture of organic materials commonly found in reactor containment vessels. Temperatures of 24 and 90 C were used. No difference in the iodine distribution was observed in composite deposition tubes before and after contact with DOP vapor using the organic iodide fraction from thermal decomposition of sodium iodide-dichromate mixture. When DOP and molecular iodine vapor were contacted ~ 5 to 15 per cent conversion of the elemental iodine to other forms was detected. The conversion of elemental iodine by the organic reactor materials appeared to be independent of temperature and aging time. A 5 - 20 per cent conversion of elemental iodine was noted in contacts with this material with 1 - 5 per cent in a form penetrating four successive charcoal beds. Some conversion of organic iodides to elemental iodine was observed in contact with these organic vapors but may be due to some thermal decomposition.

Browning, Adams and Attrill^[23] detected traces of methyl iodide in iodine vapors in a hydrogen-steam atmosphere at 100 C on passing through a bed of oxidized steel wool. The effectiveness of iron as a carrier in halide substitutions in hydrocarbons by the formation and decomposition of ferric halides was noted in a previous section.

Parker, Martin, Creek and Barton^[23] reported an increase in the "penetrating form" of iodine in the presence of a mixture of airborne elemental iodine and the organic gases generated by the hydrolysis of uranium carbide. The composition of these organic gases has been investigated by Bradley and Ferris^[26,27] and may be representative of the gases which could be generated during fuel melt down accidents for reactors using this fuel. The gases contain a high percentage of methane as well as hydrogen and more than 30 additional hydrocarbons.

A mixture of air and steam at 30 psig was placed into a tank along with 0.5 liter of the hydrocarbon mixture when required. The iodine sample was then vaporized by means of a gas torch and the iodine vapor displaced into the tank by a stream of air. A concentration of ~ 2 mg/m³ iodine was used in all experiments. The hydrocarbon gases were heated to a variable degree during the vaporization of iodine and in one case where UO₂ was melted, more intensive heating

occurred. A fan located in the tank was operated briefly to obtain mixing. After a four hour retention period, the tank was depressurized into a "Maypack" arrangement modified to allow sampling between stages. The remaining iodine was successively displaced into similar sampling trains by an argon and an air sweep.

In air, only 0.3 per cent of the iodine released was in the "penetrating" form. In an air-steam atmosphere, the percentage of "penetrating iodine" increased to 0.5 to 1.2 per cent, and the presence of acetone and solid carbon dioxide did not produce a significant effect. The presence of the hydrocarbon mixture produced an increase in the amount of "penetrating iodine" (2.5 to 21 per cent). There does not appear to be a significant desorption of iodine during the air sweep -- a potential methyl iodide formation process. Unfortunately, distribution of iodine forms during each displacement step are not reported.

Collins and Hillary^[20] found as much as 10 per cent of the iodine generated during their high activity tests penetrating the absolute filter-charcoal bed trapping system. Methyl iodide was the major portion of this penetrating fraction and was shown to be desorbing from an organic based paint used to protect the reactor vessel during construction.

In the high activity tests, 800 grams of irradiated, stainless steel clad, UO₂ fuel elements were held in a graphite boat and heated to ~ 2000 C in a carbon monoxide-dioxide atmosphere. Part of the airborne iodine was directly introduced into the trapping system during the initial 'blowdown' (depressurization). The remainder of the material was held in a steel containment vessel while heating of the fuel continued. After an hour of additional heating, a second 'blowdown' to the trapping system was performed. The material in the containment vessel was alternately circulated through the trapping system and pressure vessel presenting a mixture of "fresh" and "aged" gases to the trapping system. Finally, the pressure vessel containing the fuel was isolated from the system and gases swept through the trapping system for 20 hours.

From the results shown in Table III it is apparent that the majority of iodine arrived at the trapping system during the final phase of operation. The arrival at this time was attributed to desorption from the vessel walls. The fraction penetrating the charcoal was analyzed by gas chromatography and found to be composed of four components. Methyl and ethyl iodide were identified.

TABLE IIIIODINE ENTERING & LEAVING TRAP DURING HIGH ACTIVITY TEST(Fuel contained 200 curies of ^{131}I)

<u>Operation</u>	<u>Iodine Entering mc</u>	<u>Iodine Leaving mc</u>
Blowdown	50	1
Circulation	1000	100
Airsweep	8000	900

Methyl iodide was found to be desorbing from painted surfaces which had absorbed molecular iodine during the run. A 12' length of pipe internally painted with an organic-based graphite paint used to protect the containment vessel and baked at 400 C, was loaded with molecular iodine in air at room temperature. Air and carbon dioxide at various temperatures were passed through the pipe and desorption monitored by "Maypacks (See Table IV). At room temperatures, iodine was desorbed as elemental iodine but at elevated temperatures a substantial portion appeared as organic iodides. At 250 C, the elution was ~ 1/2 per cent per hour and confirmed as methyl iodide by gas chromatograph but, at 300 - 400 C, the iodine desorbs from the surface predominantly as molecular iodine.

TABLE IV

DISTRIBUTION OF ACTIVE IODINE ELUTED FROM 12' PIPE INTERNALLY
COATED WITH ORGANIC BASED PAINT

<u>Percentage of Loaded Iodine on Maypack Components</u>				
	<u>Copper</u>	<u>Millipore</u>	<u>Charcoal</u>	<u>Charcoal</u>
	<u>Gauze</u>	<u>Filter</u>	<u>Paper</u>	<u>Pack</u>
<u>(2.8 mg Iodine loaded in air, eluted with 5.5 CO₂/3.5 CO/l air)</u>				
During loading	35	0.2	26	0.1
4 hr @ 20 C	1.0	0.06	0.1	0.003
1/2 hr @ 290 C	0.2	0.6	0.2	0.4
<u>(4.5 mg Iodine loaded, eluted with CO₂)</u>				
During loading	50	0.01	0.03	0.02
1 hr @ 20 C	0.1	0.006	0.005	0.0003
1 hr @ 50 C	0.4	0.05	0.2	0.0004
1 hr @ 100 C	0.3	0.02	0.1	0.1
1 hr @ 150 C	0.01	0.05	0.01	0.008
1 hr @ 250 C	0.01	0.08	0.04	0.3
1 hr @ 250 C (10% air)	0.01	0.1	0.2	0.3

Parker, Martin, Creek and Barton^[23] did not succeed in producing methyl iodide by gamma irradiation of a methane-iodine mixture irradiated at 200 C in a 10,000 curie cobalt irradiation facility.

Schroth and Adloff^[28] found ~ 60 per cent of the iodine atoms produced by the electron capture of ^{125}Xe formed methyl iodide in the presence of methane. This may indicate the reactivity of newly formed atoms. Wolfgang^[29] in his review of "hot-atom" chemistry discusses this increased reactivity of newly formed atoms -- as great as 10^3 more reactive than the same material at thermal energy.

Collins, McIntosh, Taylor & Yuille^[30] identified alkyl iodides in the iodine released from irradiated AGR UO_2 heated to 1600 C. Methyl iodide constituted 1 - 10 per cent of the total iodine inventory of the fuel. AGR fuel elements irradiated to 2000 Mwd/T (containing ~ 4000 curies total fission products) were heated in a steel pressure vessel. The fission product gases were released to a steel reactor container with a trapping system. Laboratory scale tests were performed on miniature fuel elements (containing up to 100 Ci of activity) which were inductively heated to above 1500 C in a glass apparatus at atmospheric pressure. Distributions in both experiments were determined by "Maypacks".

The form of iodine released depended upon gas composition and amount of iodine released. In mixtures of carbon monoxide and dioxide virtually no iodine as elemental vapor occurs in the atmosphere upon release from fuel. The majority of activity is attached to particles. The remainder is in a form which penetrates charcoal. The amount depends upon the iodine concentration: 25 per cent at iodine concentrations of 0.01 to 10 $\mu\text{g}/\text{m}^3$, and 10 per cent at 1 mg/m^3 . The greatest amount of methyl iodide (20 per cent) was found in one run in which methane was added but small amounts of methyl iodide were found in two other runs which also had methane additions.

The only iodine vapor compounds to reach the coolant outlet from intentionally defected fuel pencils in a gas-cooled reactor were organic iodides. Approximately 0.4 per cent of the total iodine inventory was released during the test.

Collins and Hillary found 0.01 to 0.1 of the iodine inventory of Zircaloy clad, UO_2 irradiated up to 10 Mwd/T and 0.04 to 3 per cent of the inventory of the same fuel irradiated to ~ 100 Mwd/T heated to less than the clad melting point in steam as organic iodides. Three of the elements in each group showed some UO_2 melting. An additional test using tracer iodine in the presence of UO_2 and Zircaloy at 700 C in steam produced 1.7 per cent organic iodides and agrees with

TABLE V

METHYL IODIDE RELEASED FROM VARIOUS SOURCES

REF.	SOURCE	TEMP.	ATMOSPHERE DURING GENERATION	TEMP.	ATMOSPHERE DURING CONTAINMENT	METHYL IODIDE FRACTION	REMARKS
	Palladium iodide	Decomp.	Vacuum			< 0.077% (of released I)	
23	¹³¹ I tracer as elemental iodine	Gas torch	Flowing air	400 C	30 psia filtered air	.3%	In containment vessel 4 hrs.
					Air + steam	.5%	In containment vessel 4 hrs.
					Air + steam	1.2%	In containment vessel 18 hrs.
					Air + steam	1.6%	In containment vessel 5 hrs., includes undetermined amount of acetone + CO ₂
					Air + steam + hydroc.	2.5%	In containment vessel 5 hrs.
					Air + steam + hydroc.	7. %	In containment vessel 5 hrs.
					Air + steam + hydroc.	21. %	In containment vessel 9 hrs. UO ₂ melted.
5	Dried NaI (¹³¹ I tracer)	400 C	Air through -68C charcoal	Ambient	Air	1-2 %	Also chemical separation and effusion.
6	Fallout Hanford '62 Purex Stack Gas			Ambient	Environmental air	45 % 67 %	
23	Sodium Iodide + K ₂ Cr ₂ O ₇	425 C	60% RH Air	Ambient		< 2.9%	
20	2.8 mg I deposited in a 12' long pipe.	Ambient	Air	Ambient	Air	Loading 0.1	12 foot pipe painted with organic based graphite. Baked at 400 C.
				20 C		4 hr 0.003	
				290 C	5.5 CO ₂ :3.5 CO: 1 air	4 hr 0.4	
				Ambient	Air	Loading 0.02	
	4.3 mg I ₂ deposited in a 12' long pipe.	Ambient	Air	20 C		1 hr 0.0003	12 foot pipe painted with organic based graphite. Baked at 400 C.
				50 C		1 hr 0.0004	
				100 C	CO ₂	1 hr 0.1	
				150 C		1 hr 0.08	
				250 C		1 hr 0.03	
				250 C	Air	1 hr 0.33	
	0.1 mg Elemental iodine	700 C	Flowing steam	700 C		% total I released 0.35	In silica capsule, steam cooled by condensation, hot water spray + water bubbler
				200 C	Air + steam		
	0.1 mg methyl iodide					As organic iodide 0.9	
28	¹²⁵ Xe + methane gas					~60% atoms formed	

