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Gas Phase Chemistry and Removal of CH_3I during a Severe Accident

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January 2001

Abstract

The purpose of this literature review was to gather valuable information on the behavior of methyl iodide on the gas phase during a severe accident. The potential of transition metals, especially silver and copper, to remove organic iodides from the gas streams was also studied. Transition metals are one of the most interesting groups in the context of iodine mitigation. For example silver is known to react intensively with iodine compounds. Silver is also relatively inert material and it is thermally stable. Copper is known to react with some radioiodine species. However, it is not reactive toward methyl iodide. In addition, it is oxidized to copper oxide under atmospheric conditions. This may limit the industrial use of copper.

Key words

Methyl iodide, gas phase, severe accident mitigation

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The purpose of this literature review was to gather valuable information on the behavior of methyl iodide on the gas phase during a severe accident. The potential of transition metals, especially silver and copper, to remove organic iodides from the gas streams was also studied. Transition metals are one of the most interesting groups in the context of iodine mitigation. For example silver is known to react intensively with iodine compounds. Silver is also relatively inert material and it is thermally stable. Copper is known to react with some radioiodine species. However, it is not reactive toward methyl iodide. In addition, it is oxidized to copper oxide under atmospheric conditions. This may limit the industrial use of copper.

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Abbreviations

ΔH°_{298}	Reaction entalphy in 298 K.
ΔH°_f	Heat of formation
$D\Delta H^{\circ}_{298}$	Dissociation entalphy
DF	Contamination factor
E_a	Activation energy
F	Aqueous conversion factor
G	Gibb's free energy
P	Partition coefficient
RH	Relative humidity
TEDA	Triethylene diamine

1 Introduction

This is a literature review of the gas phase chemistry of methyl iodide and its catalytic decomposition. The behaviour of iodine and its compounds is not fully agreed, since the chemistry of iodine is very complex. The chemical system in the containment during a severe accident includes the released fission products from the primary circuit, steam, water, organic material, metal and concrete surfaces [Beahm *et al.* 1985]. Furthermore, iodine compounds may partition between aqueous phase, gas phase and painted surfaces [Marchand & Petit 1999].

Iodine is one of the most important fission products in the context of reactor safety. This is based on the total fuel inventory of iodine, its short half-life and diverse chemistry. Iodine is released from the core most likely as CsI during a severe accident [Mezyk & Bartels 1994]. In addition, other metallic iodine compounds such as AgI, InI and FeI are possible. A small fraction of iodine may also be released as gaseous iodine HI, I and I₂. Volatile elemental iodine is expected to form in the radiolytic oxidation from iodide ion. The formation of I₂ is strongly dependent on the pH of the sump water. The rate of formation of volatile iodine species is expected to increase considerably in acidic conditions. Thus, the pH control plays an essential role in the iodine mitigation [Beahm *et al.* 1992].

The removal of elemental iodine from the gas streams is satisfactory. It has a reasonably high diffusion coefficient in air, about 0.080 cm²/s. Therefore, a relatively high gasfilm mass transfer coefficients are possible in normal adsorption or absorption equipment. Iodine is also sufficiently reactive that a number of reagents are available to ease the removal [Chamberlain *et al.* 1963]. Painted surfaces may also act as iodine sinks, since elemental iodine has a high affinity to them [Marchand & Petit 1999]. However, the removal of other gaseous iodine species is quite different from simply removing elemental iodine from the gas streams [Chamberlain *et al.* 1963]. Organo iodides are of particular interest, when talking about iodine mitigation during a severe accident.

Organo iodides form most likely in the radiolytic reaction between elemental iodine and organic radicals during a severe nuclear accident. Iodine is a very effective scavenger of free radical reactions. This may lead to the formation of vast variety of organic iodides. The formation and decomposition of organic halides is a dynamic system, in which iodine species enter the containment and interact with a complex mixture of gases with transport to and from the surfaces and aqueous solution [Marchand & Petit 1999]. It is not fully agreed in which phase organic iodides are formed. However, the partition coefficient for example for methyl iodide is only three and it is rapidly transferred to the gas phase after its formation [Beahm et al. 1985].