TABLE VI

METHYL IODIDE RELEASE FROM UO_2 STAINLESS STEEL CLAD FUEL

REF.	DURING RELEASE			CONTAINMENT		METHYL IODIDE FRACTION, PER CENT		COMMENTS			
	TEMP °C	GAS COMPOSITION	IRRADIATION	TEMP. °C	ATMOSPHERE						
13	1700 to 1800	CO + 5% CO	Not given	Not given	Not given	Before Filtration	10 to 12 %*	* of material airborne.			
		50% CO + 50% Air				After Filtration	57 to 72 %*				
		Carbon Dioxide + Carbon Monoxide				Before Filtration	2 to 2.5%*				
						After Filtration	6 to 7.5%*				
						Per cent Total I	0.2 to 1 %*				
	Per cent Total I		0.5 to 0.7%*								
	>1800	CO ₂ + CO	2000 Mwd/T	400	CO ₂ + CO		2		(0.9% I inventory CH ₃ I with 0.5% produced in pipes.)		
						Air + CO ₂			10	0.025% reached charcoal bed.	
						Air + CO ₂			11.2	In graphite crucible in steel pressure vessel.	
										0.5% total I reached charcoal.	
								4.0% total I reached charcoal.			
Some UO ₂ melting	Steam	100 Mwd/T		% of total I released as organic iodide	0.06	Per cent total I released: 27%					
23		Air + Steam	7000 Mwd/T		Air + Steam		0.3				
23	2850	Helium	Not given	>1000	Per cent total I ₂ in second charcoal filter preceded by an absolute filter and condenser		0.018	Linear Gas Velocity fpm	350	Per Cent total I ₂ in Charcoal Trap	0.50
		Helium-Water (Dewpoint 23 C)					0.0076		60		0.36
		Air-Water (Dewpoint 23 C)					0.0011		40		0.07
		Air					0.0023 + 0.11		6		0.04
		Air 87% Steam					0.045 + 0.0001		60		0.0001
		12% Helium, 1% Hydrogen					0.45 + 0.0001		60		7.1
		87% Steam					0.0013 + 0.0001		60		15
		Air-Water (Dewpoint 23 C)									
12	Not given	Air	Simulated	Not given	Air + Steam	Percent total I inv. in "penetrating form"	 1.3				

TABLE VII
METHYL IODIDE RELEASE FROM UO_2 ZIRCALOY CLAD FUEL

REF.	DURING RELEASE		CONTAINMENT		METHYL IODIDE FRACTION		COMMENTS	
	TEMPERATURE	GAS COMPOSITION	IRRADIATION	TEMP. - ATMOSPHERE	PER CENT	PER CENT		
13	>2000 C	Steam	Not given	Not given	In dry steam In water pool After cond. & filtration Percentage total I Percentage total I	6.5 75 98 0.3 3.5		
20	Melting point Zircaloy can.	0.5 MeV/T	0.5 "		0.02	6.2	25 g UO ₂ + Zircaloy + 0.1 mg I in silica capsule. Steam cooled by cond. partial evap. water spray + water bubbler.	
			0.5 "		0.01	6.8		
			1.0 "		0.01	2.4		
			2.0 "		0.02	2.4		
			5.0 "		0.001	2.9		
	Some UO ₂ melting.		1.0 "		0.1	13.7		
			2.0 "		0.003	15.4		
			7.0 "		0.03	40		
			100.0 "		0.04	28		
					0.05	35		
1000C	Air	Tracer	700 - 200 C	Steam + Air	Percentage of total Iodine re- leased as organic iodides.	34		
					Percentage of total Iodine re- leased as organic iodides.	9		
					Percentage of total Iodine re- leased as organic iodides.	60		
					Percentage of total Iodine re- leased as organic iodides.			
					Percentage of total Iodine re- leased as organic iodides.			
12	Near melting point.	Air	Simulated	Not given	Per cent total I Inventory in "Pen- etration Form"	0.7 0.8		
30	1400 C	50% Air + 50% CO ₂	1.5 "		6	7	Percentage of total Iodine Inventory reaching charcoal beds. Percentage of total Iodine Inventory reaching charcoal beds.	
			1.5 "		6	7		
			1.5 "		6	9		
			1.5 "		4	6		
			1.5 "		6	4		
			1.5 "		4	4		
			1.5 "		0.1	4		
	1700 C to 1800 C	50% Air + 50% CO ₂	50 "		2	2		
			100 "		0.25	0.7		
			150 "		0.5	2.7		
			150 "		1.2	2		
			2000 "		1	1		
			50% CO ₂ , 35% CO, 10% Air, 1% H ₂ , 0.02% CH ₄	150 "		0.2 - 1		1
			CO ₂ + CO	150 "		0.5 - 2		0.7
	2000 C	CO ₂ + CO	150 "		4 - 5	--		
1700 C to 1800 C	CO ₂ + CO + 1000 ppm CH ₄	150 "		1 - 20	20			
2000 C	CO ₂ + CO	150 "		10	10			
1700 C to 1800 C	50% Air + 50% CO ₂	100 "		0.7 - 2	12			
	CO ₂ + 5% CH ₄	150 "		0.1 - 0.7	0.6			

TABLE VIII

[12]

RADIOIODINE DISTRIBUTION IN THE CONTAINMENT MOCK-UP FACILITY AT ORNL

Source	Tracer	UO ₂ 7000 Mwd/T	Tracer			Tracer			Simulated High Burnup UO ₂ Fuel		
			UO ₂ melted			(1)					
Gas Composition	Air		Air+Steam+Organics			Air + Steam					
Per cent Iodine Inventory Released		90.6*							100.*	86.8*	98.3*
Per cent Iodine Retained in Containment Vessel	79.6	25.2*	68.6	82.6	61.8	95.7	92.2	72.2	89.7*	63.2*	79.7*
On Walls	79.6	25.2*	20.9	24.4	18.3	60.8	38.2	19.3	33.7*	13.2*	8.1*
In Condensate			47.3	58.2	43.5	34.9	54.0	52.9	56.0*	50.0*	71.6*
Per cent Iodine Inventory penetrating 3/4" charcoal	0.01	0.08*	0.17	0.8	0.5	0.08	0.3	3.8	0.02*	0.02*	0.02*
Per cent Iodine Inventory in "Penetrating Form"	0.3	0.3*	2.5	7.	21.	0.5	1.2	1.6	1.3*	0.7*	0.8*

(1) CO₂ + acetone in capsule.

* Per cent of total iodine inventory.

Browning's value for "penetrating" iodine in air-steam mixtures.^[12]

Collins, Taylor and Yuille^[30] report 10 per cent organic iodides of the airborne iodine from stainless steel clad UO_2 fuel elements heated to > 1400 C in carbon dioxide with 5 per cent monoxide and only 2 per cent in carbon dioxide with 50% air. Using Zircaloy clad elements heated to $>> 2000$ C in dry steam, these workers found organic iodide releases were 6.5 per cent of the airborne iodide.

Parker, Lorenz and Wilhelm^[23] found 2.5 per cent of the airborne iodine from lightly irradiated stainless steel clad, UO_2 pellets heated to 2800 C in 1000 psi steam in a "penetrating form". Only 10 per cent of the iodine inventory was released during the experiment and 2.5 per cent transferred to the containment vessel.

Haller^[31] found ~ 40 per cent of chemical plant gaseous effluent activity as methyl iodide.

Data relating to the formation of methyl iodide in systems in which radioactive iodine is released are consolidated in Tables V - VIII.

THE BEHAVIOR OF METHYL IODIDE IN NUCLEAR SYSTEMS

A considerable amount of data is currently available on the behavior of methyl iodide in nuclear systems. Many authors reported the distribution of airborne iodine as a function of time after release under a variety of circumstances.^{[20][32][33][34][35]} Data in dry and condensing atmospheres indicate that methyl iodide is very slowly removed by normal mechanisms at temperatures under 100 C. At atmosphere temperature above 100 C thermal decomposition increases the removal rates.^[20]

In dry atmosphere at ~ 100 C, most charcoals show a fair retention for methyl iodide^[3] and some appear to retain their capacity at room temperature.^[11] As the humidity of the atmosphere increases, the charcoal absorbs increasing amounts of moisture interfering with its absorptive capacity.^{[12][20][23][38]} (Other materials can apparently cause the same interference.^[37]) Various organic and inorganic impregnants have been used to increase the capacity with some success.^{[3][36][39][40]} The usefulness of the impregnants is limited so far by the volatilization of some promising organic impregnants at use-temperatures and the lowering of the charcoal ignition temperature by some inorganics.^[38] Evaluation and testing is continuing.

Aqueous scrubbing solutions or sprays would not be affected by moisture but poor partition coefficients and the mass transfer resistance of methyl iodide in water almost requires a vapor phase reaction to convert the methyl iodide to a water soluble species.^[38] Some aqueous scrubbing solutions have been tested with only acid-bromate showing the required efficiency.^{[38][41]} Two studies are currently in process to evaluate the use of hydrazine in scrubbing systems for methyl iodide control.^{[41][42]}

Some information has also been reported on the behavior of methyl iodide on desiccants used for moisture removal,^{[23][39]} and studies to evaluate the use of promising chemical additives on solid support material for methyl iodide control is being contemplated.^[42]

The Distribution of Airborne Iodine

Megaw and May^[32] studied the airborne iodine distribution of tagged iodine released in air at ambient temperatures in the 7000 m³ PLUTO containment vessel. Activity distribution as a function of time after release are shown in Figure 1. Operating conditions during these runs were:

TABLE IX

OPERATING CONDITIONS DURING EXPERIMENTAL RELEASES
IN PLUTO CONTAINMENT VESSEL

Run Number	Iodine Released		Calculated Conc. Added		Max. Measured Concentration dpm/m ³
	mg ¹²⁷ I	mc ¹³² I	g/m ³	dpm/m ³	
A	0.09	28.2	0.013	8.9 × 10 ⁶	1.45 × 10 ⁶
B	0.95	22.9	0.14	7.2 × 10 ⁶	1.75 × 10 ⁶
D	99	20.1	14.1	6.4 × 10 ⁶	3.0 × 10 ⁶

Sample distributions were determined by "Maypack". The authors concluded the physical and chemical nature of iodine released inside the containment shell changes with time after release. The resulting iodine deposits out much less readily. Croft and Iles^[33] noted similar behavior using a narrower concentration range (0.3 to 0.8 µg/m³) under similar experimental conditions in the Zenith experiments (see Figure 2). Croft, Iles and Davis^[34] report similar stability in wet and dry atmospheres of the fraction trapped in the charcoal

FIGURE 1
 Variations in Airborne Iodine-132 Concentration with Time in Pluto Containment Vessel
 Megaw and May³²

granule section of a "Maypack". Molecular iodine was released into a 30 m³ room at ambient temperature. Airborne iodine distributions are shown in Figures 3 and 3b, and operating conditions are listed below.

TABLE X
EXPERIMENTAL CONDITION DURING ROOM RELEASE
OF MOLECULAR IODINE

<u>Run Number</u>	<u>Released</u>			<u>Effective Deposition Velocity, cm/sec*</u>
	<u>Moisture</u>	<u>Grams</u>	<u>mg/m³</u>	
1	dry	3.1	113	4.0×10^{-3}
2	dry	6.5	237	3.1×10^{-3}
3	wet	5.2	190	3.7×10^{-3}

* $\lambda = vA/V$ where λ = experimental exponential decay constant
 A = effective deposition surface area
 V = free volume container
 v = effective deposition velocity.

Megaw and Bridge's^[35] study of the distribution of airborne iodine generated from tagged iodine crystals held at 40 C and trace-irradiated uranium wire in air and carbon dioxide also indicate methyl iodide stability in glass. The iodine vapors were aged in a series of clean glass vessels. Samples were taken at various points using Maypacks at a sampling rate of 200 cc/min. Distributions found are shown in Figures 4a, 4b, 4c and 4d and experiment conditions listed in Table XI.

TABLE XI
EXPERIMENTS ON GAS-PHASE REACTIONS OF IODINE

<u>Figure</u>	<u>Source</u>	<u>Iodine Activity</u>	<u>Vol. Conc. of ¹²⁷I</u>	<u>Carrier Gas</u>
4(a)	Irradiated U	¹³¹ I	Carrier free	Air, unfiltered
4(b)	Irradiated U	¹³¹ I	Carrier free	Air, filtered
4(c)	Irradiated U	¹³¹ I	Carrier free	Air, filtered, dried
4(d)	Cold trap + Irradiated U	¹³² I + ¹³¹ I	0.5 mg/m ³	CO ₂ , filtered, dried

FIGURE 2
Variations in Airborne
Iodine-132 Concentration with
Time in Zenith Containment
Vessel
Croft and Dea³³

FIGURE 3
Variations in Airborne Iodine Concentration with Time in 30 m³ Room
Croft, Dea and Davis³⁴

Iodine from irradiated uranium, unfiltered air.

Iodine from irradiated uranium, filtered air.

Iodine from irradiated uranium, filtered, dried and charcoal-trap treated air.

Iodine from irradiated uranium (continuous line) and from cold trap (broken line).

FIGURE 4

Variations in Airborne Iodine Concentration with Time in Glass Apparatus
Megaw and Bridges³⁵

Collins and Hillary^[20] have studied the gasborne stability of iodine at elevated temperatures in various carbon dioxide atmospheres in a 75 ft³ steel pressure vessel. Vapors from iodine inductively heated from 750 to 1000 C in graphite or stainless steel or methyl iodide were held at various temperatures and periodically sampled. Results are listed in Table XII. Methyl iodide stability decreased from 100 C where it is relatively stable to 300 C due to thermal decomposition. Other factors may influence the decomposition at higher temperatures -- methyl iodide disappeared 30 times more rapidly at 390 C than at 370 C.

Browning, Martin and Creek^[12] report > 99.8 per cent of the methyl iodide released in a condensing system remained airborne. Unirradiated Zircaloy clad, uranium dioxide was melted in a steam-helium atmosphere while 400 µg of tagged methyl iodide was directly added to the tank containing 15 psig helium - 15 psig steam at 120 C. At the end of five hours, the temperature of the vessel was approximately 30 C and the gases were released to charcoal traps. Material still airborne in the tank was removed by an argon sweep followed by an air sweep. Only 0.08 per cent of the iodine activity was retained on the walls, 0.07 per cent found in the condensate, of which 85 per cent was still in the organic form and 99.8 per cent remained airborne. Hilliard and McCormack^[36] have also found methyl iodide relatively stable in condensing air-steam systems. (See Figure 5).

The Retention of Methyl Iodide by Charcoal

Charcoal is a widely used radioiodine clean-up media in reactor effluent gas treatment systems but, under certain conditions, has shown a poor efficiency for methyl iodide. Morris, Diffey, Nicholls and Rumary^[4] found the charcoal beds tested for radioiodine removal of iodine released in the PLUTO containment shell in dry air was 99 per cent efficient for the non-elemental forms produced. The iodine vapor released was generated by the thermal decomposition of a mixture of solid potassium iodide and dichromate and was sampled in ambient air at ambient temperature by "Maypacks". The combination of a high efficiency filter + charcoal was much superior to the other two systems tested (filter + caustic scrubber or copper mesh) and had a dF ranging from 2030 to 90.5. Chamberlain, Eggleton, Megaw and Morris^[3] concluded from tests run at 20 and 250 C in dry air and carbon dioxide that the organic iodide are well sorbed by charcoal but not removed by silver, copper or alkaline materials.

McCormack^[37] detected serious loss of charcoal absorptive capacity when the surface of charcoal was coated with dust and organic vapor. In his investigation

TABLE XII
STABILITY OF GAS BORNE METHYL IODIDE IN VARIOUS CO₂ ATMOSPHERES.
75 ft³ STEEL PRESSURE VESSEL

CORE	VESSEL TEMP. °C	GAS COMPOSITION	CORE TEMP. °C	TOTAL I CONC. mg/m ³	PER CENT METHYL IODIDE ⁽¹⁾ AT TIME AFTER RELEASE - IN MINUTES											
					0	50	100	150	200	250	300	350	400	450	500	
Graphite		50 v/o CO ₂ + 50 v/o CO	1040	2 × 10 ⁻⁴	0.0006	0.0002 in 30 min.										
			1000	0.25	0.2	0.09	0.05	0.02	in 120 min.							
			1000	7.1	0.1	0.008	0.01+	0.0002								
			900	5.5	0.007	air addn.	0.025	air add	0.015	two air addn.		0.2				
St. Stl. Fuel Can	390	(13)	550	~6	0.095			0.015	0.006 ⁽³⁾		0.03					
Thin St. Stl. Susceptor			(14)	750	6	0.2			0.08	0.06		0.06				
			(15)	~100	31 ⁽²⁾	2	0.02		air add.		0.15	0.02				
			(16)	~100	16 ⁽²⁾	10.5	(4)	(5)	10.5	(6)	8.5	(7)	4	(8)	2.5 ⁽⁹⁾	2.6 ⁽¹⁰⁾
Thick St. Stl. Susceptor	100 to 300	(17)	~100	1.2 ⁽²⁾	7.0	5.5		(12)	4	3		Air Addn.		0.9	0.8	

- (1) Per cent of initial iodine addition reaching charcoal granules of Maypack.
- (2) Added as methyl iodide.
- (3) Core reheated and air added.
- (4) 50 minutes at 100 C.
- (5) 50 minutes at 200 C.
- (6) 100 minutes at 200 C.
- (7) 100 minutes from 200 to 300 C.
- (8) 100 minutes at 300 C.
- (9) 50 minutes at 300 C + air added.
- (10) 50 minutes at 300 C.
- (11) 100 minutes at 300 C.
- (12) Temperature raised to 310 C.
- (13) 63 to 66 v/o CO₂ + 37 to 34 v/o CO + 0.01 v/o O₂.
- (14) CO₂ + 1.4 v/o CO + 1.2 to 9 v/o O₂.
- (15) CO₂ + 2.6 to 2.0 v/o CO + 0 to 3.3 v/o O₂.
- (16) CO₂ + 2.6 to 2.4 v/o CO + 0 to 2.4 v/o O₂.
- (17) CO₂ + 3.2 to 2.8 v/o CO + <0.8 to 1.8 v/o O₂.

FIGURE 5

Distribution of Airborne Iodine in Condensing Air Steam Atmosphere
Hilliard and McCormack³⁶

of efficiency of large charcoal beds used on the Hanford project he found losses in both the beds used in the Radiometallurgical Laboratory Building and the Redox Chemical Processing Plant. The charcoal from the Radiometallurgical Laboratory was dull and dusty and was only 58 per cent efficient. Absorptive capacity of the charcoal could be restored by removal of the old surface or creation of new surfaces, as indicated in Table XIII.

TABLE XIII

RADIOMETALLURGY BUILDING CHARCOAL REMOVAL EFFICIENCY

<u>Charcoal</u>	<u>Per Cent Iodine * Retained</u>	<u>Remarks</u>
	58.	As received.
Radiomet	57.	7/8" diameter, 100 fpm.
Charcoal	94.	Abraded and washed.
	99.7	Crushed to + 14-20 mesh.
New	99.9	

*Elemental iodine used in these experiments.

Collins and Hillary^[20] found as much as 10 per cent of the iodine arriving at the charcoal trapping system (0.5 per cent of the total iodine inventory of the fuel) penetrated. The iodine vapors were generated by heating irradiated, Zircaloy clad, uranium dioxide to >1800 C in a steel pressure vessel containing a mixture of carbon monoxide-dioxide gas. Greater than 90 per cent of the iodine presented to the charcoal arrived during the argon sweep and air clean up of the containment shell system. Penetration during these phases was > 10 per cent and the largest part of the material penetrating was identified as methyl iodide by gas chromatography. Subsequent investigation indicated desorption from active iodine deposited on organic-based paints used in the system.

Charcoal beds tested in air saturated with water at room temperature at 100 C showed poor retention unless allowed to stand 50 hours before elution or heating. Vapors generated by heating irradiated, Zircaloy clad uranium dioxide to the melting point of the Zircaloy can in an air-steam mixture were successively passed through a condenser, bubbler, glass wool droplet trap, and high efficiency filter before presentation to the 4" deep charcoal bed at 100 C. The gas residence time in the charcoal beds was ~ 1 second. After the charcoal was loaded the beds were eluted for 24 hours using water-saturated air at room temperature. Results are given in Table XIV.

TABLE XIVCHARCOAL RETENTION IN WATER-SATURATED AIR

<u>Charcoal Treatment</u>	<u>Iodine Penetration</u> <u>Per Cent of Loading</u>	
	<u>Loading</u>	<u>Elution</u>
None	1.3	14.
Allowed to stand 50 hr before elution	0.1	0.05
Heated bed	0.007	0.01
Morpholine impregnated	0.007	0.002*

* in 4 hr.

British Carbo-Torit Sc II, a coconut based charcoal, had a methyl iodide retention capacity for methyl iodide of only 4 grams/tonne.

Collins, Gate, Taylor and Taylor^[11] found a coal-based charcoal with much higher capacity for methyl iodide. Charcoals were tested by mixing ^{131}I tagged methyl iodide with carbon dioxide + 5 v/o carbon monoxide (preheated to temperature if required) and passing the loaded gas through a 1" diameter, 4" deep bed at a face velocity of 140 ft/min. The bed loading was generally accomplished within 30 minutes and gas flow was then continued for any length of time. Results are shown in Figure 6, along with some results using iodine generated from irradiated stainless steel clad, uranium dioxide elements heated to 1500 to 1600 C in 5 per cent CO + 95 per cent CO₂. Coconut based charcoal (British Carbo-Norit Sc II) showed a critical loading of only 4 grams/tonne at 100 C while coal-based (Sutcliffe-Speakman 207B) showed a critical loading of 500 grams/tonne under the same conditions.

Since one of the principal differences between the two charcoals is the greater amount of metallic impurities found in coal-based charcoal, metallic and other impregnants were evaluated. None was found satisfactory. The results of the evaluation of preloading Sc II with 1 gram of natural iodine is listed in Table XV.

FIGURE 6

Retention of Methyl Iodide on Coconut-and Coal-Base Charcoal
 (-8 +12 BSS, 4" x 1" Dia. Bed)
 Collins, McIntosh, Taylor and Yuille³⁰

TABLE XV

RETENTION OF METHYL IODIDE ON SC II CHARCOAL
PRELOADED WITH 1 GRAM NATURAL IODINE
 (-8+12 BSS 4" Deep x 1" Diameter Bed at 100 C)

Weight Of Methyl Iodide Loaded	Gas Flow At 140 ft/min Hr	Methyl Iodide Penetration Per Cent
7. μ g	1	8
16	4	0.4
22	2.5	0.2
180	1	10
2.6 mg	3	1.6
3.6	3	0.3
	7	14
8.3	1	3

Collins, McIntosh, Taylor and Yuille^[30] tested both coconut and coal based charcoals using three-sized systems. AGR-type stainless steel clad, irradiated uranium dioxide fuels were inductively heated in carbon dioxide, or carbon dioxide plus carbon monoxide or air, to the melting point of the stainless steel can. Miniature fuel elements containing less than 100 curies of fission product activity were heated at atmospheric pressure in an all glass apparatus. Target elements were handled in a steel pressure vessel at reactor temperatures and pressures. A single large scale test using an element irradiated to 2000 Mwd/T has been previously cited. The gases generated were passed through a cyclone to remove particles greater than 5 μ and a high efficiency filter prior to loading onto a 4" deep charcoal bed. Face velocity at the bed was 70 ft/min (a gas residence time in the bed of $\sim 1/7$ second). The charcoal beds were backed by "full-flow" "Maypacks". Gases used were filtered and dried using $\text{Mg}(\text{ClO}_4)_2$ before use. The authors concluded that iodine penetration exceeded 1 part in 10^4 when:

- a. > 100 μ g of iodine are presented to SC II charcoal at 100 C on Sc II used at room temperature.
- b. < 10^{-3} μ g of iodine presented to charcoal beds.