The gaseous organic iodides are able to penetrate most filters currently in use. Thus, better understanding of behaviour of organic iodides during a severe accident is needed, when developing new methods to prevent the source term during an accident. The potential of some new materials is discussed in this review. Transition metals such as silver, copper, palladium were introduced in the previous report “*Methods to Prevent the Source Term during a Core Melt Accident*”. Main emphasis in this literature study is on the silver compounds and their use in the filters. Properties of copper and some other compounds are also discussed.

2 Properties of Methyl Iodide

Only short introduction of the properties of methyl iodide is given here. More precise information is already covered in the previous report “*Methods to Prevent the Source Term of Methyl Iodide during a Core Melt Accident*”. Methyl iodide is a clear, colorless liquid, which has acrid odor. Its solubility is 14g / 100g of water at 20°C [J.T.Baker 2000]. Although organic iodides are relatively soluble in water, the rate of dissolution is slow. The dissolution rate can be increased for example using a mixture of organic iodides and methanol. Organic iodides have a high vapour pressure [Mezyk & Bartels 1994]. The vapor pressure of methyl iodide is about 53 kPa at 25 °C. Methyl iodide is a volatile compound and its volatility by volume is 100% at 21 °C. The half-life of methyl iodide in water is most likely over 30 days. Care should be taken when handling methyl iodide with strong oxidizers, powdered metals and reducing agents, because the reaction may be vigorous [J.T.Baker 2000].

3 Partition of Iodine and Methyl Iodide between Aqueous Phase, Gas Phase and Surfaces

A number of different iodine species may be formed during a severe accident such as I_2 , I^- , HOI , IO_3^- and CH_3I [Lutz & Kelly 1987]. These compounds may be partitioned between aqueous phase, gas phase and painted surfaces. Methyl iodide is more volatile compound than elemental iodine. At 298 K the partition coefficient for methyl iodide is around 3, whereas for elemental iodine is about 86. Thus, the formation of methyl iodide adds to the partitioning of iodine species to the containment atmosphere [Beahm et al. 1985]. Methyl iodide and other organic iodides are of particular interest during a severe accident, since they are difficult to remove from the gas streams. Methyl iodide is also able to penetrate most of the filters currently in use [Marchand & Petit 1999].

The partition coefficient depends significantly on temperature. This is inversely related to Henry's law constant K . Gas-liquid partitioning of volatile elemental iodine can be presented by partition coefficient [Beahm et al. 1992]:

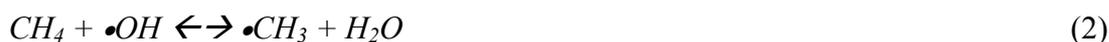
$$P = \frac{[I_2(aq)]_{eq}}{[I_2(g)]_{eq}} \quad (1)$$

There is a large amount of water present in the containment, which affects iodine volatility. Large volumes of water also lower the dose rate and retain dissolved I_2 . Iodine volatility is strongly dependent on the aqueous conversion factor. Aqueous conversion factor was estimated according to ORNL data to be $F = 3 \cdot 10^{-4}$. This number indicates that only a small amount of iodine would be released to the gas phase, when pH of the sump is maintained above seven. In acidic pH a large fraction of non-volatile I^- is converted to volatile I_2 . Therefore, evaporation of volatile iodine species increases in order to recover equilibrium partitioning. I_2 concentration in the containment atmosphere increases. A higher I_2 concentration also enhances the formation of organic iodides and leads to even greater total iodine concentration in the gas phase [Beahm et al. 1992].

The studies of Weaver et al. show that organic iodide concentration in the gas phase can be accounted using a mechanism involving the formation of organic iodides in the aqueous phase and the subsequent partitioning of these species to the gas phase. This suggests that the formation of organic iodides in the gas phase would be of minor importance [*Weaver et al. 1996*].