Results are listed in Table XVI.

Parker, Martin, Creek and Barton^{[12][23]} found poor methyl iodide removal efficiencies using charcoals in helium-steam mixtures. During tracer runs in the Containment Mock-up Facility (CMF) in helium-steam atmospheres, a large amount of the iodine arriving at the charcoal beds penetrated (See Table XVII). Sub-

TABLE XVI

PENETRATION OF COCONUT- AND COAL BASED CHARCOAL BY IODINE RELEASED BY
IRRADIATED UO₂ FUEL -- COLLINS, McINTOSH, TAYLOR AND YUILLE^[30]

GAS COMPOSITION	FUEL TEMP. (°C)	FUEL IRRAD. Mwd/T	PER CENT OF FUEL I INVENTORY REACHING TRAPPING SYSTEM	DEPTH (in.)	TYPE	CHARCOAL BEDS		DURATION OF GAS FLOW (Hr.)	IODINE PENETRATION OF CHARCOAL (Part/10 ⁴ Released)
						TEMP. (°C)	PER CENT AIRBORNE IODINE AT CHARCOAL BEDS METHYL IODIDE		
CO ₂	--	--	--	4	II	100	89	1	57
				4	II	100	--		170
				1.5	II		99		4.3
				1.5	II		100		0.5
				1.5	II		99		4
CO ₂ + CO	1700 to 1800	1.5	31	4	II		99.5	1	0.7
			32	4	II		100		2
			37.5	4	II		99.5		0.8
			25	12	II	100	100		1
			7.5	4	II		99.5		0.2
	2500	150	9	4	II		99	1	0.25
			31	4	II		100		0.2
			27	4	II		99		0.16
			35	4	I	20	99.5		0.4
			33	4	II	150	100		0.2
Air + CO ₂	1700 to 1800	2000	14	4	II	100	100	1	0.2
			70	4	II		99		0.2
			--	4	II	--	--		0.2
			--	4	II	100	--		0.2
			--	4	II	--	--		0.2
	1400	1.5	10	4	II	100	97	1	0.5
			36	4	II	100	18		0.3
			47	4	I	20	28.4		0.3
			2.8	4	II		68		22
			40	4	II	20	--		34
H ₂ O sat'd CO ₂ + CO	>2000	150	40	4	II		--	1	0.2
CO ₂ + CO + 1000 ppm CH ₄	1700 to 1800	150	33	4	I		--	1	0.03
CO ₂ + 5% CH ₄	1700 to 1800	150	27	4	I		83	1	4.5
Air + CO ₂	1500	1.5	20	4	II	100	--	1	

* H₂O saturated 54% CO₂ + 35%
CO + 10% Air + 1% H₂ + 0.02% CH₄.

Type I -- Coal based charcoal, Sutcliffe Speakman 207B.

Type II -- Coconut based charcoal, Carbo Torit SC II.

TABLE XVII

DISTRIBUTION OF IODINE ACTIVITY FROM RELEASE OF TAGGED METHYL IODIDE IN CMF

	4-28			5-25			
	Heated Pack	Unheated Pack	Total	First Loading		Second Loading	
				Coconut Charcoal	Coal Charcoal	Coconut Charcoal	Coal Charcoal
	Per Cent Original Inventory						
Roughing + Absolute Filters	0.002	0.002	0.004	0.001	0.001	0.0005	--
Silver Coated Screens	0.02	0.00	0.02	--	--	--	--
Charcoal Papers	21.3	0.2	21.5	--	--	--	--
Charcoal Cartridges	26.6	46.4	73.0	--	--	--	--
Side streams	2.7	2.7	5.4	--	--	--	--
		99.9					
Amount Penetrating 3/4" Charcoal	0.4	1.8	2.2	4.9	81	49	83
Amount Penetrating 1-1/2" Charcoal	0.05	0.07	0.1	--	--	--	--
Amount Penetrating 4" Charcoal	--	--	--	2.4	20.6	24	31.4
Treated Back-Up Charcoal	--	--	--	2.1	16	2.0	22.4
Scavenger Charcoal	--	--	--	0.3	4.6	0.4	12.4
Condensate	--	--	--	0.2	0.2	0.4	0.4

sequently, two experiments were run to determine the effects of humidity, charcoal temperature, total amount of water absorbed by the charcoal, and gas velocity upon the retention of methyl iodide by coconut-based charcoal.

Methyl iodide, in a steam-helium atmosphere, was "aged" in the stainless steel CMF and vented through 4" deep coconut-based charcoal beds backed by 3" 5% morpholine impregnated coal-based charcoal. Unirradiated Zircaloy-clad, uranium dioxide was melted in a steam-helium atmosphere to provide a realistic aerosol atmosphere. Methyl iodide was directly added to the tank held at 120 C. During the "ageing" period in the condensing system, no significant changes occurred in the methyl iodide due to deposition, absorption or decomposition.

In the first experiment, 400 μ g of methyl iodide was added and the system cooled for five hours by stopping steam additions. At the end of this period, the water-saturated gases at $\sim$ 30 C were vented to parallel "Maypack" type cartridges -- one at 120 C and one unheated. Results are shown in Table XVII. The methyl iodide absorption on charcoal retained an exponential profile on the charcoal probably due to the small amount of water absorbed. (Later experiments under similar conditions indicated under the conditions used, the first charcoal cartridge would only absorb 10 per cent of its own weight of water while $\sim$ 60 per cent weight increase is necessary for saturation.) It was also noted that in the heated pack, 40 per cent of the methyl iodide was retained on the six charcoal papers (equivalent to a 1/16" bed of charcoal) while the charcoal papers in the unheated pack held only 0.1 per cent. Ten times greater retention on the silver screens in the heated pack was also found.

In the second run, 3 mg of tagged methyl iodide was used and the gas vented at 75 C into parallel charcoal packs at 3 liters/min (30 fpm). Prior to use the coal- and coconut-based charcoal were preequilibrated to constant weight and inlet-outlet dewpoint using air water-saturated at room temperatures. Weight gained was 40 and 55 per cent respectively. Results are listed in Table XVII.

Browning, Adams, Hensley, Dake and Evans^{[12][23]} determined the effects of moisture and gas velocity on the methyl iodide retention by commercially available charcoals. One and a half-inch beds of commercially available charcoals were tested using both molecular and organic iodine in air-steam mixtures at $\sim$ 100 C in gas velocities ranging from 21.8 to 40.9 fpm. Results are listed in Table XVIII. All types of charcoals were effective in removing methyl iodide at room temperature and 100 C in low humidity. All charcoals tested were ineffective at high humidities. Coconut-based charcoal was the most effective at room temperature

and high humidities.

TABLE XVIII

Efficiency of Charcoal Adsorbers for Removing Different Forms
of Iodine from Steam-Air Mixtures

Charcoal bed depth: 1.5 in.
Charcoal mesh size: 12/30

Experiment	Charcoal Type	Charcoal Temperature (°C)	Iodine Fraction ^a	Steam Saturation ^b (%)	Linear Velocity of Gas (fpm)	Duration of Run (hr)	Iodine Removal Efficiency (%)
LS-1	Coconut, PCB	130	A	29.1	21.8	5	78.37
		108	B	56.3	28.6	5	99.84
LS-2	Coconut, PCB	98	A	83.2	40.9	5	4.93
		95	B	88.7	39.6	5	98.53
LS-3	Whetlerite ^c	96	A	82.4	33.8	5	10.94
		97	B	79.3	34.1	5	99.40
LS-4	Coconut, PCB	100	A	73.7	34.6	5	41.73
		95	B	90.7	37.0	5	95.69
LS-5	Coke, BPL	95	A	80.7	30.2	5	8.77
		96	B	78.2	27.9	5	99.38
LS-6	Coke, BPL	94	A	83.5	27.3	5	33.69
		96	B	85.1	34.1	5	96.76
LS-7	Coke, 207B ^d	96	A	85.7	34.9	5	6.98
		95	B	85.2	31.2	5	97.89
LS-8	Coke, 207B	95	A	85.8	31.6	5	8.19
		97	B	82.6	34.9	5	97.19
LS-9	Coke, BPL	108	A	63.0	55.0	2	90.80
		98	B	69.7	25.9	1	99.96
LS-10	Coconut, PCB	94	A	86.9	29.9	1	66.05
		93	B	66.6	18.5	1	98.42
LS-12	Coke, 207B	100	A	66.9	27.3	0.7	32.36
		94	B	88.1	30.8	0.6	98.22
LS-13	Whetlerite	94	A	82.5	26.6	1	8.94

^aA is the volatile fraction (primarily methyl iodide) and B is the less volatile fraction (primarily elemental iodine), when the iodine source is at -70°C. A is injected during the initial 10 min of the test at a concentration of $\sim 5 \times 10^{-2}$ mg/m³; B is injected over a 5-hr test period at a concentration of $\sim 1 \times 10^{-2}$ mg/m³.

^bSteam partial pressure expressed as percentage of vapor pressure of water at indicated temperature.

^cBPL charcoal impregnated with salts of silver, copper, and chromium.

^dSutcliffe, Speakman 207B, 10/14 mesh U.S. equivalent.

Since moisture content of the charcoal depends upon the relative humidity of air over it, the effects of humidity on methyl iodide were determined. Results are plotted on Figure 7 and experimental conditions stated. Retention of methyl

iodide was good in < 3 and 71 per cent RH air (99.9 per cent for 65 and 15 hours respectively). In 97% RH air penetration exceeded 0.1% within 1 hour.

The effect of linear gas velocity upon methyl iodide is shown on Figure 8. High relative humidity air (60-71 per cent) at room temperature was used with various methyl iodide concentrations to keep methyl iodide loading constant at various gas velocities. Greater than 10 per cent penetrations occurred in < 1 hour under these conditions at 50 and 100 fpm..

Humidity control as a means of methyl iodide retention was tested by cooling methyl iodide loaded air-steam mixtures using a tap water and ice water cooled condenser in series. The air, at approximately 20°C and approximately 25 per cent RH, was passed into the charcoal bed plus three back up beds. Experimental conditions and results are shown on Figure 9. Although this method is effective in improving methyl iodide retention in charcoal, it is an unattractive solution for use in reactor operation due to its dependence upon mechanical refrigeration.

Browning, Miller, Shields, Roberts, Wilhelm, Montgomery and Roberts^[23] found < 0.5 per cent of the total iodine inventory of the irradiated miniature uranium dioxide fuel melted in the ORR in-pile melting test penetrated the first charcoal filter. Fuel temperatures were approximately 2850°C with the high temperature zone adjacent to the fuel at < 1000°C. An air-steam-helium atmosphere was used.

Collins, Taylor and Taylor^[38] also found that the retention of methyl iodide on coconut and coal based charcoals was seriously affected by high humidities. They ascribed this deterioration to the blocking of the charcoal surfaces by absorbed water preventing adsorption of methyl iodide and its subsequent migration to sites where it can be decomposed and the iodine retained. The delay-time of methyl iodide in the charcoal decreases from hours in dry air to a matter of minutes in air saturated with water vapors. No commercially available charcoal was found which exhibits superior high humidity methyl iodide retention than the performance of coal-based charcoal. The capacity of the charcoal can be restored by preheating the air to reduce the relative humidity to < 30 per cent. The effects of relative humidity upon methyl iodide retention is shown on Figure 10.

Parker and Farrell^[12] have determined the effects of residence time and bed depth upon the penetration of methyl iodide in water-saturated air at 75°C through coconut-based charcoal. Air was loaded with 690 $\mu\text{g}/\text{m}^3$ of methyl iodide by passing air through a solution of methyl iodide in n-decane. Water and n-decane are removed by passage through a trap held at -78°C. The air was then saturated

FIGURE 7

Effect of Humidity on the Retention of CH₃I by Activated Charcoal
ORNL 3843¹²

FIGURE 8

Effect of Sweep Gas Velocity on the Retention of CH₃I by Activated Charcoal
ORNL 3843¹²

Trapping System: Ice Water Condenser and 1.5 in.
Charcoal Bed (P/C B)
Steam-Air Composition: 83% Steam
Concentration CH_3I : 0.1 g/m³ Continuous Injection
Face Velocity at Charcoal: 24 fpm
Relative Humidity at Charcoal: ~ 25%

FIGURE 9
Removal of Methyl
Iodide from Steam-Air Mixture
ORNL 384312

FIGURE 10
Effect of Relative Humidity of the Carrier Gas on the
Penetration of Methyl Iodide Through a Bed of Coal-Based
Charcoal
Collins Taylor and Taylor³⁹

with water by bubbling through a water bath at controlled temperatures. The methyl iodide was then loaded on two charcoal cartridge packs mounted over the water to insure the correct temperatures. Two depth charcoal cartridges were used, one size in each pack -- 1 and 2 cm deep. Both contained the same quantity of charcoal -- 4 cm^3 , 1.6 grams. Residence was varied by using flows ranging from 1.75 to 14 liters/min. Tests were 1 hour in duration.

Under the stated conditions, the controlling factor in the penetration of the charcoal bed by methyl iodide was the amount of water absorbed by the charcoal. The removal efficiency of the charcoal for methyl iodide increased with residence time (See Figure 12). The longer cartridges appeared more efficient though this may be an artifact due to the smaller air volume (and therefore smaller amount of moisture) seen by the longer cartridges. Efficiency also increased with cartridge number (See Figure 13) but again the water content of subsequent cartridges is lower due to the water removal by the previous cartridges. The charcoal was not saturated with water (water content was 35 per cent of the dry weight of the charcoal at a residence time of 0.42 second and 47 per cent at 0.105 second). In a 12 cm charcoal bed with a gas residence time of 0.21 second, 0.07 per cent of methyl iodide penetrated with a weight gain for moisture of 41 per cent. but was 24 per cent with a weight gain of 63 per cent. Figure 14 shows methyl iodide penetration of charcoal beds as a function of bed depth and residence time.

Negligible desorption of methyl iodide was found when water saturated air at 25° to 95°C was passed through 1 and 2 cm cartridge packs at 60 and 120 fpm. The charcoal was loaded to an approximate concentration of $2.8 \text{ } \mu\text{g/g}$ CH_3I charcoal in 1 hour. Each cartridge pack contained six cartridges of a single depth. Distribution in the beds are shown on Figures 15a and 15b. The large loss (~ 35 per cent) from the shallow beds was all found in the condenser in the form of iodates.

Collins, Taylor and Taylor^[38] evaluated a series of chemical compounds as impregnants on charcoal to improve its removal efficiency at high humidities. The compounds were selected for their chemical reactivity towards methyl iodide -- particularly heterocyclic amines. Generally, the coal-based charcoals were used. The few tests using coconut-based charcoals were disappointing. Charcoals were loaded with $\sim 100 \text{ } \mu\text{g}$ of methyl iodide from a condensing air-steam mixture in ~ 15 minutes. Gas residence time in the beds was $\sim 1\text{-}1/2$ seconds.

The best results were obtained with charcoal impregnated with 5 w/o piperazine. In a condensing water system where the bed temperatures increased from 20° to

FIGURE 14
Fraction of Methyl Iodide Penetrating Charcoal Beds as a Function of Bed Depth and Residence Time
ORNL 384312

FIGURE 13
Efficiency of Cartridges at Various Bed Positions
ORNL 384312

FIGURE 15a

Distribution of Methyl Iodide After Sorption at 25 °C in Water-Loaded 1-cm Coconut Charcoal and After Exposure to Flowing Saturated Air at Temperatures up to 95 °C

FIGURE 15b

Distribution of Methyl Iodide After Sorption at 25 °C in Water-Loaded 2-cm Coconut Charcoal and After Exposure to Flowing Saturated Air at Temperatures up to 95 °C

100°C, the penetration in 10 hours was 0.03 per cent. The penetration only increased to 0.034 per cent after eluting the loaded bed an additional 125 hours with water-saturated air at room temperature. After an additional loading of 200 µg of methyl iodide in saturated air at room temperature, the penetration increased to 1.5 per cent but did not increase during the next 135 hours of exposure to flow of saturated air. The chief disadvantage to other effective impregnants, morpholine or piperdine, is their low boiling points (126° to 130°C and 106°C respectively). Results are listed in Table XIX.

Browning, Adams and Attrill^[12] also studied the effectiveness of charcoal impregnants. Each 10 gram charcoal bed was impregnated with 3 w/o of an organic compound or ~ 10 w/o of the inorganic compound under investigation. The beds were pre-equilibrated with air at the required relative humidity and then loaded with the same relative humidity air containing 100 to 300 mg/m³. The flow was continued and penetration was clearly indicated by the inlet and exit air samples analyzed by a gas chromatograph with electron capture detection. Duration of tests ranged from 4 to 200 hours. Results are plotted in Figure 11 and entered in Table XIX. The loading used is higher than in the test mentioned above with a gas residence time only 1/6th as long. In general, the heterocyclic amines were the best impregnants. Inorganics were found to be detrimental to methyl iodide retention.

Taylor and Taylor^[39] (using a standard procedure) evaluated organic and inorganic impregnants and found triethylene diamine and potassium iodide to be the most effective charcoal impregnants. The charcoal beds under study were pre-equilibrated with the proper relative humidity air for at least 16 hours. Methyl iodide was loaded upon the charcoal usually within 10-15 minutes. The bed was then eluted using the same relative humidity gas for periods ranging from 4 hours up to a week. Critical loading for 0.5 per cent KI impregnated charcoal was 100 to 150 gram/tonne and 200 to 300 gram/tonne for a 1 w/o diethylene triamine impregnation. Coal-based charcoals were used in most of the study. Results are shown in Table XIX. Impregnation with potassium iodide reduced the ignition temperature of the charcoal from 440° to 250°C.

The results of "ageing" were determined and are listed in Table XX. Impregnation with triethylene diamine remained the most effective. The effects of contact time upon the penetration of methyl iodide through various impregnated charcoals in air and carbon dioxide atmospheres is shown in Figure 16.

More recently ORNL^[40] has found an iodine-impregnated coconut-based charcoal effective even after long exposure to humid air. The charcoal was found 99.7 per cent

FIGURE 16

Penetration of Methyl Iodide Through Impregnated Charcoal
Taylor and Taylor³⁹

TABLE XIXa

METHYL IODIDE PERFORMANCE OF COCONUT BASED CHARCOAL IN DRY AIR

REF.	CONCENTRATION ($\mu\text{g}/\text{m}^3$)	ADDITIVES	BED DEPTH (in.)	GAS FLOW (fpm)	TEMP. (°C)	PENETRATION (%)	REMARKS
3	8 g CH ₃ I/te 0.4 g CH ₃ I/te		4	140	100 Ambient	1-10 hr, 1% 1 hr, 1%	
3	50 Iodine		1.5	25	23 100 100 150	0.02 <0.01 0.09 0.05	4% Relative Humidity <0.1% Relative Humidity 2.7% Relative Humidity <0.1% Relative Humidity
32	100 $\frac{\text{g CH}_3\text{I}}{\text{g charcoal}}$	0.5% Potassium Iodide 5% Triethylene Diamine 10% Piperazine 1% Morpholine			Ambient	0.1 hr, 1% 0.12 hr, 1% 0.15 hr, 1% 0.4 hr, 1% >1.5 hr, 1% >>>1.5 hr, 1%	+ 1 v/o CO ₂ Air + CO ₂
4	80 Iodine		3	10	24	<1 hr., 0.1%	

TABLE XIXb

METHYL IODIDE PERFORMANCE OF COCONUT BASED CHARCOAL IN HUMID AIR

REF.	IODINE CONCENTRATION ($\mu\text{g}/\text{m}^3$)	ADDITIVE	BED DEPTH (in.)	BED TEMP. (°C)	FLOW fpm	GAS TEMP. (°C)	RELATIVE HUMIDITY (%)	PENETRATION (%)	REMARKS
20	50	50 hr. standing before elution.	100					400 Steam During loading: 1.3	
								Ambient Water sat'd During elution: 14.	
								400 Steam During loading: 0.1	
								Ambient Water sat'd During elution: 0.05	
								400 Steam During loading: 0.007	
								Ambient Water sat'd During elution: 0.01	
								400 Steam During loading: 0.007	
								Ambient Water sat'd During elution: 0.002	
3	50		1.5		25	20	77		0.66
					21.8	130	29.1% Steam		21.63
					40.9	98	83.2% Steam		95.07
					34.6	100	73.7% Steam		58.27
43	5 $\frac{\mu\text{g CH}_3\text{I}}{\text{g charcoal}}$	Iodine 1% Potassium Iodide Iodine, Bromine & Salts Triethylenediamine	2		40	24	70		.03
									0.001
								Effective	
								In 5 hr: Effective	~ 63%
4	100 $\frac{\mu\text{g CH}_3\text{I}}{\text{g charcoal}}$		1.5	70		94	86.9	In 1 hr:	32.95
			0.75						0.8
			1.5						0.1
			0.75			30	Water sat'd		3.6
	8 x 10 ⁴		1.5		10	24	71	In 15 Hr:	0.1
									Charcoal pre equilibrate at same P.H. Air as in Run
			3					In < 1 hr:	0.1
									Constant Dewpoint on Inlet & Exhaust Air.

TABLE XIXb

METHYL IODIDE PERFORMANCE OF COCONUT BASED CHARCOAL IN HUMID AIR

REF.	IODINE CONCENTRATION ($\mu\text{g}/\text{m}^3$)	ADDITIVES	BED DEPTH (cm)	BED TEMP. ($^{\circ}\text{C}$)	GAS FLOW (cfm)	GAS TEMP. ($^{\circ}\text{C}$)	RELATIVE HUMIDITY (%)	PENETRATION (%)	RESIDENCE TIME (sec/cm)	TOTAL CH ₃ I LOADED (μg)	
12	690		1		1.75 liters/min	Ambient	67 ± 18*	33.2	0.16	71.8	
			2				45 ± 6 *	5.4			
			3				39 ± 12*	1.0			
			4				39 ± 9 *	0			
			5				37 ± 10*	0			
			6				31 ± 12*	0			
			2				52 ± 5 *	27.6			
			4				45 ± 6 *	3.9			
			6				45 ± 6 *	0.3			
			8				41 ± 8 *	0			
			10				40 ± 7 *	0			
			12				39 ± 7 *	0			
			1		3.5 liters/min			57.2	0.07	145.2	
			2					23.9			
			3					6.4			
			4					1.8			
			5					0.5			
			6					0.3			
			2					55.2			
			4					21.7			
			6					6.1			
			8					1.4			
			10					0.5			
			12					0.2			
			1	7.0 liters/min				67 ± 18*	71.5	0.035	284.9
			2					45 ± 6 *	45.6		
			3					39 ± 12*	25.9		
			4					39 ± 9 *	12.9		
			5					37 ± 10*	5.4		
			6					31 ± 12*	2.1		
			2					52 ± 5 *	61.5		
			4					45 ± 6 *	32.8		
			6					45 ± 6 *	13.4		
			8					41 ± 8 *	4.9		
			10					40 ± 7 *	1.8		
			12					39 ± 7 *	0.7		
			1	14.0 liters/min				79.3	0.0175	569.4	
			2					57.9			
			3					39.7			
			4					26.5			
			5					17.1			
			6					10.5			
			2					81.0			
			4					58.5			
			6					36.0			
			8					19.2			
			10					11.4			
			12					5.7			