4 Formation of Methyl Iodide

The conversion of elemental iodine to organic iodides during a core melt accident is not fully understood. This may lead to the formation of vast variety of compounds. Postma and Zavadoski stated in their article in 1972 that the formation of organic iodides under irradiation in the gas phase was significant. Also surface reactions were considered at the time. On the other hand, methyl iodide was believed to undergo hydrolysis in an aqueous phase forming methanol and iodide [Beahm *et al.* 1985]. This is quite the opposite compared to the current data. It is generally accepted that the homogeneous gas phase reactions are of minor importance in the formation. This is due to the relatively low concentrations of both organic radicals and elemental iodine in the gas phase. Thus, the formation of organic iodides proceeds either via the heterogeneous gas phase reactions on the surfaces or via aqueous phase reactions. It is difficult to determine, which one is the most important pathway. The large impact of pH of the sump water should be also taken into account, when considering the formation of organic iodides and iodine volatilisation [Wren *et al.* 1996]. The formation of organic iodides is a dynamic system between different reaction paths such as sorption and desorption, radiation-induced formation, decomposition etc. In the table 1. a list of different gaseous species, which may affect the formation or decomposition of organic iodides, is presented. For example organic compounds form readily free radicals as a result of ageing, thermal degradation or irradiation. These radicals may easily react further and form organic iodides and other halides [Beahm *et al.* 1985]. For example, methyl radicals may be formed in aqueous media in the reaction of methane and hydroxyl radicals [Paquette & Ford 1990]:



The rate constant for the reaction $1.1 \cdot 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ in buffered aqueous media as referred to results of Buxton by Paquette and Ford. On the other hand, methyl radicals react rapidly with elemental iodine in both gas and aqueous phase, since iodine is an

effective scavenger in free radical reactions. The production of methyl iodide is proportional to the concentration of I₂ [Paquette & Ford 1990]:



The rate constant for the reaction of elemental iodine and alkyl radical depends on the structure of the radical. The larger the radical fragment is, the greater the rate constant for the reaction [Garibyan et al. 1987].

Table 1. A list of gaseous compounds, which may affect the formation of organic iodides [Beahm et al. 1985].

CH ₃ I	C ₂ H	CH ₃ CH ₂ OH	N ₂ O ₅	CH ₃ NO ₃
C ₂ H ₅ I	C ₂ H ₂	CO ₂	N ₂ O ₄	N ₂ H ₄
CH ₂ I ₂	C ₂ H ₄	CO	N ₂ O ₃	N ₂ H ₂
I ₂	C ₂ H ₅	H ₂ O ₂	NO ₃	NH ₃
HI	C ₂ H ₆	HO ₂	NO ₂	NH ₂
HOI	CH ₃ OH	H ₂ O	NO	NH
NOI	CH ₃ OOH	OH	CN	N ₃
IO	CH ₂ O	O ₃	HCN	N ₂
CNI	HCO	O ₂	CN ₂	N
COI ₂	C ₂ H ₄ O	O	C ₂ N ₂	H ₂
CH ₄	CH ₂ CO	HNO	CNO	H
CH ₃	HCOOH	HNO ₂	CHNO	
CH	CH ₃ COOH	HNO ₃	CH ₃ NO ₂	

4.1 Formation of Methyl Iodide in the Gas Phase

Irradiation in the gas phase affects significantly iodine chemistry, even though the radiation stopping power in the gas phase is much smaller than in the aqueous phase. This is due to a large difference in the density. Without irradiation the extent of the reaction between alkane and elemental iodine is small and the equilibrium lies well on the left. Therefore, the radiation is most likely the main driving force in the formation of organic iodides in the gas phase. The formation of organic iodides is believed to proceed in the reaction between elemental iodine and free organic radical, which is formed by irradiation. Organo iodides are also observed in radiation chemistry experiments, where iodine is used as a free radical scavenger during radiolysis of gases. According to studies of Postma and Zavadoski a free energy value, $G(\text{CH}_3\text{I})$, of radiolysis of methane and iodine can be presented as a function of iodine concentration. They have also calculated a conversion of 2.2% of iodine to methyl iodide in a postulated accident with the adsorbed dose around 32 kGy. This value was decreased with the addition of water vapor, oxygen or both. The value was increased with the increase of the ratio of methane to iodine [Wren 1987].