* $\frac{\text{Wt. of Water on Charcoal}}{\text{Dry Wt. of Charcoal}} \times 100$

METHYL IODIDE PERFORMANCE OF COCONUT BASED CHARCOAL IN HUMID AIR

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TABLE XIXc

METHYL IODIDE PERFORMANCE OF COCONUT BASED CHARCOAL IN OTHER GASES

REF.	IODINE CONCENTRATION ($\mu\text{g}/\text{m}^3$)	ADDITIVES	BED DEPTH (in.)	BED TEMP. ($^{\circ}\text{C}$)	GAS COMPOSITION	GAS FLOW (fpm)	GAS TEMP. ($^{\circ}\text{C}$)	RELATIVE HUMIDITY	PENETRATION (%)			
40	Wt. Loaded	Carbo Torit Sc II	1" Diameter x 4" Deep		$\text{CO}_2 + 5\% \text{ CO}$	140	100	Ambient	In 1 hr.	0.002	In 16 hr.	0.007
		Amb.					In 1 hr.		0.2	In 5 hr.	5.	
		2. mg Sc II Pyridine					In 1 hr.		7			
		600. Sc II Silver					In 1 hr.		2			
		140. Exp. 364 Copper					In 1 hr.		95			
		21. ASC 324 Ag + Cu + Cr					In 1 hr.		7			
		7. μg					In 1 hr.		8			
		16.								In 4 hr.	0.4	
		22								In 2.5 hr.	0.2	
		180 Sc II-Preloaded with					In 1 hr.		10			
		2.6 1 gram ^{127}I								In 3 hr.	1.6	
		3.6					In 3 hr.		0.3	In 7 hr.	14	
	8.3	In 1 hr	1	2.7% of 50 mc I load during 1/2 hr. blowdown.								
	Ultrasorb Sc II	4	50% $\text{CO}_2 +$ 50% CO	300 cc/min			10.2% of 935 mc I load during 1/2 hr. circulation					
							10.1 of 9000 mc I load during 20 hr clean up					
			10	CO_2		20						

TABLE XIXd

METHYL IODIDE PERFORMANCE OF COAL BASED CHARCOAL IN DRY AIR

REF.	IODINE CONCENTRATION ($\mu\text{g}/\text{m}^3$)	ADDITIVE	BED DEPTH (in.)	BED TEMP. (°C)	GAS FLOW (fpm)	GAS TEMP. (°C)	RELATIVE HUMIDITY (%)	PENETRATION (%)	REMARKS
29	50	Whetlerite	1.5		25	23 100 150 100	<3 <0.1 0.03 <2.7	0.09 0.02 0.03 0.06	
3	50		1.5		25	24 100 100 150 24	<3 <0.1 ~2.7 <0.1 <3	0.03 0.11 0.13 0.06 0.71 0.01	
		Sutcliffe-Speakman							
30		Sutcliffe-Speakman 207-B	4		140	100 Amb.			1% penetration at loading of 400 g $\text{CH}_3\text{I}/\text{T}$, 1 - 12 hours flow 1% penetration at loading of 4 Kg $\text{CH}_3\text{I}/\text{T}$

TABLE XIXe

METHYL IODIDE PERFORMANCE OF COAL BASED CHARCOAL IN HUMID AIR

REF.	IODINE CONCENTRATION ($\mu\text{g}/\text{m}^3$)	ADDITIVES	BED DEPTH (in.)	BED TEMP. ($^{\circ}\text{C}$)	GAS FLOW (cpm)	GAS TEMP. ($^{\circ}\text{C}$)	RELATIVE HUMIDITY (%)	PENETRATION (%)
39	100	1 w/o Pyridine	1.5		1.5		99-100%	~5.
		1 w/o Morpholine						0.05
		10 w/o Morpholine						0.0054
		30 w/o Morpholine						38.2
		1 w/o Piperidine						0.0048
		30 w/o Piperidine						3.2
		5 w/o 4 Amino Pyridine						0.066
		5 w/o Piperazine Hydrate						0.07
		5 w/o p Phenylene Diamine						67.8
		5 w/o 2,2' Dipyridyl						77.0
		5 w/o Iminazole						14.5
		5 w/o Succinimide						7.9
		10 w/o Succinimide + Ag Succinimide						33.6
		5 w/o Guanidine Carbonate						45.0
		5 w/o 4 Amino Phenazone						78.4
		5 w/o 2 Amino Pyridine						32.1
		5 w/o Toluene P Sulpho- namide						76.6
		5 w/o Aminoacride						25.7
		5 w/o Ethanolamine						10.9
		3 w/o Dicyclo Hexylamine						32.7
		2 w/o 2 Amino 2 Methyl Propyl 1,3 Diol						35.3
		2 w/o Isopropanol Amine						16.7
		2 w/o Hexamethylene tetramine						1.71
		2 w/o 3 Amino Propanol						28.4
		3 w/o p Amino N,N' Diethylaniline						45.1
		3 w/o Acridine						41.4
		2 w/o N (2 Aminoethyl) Ethanolamine						~9.0
		2 w/o N,N Diphenyl Benzylamine						63.4
		1 w/o N Methyl N Phenyl Benzylamine						66.3
		2 w/o N,N Dimethyl Benzylamine						29.4
		1 w/o N,N Diphenyl Guanidine						
		Whetlerite						38.13
								82.4 Steam
								49.75
								26.58
								91.23
								66.21
								93.02
								25.76
								60.
								0.008
								0.03
								0.07
								0.0073
								2.5
								0.004
								1.5
								No improvement over unimpregnated charcoal
								0.003
								<0.001
								0.002
								1.01
								3.20
								1.38
								0.83
								10.3
								12.2
32	100	1 w/o Morpholine	1.5		1.5		99-100% RH Air	0.008
		1 w/o Piperidine						0.03
		5 w/o 4 Amino Pyridine						0.07
		10 w/o Piperazine						0.0073
		5 w/o Diethylene Diamine						2.5
		40 Appn. Org. Imp.						0.004
		5% Potassium Bromate						1.5
		5% Potassium Bromide						No improvement over unimpregnated charcoal
		5% Potassium Iodide						0.003
		0.5% Cesium Iodide						<0.001
		2% Cesium Iodide						0.002
		2% Calcium Iodide						1.01
38		2% Ferrous Iodide	1.5		0.1			3.20
		2% Ferrous Bromide						1.38
								0.83
								10.3

TABLE XIXe

METHYL IODIDE PERFORMANCE OF COAL-BASED CHARCOAL IN HUMID AIR

Ref.	Iodine Concentration ($\mu\text{g}/\text{m}^3$)	Additives	Bed Depth (In.)	Bed Temp. (°C)	Gas Flow (fpm)	Gas Temp. (°C)	Relative Humidity (%)	Penetration (%)
32	100 $\frac{\mu\text{g CH}_3\text{I}}{\text{g charcoal}}$	2% Sodium Chloride	Sutcliffe-Speakman	—	0.1	—	99-100	8.5
		2% Magnesium Iodide						0.37
								97.0
		10 w/o Piperazine						Log ₁₀ DF 5.0 at 0 × 10 ⁶ BV*
		5% Triethylene Diamine						3.0 at 5 "
								2.0 at 100 "
		0.5% Potassium Iodide						10.0 at 0 "
								7.6 at 50 "
								5.4 at 100 "
								10.0 at 0 "
								6.4 at 30 "
								4.4 at 100 "
4	100 $\frac{\mu\text{g CH}_3\text{I}}{\text{g charcoal}}$	Sutcliffe-Speakman	1.5	—	31.6	95	85.8%	In 5 hrs. 91.81
		Coke BPL			55	108	63%	In 2 hr 9.20
		Sutcliffe-Speakman			27.3	100	66.9%	In 0.7 hr 67.64
		Whetlerite			26.6	94	82.5%	In 1 hr 91.06
			3/4	30	—	—	Water Saturated	81 1st loading [†]
			1					83 2nd loading [†]
								20.6 1st loading [†]
								34.8 2nd loading [†]
		Sutcliffe-Speakman	1.5	—	25	31.6	20 ~25	In 5 hr. 91.81
		Coke BPL			108	55		In 2 hr. 9.2
		Sutcliffe-Speakman			100	27.3		In 0.7 hr. 67.64
		Whetlerite			94	82.5		In 1 hr. 91.06
50	$\frac{\mu\text{g CH}_3\text{I}}{\text{m}^3}$	Sutcliffe-Speakman	1.5	—	—	—	20 ~25	In 5 hr. 91.81
		Coke BPL						In 2 hr. 9.2
		Sutcliffe-Speakman						In 0.7 hr. 67.64
		Whetlerite						In 1 hr. 91.06

* BV = Bed Volumes ambient air through charcoal during ageing tests. If contact time is 0.5 sec., 100 × 10⁶ BV = 18 months oper.
1.0 sec., 100 × 10⁶ BV = 3 years oper.

† Charcoal absorbed 40% own weight in condensed moisture, loading period = 30 minutes.

** 10 $\frac{\text{mg I}_2}{\text{m}^3}$ during remainder of run.

TABLE XIXf

METHYL IODIDE PERFORMANCE OF COAL-BASED CHARCOAL IN OTHER GASES

Ref.	Iodine Concentration ($\mu\text{g}/\text{m}^3$)	Additives	Bed Depth (in.)	Bed Temp. ($^{\circ}\text{C}$)	Gas Composition	Gas Flow (fpm)	Gas Temp. ($^{\circ}\text{C}$)	Relative Humidity (%)	Penetration
32		Sutcliffe-Speakman	4		$\text{CO}_2 + 5\% \text{ CO}$	140	100		In 1 hour — 0.001 In 24 hours — 0.01 In 72 hours — 0.02
32	100 $\frac{\mu\text{g CH}_3\text{I}}{\text{g charcoal}}$	Sutcliffe-Speakman			CO_2	0.25 sec*	Ambient	99-100	0.004
						0.15 sec			0.01
						0.22 sec			0.1
						1.1 sec			0.1
						>>1.5 sec			0.1
						>>>1.5 sec			0.1
					Air + CO_2				

*Contact time.

efficient for methyl iodide in 70 per cent RH air at 24°C at a velocity of 40 ft/min at a loading of 5 gram/tonne. Under similar conditions, unimpregnated charcoal was only ~ 39 per cent efficient in 5.5 hr. The evaluation of various compounds as impregnants is continuing.

TABLE XX

RESULTS OF AGEING TESTS ON IMPREGNATED CHARCOAL

(Ageing in air at ambient relative humidity followed by standard test in 99 - 100% R.H. air; 100 µg CH₃I/g charcoal)

<u>Impregnant</u>	<u>Bed Volume Of Air Passed During Ageing X 10⁻⁶</u>	<u>Log₁₀DF In Standard Test After Ageing</u>	<u>'Contact Time' In Test</u>	<u>Log₁₀DF Normalized To 0.5 Sec. 'Contact Time'</u>
10 w/o Piperazine	0	5.0	0.5 sec	5.0
	1	4.4		4.4
	5	3.0		3.0
	100	2.0		2.0
5 w/o Triethylenediamine	0	5.0	0.25 sec	10.0
	50	3.8		7.6
	100	2.7		5.4
0.5 w/o Potassium Iodide	0	5.0		10.0
	1	5.0		10.0
	30	3.2		6.4
	100	2.2		4.4

(Note: 100 × 10⁶ bed volume changes is equivalent to 18 months operation at 0.5 second 'Contact Time' or 3 years at 1.0 second 'Contact Time'.)

The Removal of Airborne Methyl Iodide By Aqueous Solutions

The removal of methyl iodide from reactor atmospheres by aqueous solutions has some very desirable advantages. The removal is not affected by moisture in the air and requires no mechanical equipment. Many current reactors use pressure suppression as a means of controlling post-accident pressures and already have a large water pool available. Collins, Taylor and Taylor^[38] evaluated a number of aqueous solutions for methyl iodide removal efficiencies in a series of glass bubblers. Methyl iodide in an air- or carbon dioxide-steam atmosphere was passed

through a series of bubblers with up to 3 seconds contact time. Solution temperatures up to 60°C were used. Most of the solutions tried showed less than 1 per cent efficiency. Only acid-bromate demonstrated a useful efficiency ranging from 94 per cent at 20°C liquid temperature and a 3.2 second contact time to 99.99 per cent at 60°C with the same contact time. The results of all experiments are listed in Table XXI. The authors noted that the poor methyl iodide partition from a gas phase into water makes aqueous solutions virtually ineffective unless a gas phase reaction occurs first to convert methyl iodide to a water soluble compound.

Diffey, Rumary, Smith and Stinchcombe^[22] found mass transfer resistance in the removal of methyl iodide by aqueous solutions under simulated reactor accident conditions. Decontamination was not improved by the various additives tried. Two sizes of experimental equipment were used.

Simulated fission products were carried in an air-steam mixture at a flow of 34 m/sec and fed through "lutes"* 3 and 50 mm in diameter immersed 6 and 50 cm respectively into a cold water pond. In the all-glass small scale apparatus, air, containing iodine species, was injected into a 90 per cent dry-saturated steam and passed through the 3 mm "lute" into the water pool at a velocity of 34 mm/sec. Filtered air was swept over the liquid surface at 32 liters/min and through a condenser and charcoal bed to remove iodine. The iodine was injected into the system for 30 minutes followed by a 30 minute air sweep to determine loss of iodine from the pool.

In the larger experimental apparatus the iodine species in air are mixed with the required amount of steam and passed into a 1-1/2' x 3' x 4-1/2' stainless steel vessel through a 50 mm single or multiple "lutes". Constant temperature is maintained by a cooling coil. The tank is equipped with two 2' x 2' viewing windows. Gas sampling for both experiments were by "Maypack" with inlet gases heated to ~ 90°C to prevent condensation of moisture.

Methyl iodide exhibits a considerable mass transfer resistance limiting the decontamination factor and, is rapidly and virtually completely lost when air is passed over the surface of the pool. Figure 17 shows the measured decontamination factor compared to theoretical curve calculated on the assumption that

* A "lute" is a liquid sealed tube, e.g.

TABLE XXIa

REMOVAL OF AIRBORNE METHYL IODIDE BY AQUEOUS SOLUTIONS

Chemical Additives	Concentration	Apparatus	Atmosphere	Temp. (°C)	CH ₃ I		Remarks
					Concentration	Behavior (% Penetration)	
Silver Nitrate	0.1 M	$\frac{3}{4}$	Air or CO ₂	20	0.1 - 10 mg/m ³	99	Gas flow in bubblers dispersed with sintered glass disc. Flow: 5 l/min Residence Time: ~ 0.8 sec
		$\frac{4}{4}$		80		25	
Silver Nitrate + Foaming Agent	0.1 M	3				93	
Silver Fluoride	1%	4		60		96	
Morpholine + Sodium Hydroxide	10% 1 N	4		60		93	
Potassium Permanganate + Sulfuric Acid	0.1 M 0.1 N	4		60		82	
		$\frac{4}{4}$		20		6	
Potassium Bromate + Sulfuric Acid	0.1 M 0.6 N	$\frac{8}{4}$ $\frac{4}{4}$		20		1	
		$\frac{4}{4}$		30		0.75	
		$\frac{4}{4}$		45		0.1	
		$\frac{4}{4}$	Air	60	30 µg/m ³	0.01	
	0.3	3		20		20	
Chlorine in Air	$\frac{60}{42}$ g/m ³	$\frac{2}{4}$		20		0.04	
		$\frac{2}{4}$		20		<0.01	
Bromine in Air	0.5 g/m ³	$\frac{3}{3}$		60		50	
		$\frac{3}{3}$		20		50	
Water + Iso Quinoline + Triethanoline + Ionic Detergent + Non Ionic " + Foaming Agent		32 l/min flow over a 10 l pond	Air	35	5×10^{-9} to * 10^{-6} M	40 to 55% loss in 30 min.	* Concentration in pond water.

TABLE XXIIb

METHYL IODIDE BEHAVIOR IN AQUEOUS SOLUTION

Chemical Additive	Concentration	Apparatus	Atmosphere	Temp. (°C)	CH ₃ I Concentration	CH ₃ I Behavior
Water		5cm lute 50 cm immersion	2.5 Kg/min steam 200 l/min air	50	4×10^{-6} M*	90% loss in 30 min
Sodium Thiosulfite	0.02 N	Flowing stream over 10 l pool	Air Flow: 200 liters/minute	35	5×10^{-9} M*	40% loss in 30 min
Paraffin on Water	5mm				4×10^{-7} M	7% loss in 30 min
Methylated Spirits	--				3×10^{-6} M	1.7% loss in 30 min
Distilled Water						
Chlorinated Water		Series of bubblers < 3 sec contact time	Air or CO ₂	<65		< 1% Extraction
Sodium Hydroxide	1 N					
Sodium Bicarbonate	1 N					
Sodium Thiosulfate	0.1 N					
Ammonium Hydroxide	0.1 N					
Pyridine in Water	5%					
Morpholine in Water	5%					
Pyridine in	10%					
Sodium Hydroxide	1 N					
Potassium Dichromate	0.1 M					
in Sulfuric Acid	0.1 N					
Hydrogen Peroxide	0.1 M					
in Sulfuric Acid	0.1 N					
Potassium Iodate	0.1 M					
in Sulfuric Acid	0.1 N					
Ceric Sulfate	0.1 M					
in Sulfuric Acid	0.1 N					
Chlorine Water						

* g mol/liter in 500 liter pool.

FIGURE 17

Comparison of Experimental and Theoretical Decontamination Factors
for Removal of HI and CH_3I by a Water Lute
A. E. R. E. - R. 4882²²

the methyl iodide in the pond is in equilibrium with the air leaving the pond. The theoretical curve was calculated by:

$$dF = \left[1 - \frac{1 - e^{-x}}{x} \right]^{-1}$$

where $x = \frac{vt}{VK}$

v = volume flow rate of air

V = volume of pool

t = time of run

K = partition coefficient = $\frac{\text{g mol/liter in water}}{\text{g mol/liter in air}}$.

The partition coefficient from the measured values in experiments in the large apparatus at 50°C was 1.3 (at a methyl iodide concentration of 10^{-5} M) as compared to a 2.5 calculated at this temperature for equilibrium conditions. The true value for build up and loss of methyl iodide in the pond (VK/v) was measured to be 7 and 13 minutes as compared to a calculated value of 3.3 minutes for both. Figure 18 shows the variations of methyl iodide concentration with time. Figure 19 is the calculated fraction of methyl iodide removed by the pond water as a function of the ratio of the total volume of air carrying the methyl iodide to the water volume. The measured partition coefficients indicate a limit of 3 for decontamination factor.

More recently, Mishima^[41] found low methyl iodide removal efficiencies by water and hydrazine hydrate solution in steam and hot air atmosphere. Steam or air containing ~ 25 mg/m³ methyl iodide was bubbled through water or hydrazine hydrate solution at 3 liters/min. Liquid temperatures increased during the 10 minute run from ambient to $> 80^\circ\text{C}$. Water extracted $\sim 0.2\%$ of the methyl iodide under these conditions while 17.5 to 35 per cent hydrazine hydrate extracted 11 - 14 per cent. Figure 20 is a schematic diagram of the apparatus. Results and experimental conditions are listed in Table XXII.

Methyl Iodide Vapor Phase Reactions

Very little work has been done to utilize a vapor-phase reaction for the removal of methyl iodide from reactor containment atmosphere following a meltdown accident. Collins, Gate, Taylor and Taylor^[11] found high concentrations of halogens to be effective in removing methyl iodide but not practical for reactor use. The effectiveness of acid-bromate was attributed to the formation of water-soluble iodine-bromides by the intimate contact of "nascent"

FIGURE 18

Variation with Time of the Methyl Iodide Concentration in the Water of the Large Pond at 50 °C
A.E.R.E. - R. 488222

FIGURE 19

Dependence of the Percentage of Methyl Iodide Trapped on the Relative Volumes of Air and Water at 50 °C
A.E.R.E.-R.488222

FIGURE 20

Schematic Diagram of Gas Washing Apparatus used in Methyl Iodide Extraction Experiment
Mishima⁴¹

TABLE XXII

METHYL IODIDE EXTRACTION BY HYDRAZINE SOLUTION - STEAM ATMOSPHERE

Run	Liquid	Volume (cc)	Temperature Liquid (°C)	Volume Condensate (cc)	Temperature Sample (°C)	Temperature Condensate (°C)	Flow (l/min)	Length Of Run (min)	Per Cent Extracted	Atmosphere	CH ₃ I Concentration (mg/m ³)	Contact Time (sec)
1	Water	50	30 - 81	50	73 - 91	22	13.5	10	.2	Steam	25	~0.25
2	Water	50	34 - 84	32	77 - 92	23 - 70	3	10	.2	Steam	25	1
3	35% N ₂ H ₂	50	25 - 83	41	92 - 93	22 - 74	3	10	14	Steam	25	1
4	17.5% N ₂ H ₂	50	25 - 85	40	91.5 - 97	22 - 73	3	10	11	Steam	25	1
5	Water	50	23	—	> Ambient	21	3	8	.2	Hot Air	21.7	1
6	35% N ₂ H ₂	50		--			3	8	11	Hot Air	21.7	1

ID gas washing bottle: 1.625" OD gas inlet tube: 0.3125"
 Depth of immersion tube: ~ 2.5"

bromine and methyl iodide in bubbles. Various concentrations of gaseous bromine and chlorine followed by a series of bubblers were tested and > 99.99 per cent removal attained with an airborne chlorine concentration of 42 grams/m³. Results are listed in Table XXIII. The method does not commend itself to reactor application because of the corrosiveness and dispersal problems with large concentrations of halogens and the long contact time required by the reaction.

Viles and Silverman^[42] at the Harvard Air Cleaning Laboratory briefly investigated the vapor phase reaction between methyl iodide and hydrazine. In neutral or alkaline atmosphere, hydrazine and methyl iodide have been found to form an aerosol effectively removed by high efficiency filters. The carbon dioxide in normal air interferes and must be neutralized. This work is continuing.

Mishima^[41] obtained high methyl iodide removal efficiencies by spraying a 35 per cent hydrazine hydrate solution through methyl iodide in ambient air at room temperatures. Tagged methyl iodide, and in some tests molecular iodine, were released into an aluminum tank 45" tall x 14" in diameter, with a volume of 0.114 m³, from alcohol and carbon tetrachloride solutions (See Figure 21). Various aqueous solutions were sprayed through the tank to evaluate their removal efficiencies. Methyl iodide concentrations were 1000 and 0.57 mg/m³. Spraying times ranged from 10 to 30 minutes, using 4 and 1 liter of liquid single-pass or recycled through the system. Residual airborne activity remaining was collected on charcoal at -78°C. Removal efficiency for 35 per cent hydrazine hydrate solutions ranging from 93-100 per cent were obtained. Results of all runs are listed in Table XXIV. Additional spraying tests using a larger facility and under more realistic post-reactor accident atmospheres* are planned.

The Behavior of Methyl Iodide in "Maypacks"

The distribution of tagged methyl iodide in "Maypacks" under various conditions has been reported by several authors^{[12][30][44]}. (A "Maypack" is a composite air sampler pack to differentiate the various airborne iodine species. It usually consists of: silver or copper screens for elemental iodine and HI, high efficiency filters for particles, charcoal paper for reactive vapor forms and charcoal granules.) Results are listed in Table XXV. In dry gases and low concentrations, methyl iodide appears to distribute between charcoal paper and granules.

*Atmospheres approximating those expected in a reactor containment vessel five days after a fuel melt-down accident will be used, an air-steam mixture at atmospheric pressure at 75°C. Methyl iodide concentrations ranging from 0.01 to 10 mg/m³ and a total iodine concentration ranging from 2.5 to 50 mg/m³.

TABLE XXIIIVAPOR PHASE REACTION OF METHYL IODIDE WITH CHLORINE AND
BROMINE AND RETENTION OF THE PRODUCT IN WATER

<u>Methyl Iodide Concen- tration In Air (mg/m³)</u>	<u>Halogen Concen- tration In Air (mg/m³)</u>	<u>Number Of H₂O Bubbles</u>	<u>Water Temp. (°C)</u>	<u>% Penetration Of Activity Through Water</u>
30	0.3 Chlorine	3	20	20
	0.5 Bromine	3	20	50
	0.5 Chlorine	3	60	50
	60.0 Chlorine	2	20	0.04
	42.0 Chlorine	4	20	<0.01

TABLE XXIV

PER CENT METHYL IODIDE SCRUBBED FROM AIR BY VARIOUS
SOLUTIONS SPRAYED INTO 114 LITER CHAMBER

<u>Extractant</u>	<u>Volume</u>	<u>Contact</u>	<u>I₂</u> <u>Concentration</u> <u>(mg/m³)</u>	<u>CH₃I</u> <u>Concentration</u> <u>(mg/m³)</u>	<u>%</u> <u>Extracted</u>
Water	4 liter	Single Pass	--	1000	5
	1 liter	Recycle	--	1000	--
			--	1000	5
			50.5	0.57	4
35% Hydrazine	4 liter	Single Pass	--	1000	93
	1 liter	Recycle	--	1000	--
			--	1000	100
				1000	100
			50.5	0.57	99
10% Hydrazine		Recycle	50.5	0.57	88
5% Hydrazine			--	1000	74
5% Ammonium Hydroxide			50.5	0.57	19
1% Ammonium Hydroxide			--	1000	30
5% Ethanol			--	1000	5

FIGURE 21

Schematic Diagram of Aerosol Spray System used in Methyl Iodide Extraction Experiment
Mishima 41

TABLE XXV

DISTRIBUTION OF ^{131}I TAGGED METHYL IODIDE IN A MAYPACK
FROM TRG-R 956(W), EXPERIMENTS RELATING TO THE CONTROL
OF FISSION PRODUCT RELEASE FROM AGR
 (Sampling Rate 300 cc/min)

	Weight CH_3I To Maypack (μgm)	Per Cent ^{131}I Activity			
		Copper	Millipore	Charcoal Paper	Charcoal
In dry gas	$10^{-3} - 10^{-2}$	<0.1	~0.2	~2.5	~75
	~1	--	0.2	~15	~85
	~10	--	0.1	~5	~95
In wet gas	$10^{-3} - 10^{-2}$	--	--	~5	~95
	~1	--	--	~5	~95
	~10	--	--	~2	~98

From AERE-M-1211 Iodine Compounds Formed On Release of Charcoal-free ^{131}I

	Wiggin Teape Charcoal Paper			
Sampling Rate 10 l/min	3.2	1.2	3.6	92

as the concentration and flow increase (reducing contact time), the methyl iodide concentrates in the charcoal granules. In the presence of moisture in a condensing system (an unheated "Maypack"), almost all the methyl iodide in the pack appears in the charcoal granules and may penetrate the entire pack. If the "Maypack" is maintained at or above the gas temperature, a dry gas distribution is again obtained.

The Behavior of Methyl Iodide in Liquid Gas Chromatographs

Liquid gas chromatography is a simple and efficient means of separating volatile materials. The use of gas chromatography as a means of analysis^[5]^{[12][13]} for, and in the preparation of^{[22][24]} methyl iodide is increasing. Eggleton and Atkins^[5] used a combination of gas chromatography-effusion techniques to analyze one fraction from the thermal decomposition of solid sodium iodide. Purified helium at a flow of 50 cc/min was used as carrier gas and 15 w/o di-nonyl phthalate or silicone oil on 60/80 mesh celite web used as stationary phase. The temperature of the 0.6 × 200 cm glass column was 40°C. These conditions are followed closely in almost all British work. Figure 22 is the chromatograph obtained for fraction "A" and Figure 23 a chromatograph of the vapors released from heating a highly irradiated uranium dioxide fuel element. Retention volumes were accurately determined by splitting the methyl iodide peak produced and combining each half with a spike of untagged methyl iodide. Each "spike" half was again chromatographed and divided. Comparison of the activity in each half would reveal small differences in retention volumes.

Collins, Taylor and Yuille^[13] used the above procedure in the analysis of iodine vapors from the heating of irradiated uranium dioxide fuel (see Figure 24). Diffey et al^[22] and Atkins and Arkell^[24] have used modifications of this procedure for purification of tagged methyl iodide.

Browning, Adams and Attrill^{[12][23]}, at ORNL, used silicone rubber as a stationary phase in the analysis of iodine from the thermal decomposition of solid palladium iodide (See Figure 25). Argon at 90 cc/min was used as the carrier gas with silicone rubber on inert support material as the stationary phase. The column was a 0.25" × 8' stainless steel tube with a column temperature at 75°C.

Haller^[31] used a silicone oil as a stationary phase and linear temperature programming to separate the alkyl iodides found in the gaseous effluent from a chemical processing plant. Helium was used as a carrier gas with silicone oil on 45/65 chromosorb in a 0.25" × 20' stainless steel column. Initial temperature

FIGURE 22
Gas Chromatogram of Activity
Released from Highly Irradiated
Uranium Dioxide
Eggleton and Atkins⁵

FIGURE 23
Gas Chromatogram of Fraction 4
from NaI Thermal Decomposition
Eggleton and Atkins⁵

FIGURE 24
Gas Chromatogram of Gaseous
Activity Released from Heated
Irradiated Uranium Dioxide
Collins, Taylor and Yuille¹³

FIGURE 25
Iodine Compounds Present in
Elemental Iodine Produced by
P415 Method
ORNL 1776²³

was 40°C with a linear rate of 6 to 10°C per minute. Activity in the effluent gases was collected at liquid nitrogen temperature in a mixture of untagged alkyl iodides and "peak splitting" used to determine retention volumes.

Methyl iodide retention volumes under various conditions using several stationary phases found in the literature are listed in Table XXVI.

TABLE XXVI

RETENTION VOLUMES OF METHYL IODIDE ON VARIOUS STATIONARY PHASES AND CONDITIONS

Carrier Gas	Flow (cc/min)	Column Material	Size	Temp. (°C)	Stationary Phase	Support Material	Retention Volume (ml)	Ref.	Remarks
Helium	50	Glass	0.6 × 200 cm	40	15 w/o Dinonyl Phthalate	60/80 Celite	346	3	
Helium	48	Glass	0.6 × 200 cm	40 ± 1	15 w/o Silicone Oil	60/80 Celite	214	6	Uncorrected for system dead space.
Helium	50	Glass	0.6 × 200 cm	40 ± 1	15 w/o Silicone Oil	60/80 Celite	214	26	
Argon	93	SS	0.25" 8'	75	Silicone rubber	--	90 sec*	8	
Helium	60	Copper	0.25" 4'	55	1,2,3 - Tris (2 Cyanoethoxy) Propane	60/80 Chromosorb	31.2	40	Corrected for system dead time.
				100			12.4		
				153			4.75		
				53			0.865†		
Helium	52 - 56	Glass	5 mm × 2 m	73	88' Oxydipropionitrile	60/80 Chromosorb	0.930†	41	Reference solute CCl ₄ . Peak retention time 4.0 min.
	48 - 54			93			0.550†		Reference solute CCl ₄ . Peak retention time 2.9 min.
	49 - 54			113			0.645†		Reference solute CCl ₄ . Peak retention time 4.3 min.
	56 - 60				Tri-M-Tolyl Phosphate				Reference solute CCl ₄ . Peak retention time 1.9 min.

* Retention time.

† Relative retention ratio — Retention Time Material:Retention Time Reference Solute

CONCLUSIONS

A considerable amount of information has been generated concerning methyl iodide and its behavior in the short time since its identification as a radioiodine vapor component. The vast majority of this data is limited to the elucidation of only certain limited circumstances and the theoretical expressions required to extrapolate this information to other applications are lacking.

The wide range of potential situations accompanying postulated reactor accidents introduces a considerable uncertainty into even the most realistic application of the data presented in this review. In some cases the data would prove entirely adequate, in others specific research will be required. Eventually, the data will be amplified to provide a broader understanding of methyl iodide. Some broad generalizations can be deduced from the information currently reported in the literature.

1. Methyl iodide has been identified as a compound of radioiodine released from fuel under many circumstances expected in and around a reactor, particularly CO₂ cooled reactors.
2. The amount of methyl iodide present under any given set of conditions is not easily calculated and is the result of many competing processes. The mechanisms of formation are not known. Direct substitution of radioiodine in the organic in a vapor phase reaction does not appear to be a likely process. The reaction does not occur readily even in solution.^[7] Direct substitution in the vapor phase of "hot", newly formed radioiodine does occur.^[28] Methyl iodide is also formed by some reaction in organic surfaces under reactor conditions.^[20]

Methyl iodide is decomposed by heat, light and radiation. Any methyl iodide present in the melting fuel would be virtually all decomposed.^[20] The radiation present in irradiated fuels may well be sufficient to preclude the presence of any significant amounts of methyl iodide.^[18,19] The temperature and atmospheric conditions present in reactor containment vessel after a fuel melt-down accident may well limit the methyl iodide concentration.^[20] Before the data currently available can be properly evaluated, the formation and decomposition mechanisms and the parameters affecting them need better definition.

3. Methyl iodide remains airborne for long periods of time, and may well be the predominant species airborne in time. The material does not go readily

into aqueous solutions^[22] and does not get carried down in condensate.^[12]

4. Several removal processes -- impregnated charcoals and vapor phase reactions (sprays) -- appear promising and are currently being investigated.^[39,40,41,42] The behavior of methyl iodide on charcoals has been studied extensively but has not been fully resolved. Charcoals and impregnated charcoals effectiveness under a variety of conditions have been reported.^[3,11,12,13,20,23,37,38,39,40] British workers find coal-based charcoal most effective^[10] while ORNL scientists find coconut-based superior.^[23] ORNL has reported good efficiencies using an iodine impregnated charcoal.^[39] British workers have previously reported iodine impregnation ineffective.^[11] Both agree that heterocyclic amines are effective impregnants but some volatilize at relatively low temperatures. Iodine^[39,40] and triethylene diamine^[40] are effective but iodides lowered the ignition temperature of coal-based charcoal from 440° to 250°C. Its effect upon coconut-based charcoal is not known. Since the mechanism controlling the adsorption of iodine by charcoal is not known, explanation of the effectiveness of impregnants can only be theorized. The effectiveness of charcoal for other iodine forms and its freedom from mechanical equipment commends its use in reactor air cleaning systems. Additional work to define the mechanism governing the adsorption of iodine on charcoal and controlling the effectiveness of impregnants is needed.

The effectiveness of vapor phase reactions has been demonstrated in several experiments.^[11,41,42] Hydrazine hydrate vapor appear to be effective although a great deal of work is still required to define the mechanisms involved and optimize removal efficiency. The usefulness of bubbling through aqueous pools appears to be severely limited.^[22,41]

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