Goy and Pritchard have studied the formation of methyl iodide in the gas phase. They performed equilibrium experiments with I_2 and CH_4 . The results of the experiments with varying temperature and constant concentrations are shown in table 2. [Goy & Pritchard 1965]. Paquette and Ford observed in their studies that the concentration of methyl iodide was increased, when the volume of the gas phase was increased to 40 vol% at pH 3 and after adsorption of 3.5 kGy radiation dose. Thus, methyl iodide is likely to be formed in the gas phase under these conditions [Paquette & Ford 1990].

Table 2. The equilibrium $\text{CH}_4 + \text{I}_2 \leftrightarrow \text{CH}_3\text{I} + \text{HI}$ at temperatures between 585 – 748 K [Goy & Pritchard 1965].

T, K	$\text{Log } K_T$	$\Delta[-(F_T^\circ - H_{298}^\circ)/T], \text{J/mol deg}$	$\Delta H_{298}^\circ, \text{kJ/mol}$
748	-2.9455	14.570	53.110
732	-3.0627	14.595	53.076
717	-3.0871	14.474	52.783
708	-3.1588	14.449	53.076
688	-3.2595	14.386	52.863
620	-3.7300	14.181	53.097
616	-3.7110	14.172	52.523
607	-3.8063	14.143	52.850
585	-3.9688	14.084	52.720
			Average: 52.900

$\Delta[-(F_T^\circ - H_{298}^\circ)/T]$ is the free energy function that is tabulated in JANAF tables for CH_4 , I_2 and HI . Both calculations and experiments showed that the change in the free energy is precisely linear over the temperature range 600 – 800 K. ΔH_{298}° is the heat of the reaction. It can be calculated with the following equation [Goy & Pritchard 1965]:

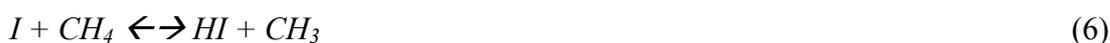
$$\Delta H_{298}^\circ = -RT \ln K_T + T\Delta[-(F_T^\circ - H_{298}^\circ)/T] \quad (4)$$

Golden et al. have also studied the heat of the reaction. The results of their studies are given in table 3 [Golden et. al. 1965].

Table 3. Thermodynamic data of $\text{CH}_4 + \text{I}_2 \leftrightarrow \text{CH}_3\text{I} + \text{HI}$ [Golden et. al. 1965].

T, K	$\Delta H_{298}^\circ, \text{kJ/mol}$
605.6	52.88±0.80
630.4	52.59±0.54
666.9	52.71±0.75

The average change in enthalpy for the reaction $\text{CH}_4 + \text{I}_2 \rightleftharpoons \text{CH}_3\text{I} + \text{HI}$ is $\Delta H = 52.92 \pm 0.21$ kJ/mol. This includes eight of the nine results obtained by Golden et al. The heat of formation obtained from these results is $\Delta H_f^\circ_{298} = 14.24 \pm (2.09 \pm x)$ kJ/mol. x is an uncertainty in the heats of formation for CH_4 , $\text{I}_2(\text{g})$ and HI given in JANAF tables [Goy & Pritchard 1965]. The heat of formation given in CRC, $\Delta H_f^\circ_{298} = 12.98$ kJ/mol [Weast 1984]. Also Golden et al. have reported a value $\Delta H_f^\circ_{298} = 13.73 \pm 0.67$ kJ/mol [Golden et. al. 1965]. The values are in relatively good agreement with each other. The overall activation energy for the formation of methyl iodide was found to be 221.9 ± 4.6 kJ/mol. The rate of formation was found to be half order for I_2 and first order for CH_4 at temperatures between 548 – 618 K. The following mechanisms were introduced [Goy & Pritchard 1965]:



However, according to Sykes, iodine radical is not capable of capturing hydrogen atom from methane without extra energy. The ΔH for following reactions is [Sykes 1986]:



4.2 Formation of Methyl Iodide in the Heterogeneous Reactions

The heterogeneous reactions on the surfaces play most likely an important role in the formation of organic iodides. Painted surfaces are able to trap elemental iodine, since volatile I_2 has a high affinity to them [Marchand & Petit 1999]. Elemental iodine may react further with the compounds and coatings on the surface. The studies of Dickinson et al. showed that a significant amount of organic iodides might be formed on the painted surfaces under irradiation. According to these studies, organic iodides were also formed

even without irradiation on the surfaces at very high temperatures. However, the rate of formation was much lower without irradiation. At low temperatures without irradiation, no formation of organic iodides could be detected. The formation was also decreased, when the surface was submerged in water at pH 7 [Dickinson et al. 1999b].

4.3 Formation of Methyl Iodide in the Aqueous Phase

The formation of methyl iodide in the aqueous phase is only shortly discussed here. The formation of methyl iodide is largely affected by pH in the aqueous phase. The studies of Paquette and Ford shows that about 40% of initial iodine concentration is converted to methyl iodide, when a dose rate around 2.0 kGy is adsorbed by the buffered solution at pH 7. The remaining iodide species are most likely iodates [Paquette & Ford 1990].

5 Decomposition of Methyl Iodide

Both elemental iodine and methyl iodide are susceptible to thermal and radiolytic decomposition in the containment atmosphere. Methyl iodide undergoes complete thermal decomposition below 400 °C [Bartonicek et al. 1975]. Golden et al. received the value for bond dissociation energy of CH₃-I:

$$\begin{aligned} DH_{298}^{\circ}(\text{CH}_3\text{-I}) \\ = \Delta H_f^{\circ}(\text{I}(\text{g})) + \Delta H_f^{\circ}(\text{CH}_3(\text{g})) - \Delta H_f^{\circ}(\text{CH}_3\text{-I}(\text{g})) = 235.7 \pm 2.1 \text{ kJ/mol} \end{aligned} \quad (10)$$

The tabulated heats of formation of H and I were used in the calculations [Golden et al. 1965]. Methyl iodide decomposes also on exposure to light. Burning methyl iodide produces toxic iodine vapors [J.T. Baker 2000].

Iodine and methyl iodide are able to react easily with a number of compounds, which may be present in the containment during a severe accident. Elemental iodine reacts for example with ozone producing solid oxides. Ozone is produced by the irradiation of O₂ [Wren et al. 1987]. It has been proposed that mitigation of gaseous iodine could be enhanced by increasing the production of ozone using ultraviolet photolysis of oxygen. However, the gas phase reaction of iodine with ozone is slow and a high concentration of ozone would be needed [Funke et al. 1999].

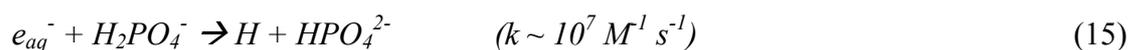
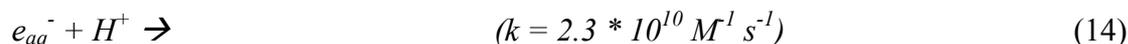
The competitive reactions of organic free radicals with other compounds such as oxygen radicals may also decrease the overall formation rate of organic iodides. The reactions of organic radical with oxygen and nitrogen oxide are shown below [Wren 1987]:



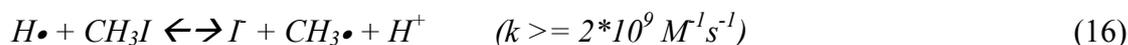
Irradiation of N₂ in air may lead to the formation of N₂⁺ or N⁺, which may in turn react with water vapour and oxygen producing nitric acid. This may have a large impact on iodine chemistry, since nitric acid decreases the pH of the sump water. Thus, more iodine is volatilised [Wren *et al.* 1987]. Also the radiolysis of water affects the iodine chemistry. Following species may be in the radiolysis of water [Neta 1972]:



Hydrogen atoms may also be formed in the reaction of hydrated electrons with acids in aqueous solution [Neta 1972]:



Hydrogen radical may also abstract atoms or radicals from saturated compounds [Neta 1972]:



It was concluded that the reaction mechanism is most likely dominated by a halogen atom abstraction as is the case also in the reaction between C₂H₅I and hydrogen. The reaction is partially in the diffusion-limited category. The gas phase activation energy for the reaction of hydrogen with methyl iodide is $E_a < 13.4$ kJ/mol. The room temperature rate constant is $(5.86 \pm 0.29) * 10^9$ dm³ mol⁻¹s⁻¹, which is almost two times slower than the reaction in the aqueous phase. This is typical for halogen abstraction by •H. The rate constant of the reaction of hydrogen with methyl iodide, ethyl iodide or 1-iodopropane in aqueous solutions has been determined by Mezyk and Bartels. The rate constants for these reactions are given in table 4. Although organic iodides used in this study are relatively water soluble, their dissolution rate is slow. Also the rate constants for the reaction of hydrogen and methyl iodide at different temperatures are calculated. They are

presented in table 5 [Mezyk & Bartels 1994].

Table 4. The rate constants for the reaction of hydrogen and organic iodides in aqueous solution. The respective activation energies are calculated over the temperature range of 9 to 52 °C [Mezyk & Bartels 1994].

	CH ₃ I	CH ₃ CH ₂ I	CH ₃ CH ₂ CH ₂ I
Rate constant (dm ³ /mol*s)	(1.17 ± 0.07)*10 ¹⁰	(1.39 ± 0.05)*10 ¹⁰	(1.142 ± 0.06)*10 ¹⁰
Activation Energy (kJ/mol)	(10.4 ± 0.4)	(11.8 ± 0.4)	(11.9 ± 0.4)

Table 5. Summary of the temperature-dependent rate constant data for hydrogen atom reaction with methyl iodide in aqueous solution [Mezyk & Bartels 1994].

Temperature (°C)	Scavenging rate constant dm ³ /mol*s
8.5	(9.44 ± 0.13)*10 ⁹
17.4	(1.06 ± 0.03)*10 ¹⁰
24.1	(1.17 ± 0.07)*10 ¹⁰
24.2	(1.21 ± 0.05)*10 ¹⁰
40.4	(1.44 ± 0.06)*10 ¹⁰
50.5	(1.69 ± 0.13)*10 ¹⁰

6 Removal of Iodine Compounds from the Containment Atmosphere

Filters are required to remove low concentrations of gaseous iodine species from the gas streams. Other requirements are high removal efficiency of iodine compounds and a good performance even in high RH [Funabashi *et al.* 1994]. The active carbon filters are commonly used in the nuclear industry to remove radioactive iodine species [Billinge *et al.* 1984]. However, active carbon filters are flammable and they release adsorbed iodine again around 150 °C [Lothar & Jurgen 1990]. There are also studies of zeolite filters, since they have shown a high affinity toward methyl iodide. However, neither of these base materials tolerates high relative humidity, and the penetration of methyl iodide through the filter may occur during a severe accident. When the relative humidity is over 50%, only a small fraction of the surface area of the porous filters is available according to Billinge *et al.* The adsorption in these conditions occurs mainly through meso- and macropores. Thus, an addition of impregnants such as TEDA and KI is essential in order to maintain the capacity of the filter in an acceptable level. These impregnants have some limitations, which limits their use in certain conditions [Billinge *et al.* 1984]. The impregnated filters and sprays are discussed in more detail in the previous literature review “*Methods to Prevent the Source Term of Methyl Iodide during a Core Melt Accident*”. In general, there is a need for more reactive and stable impregnants and bed materials.

A catalytic filter may provide a solution for removing methyl iodide from the gas streams. The catalysts are membranes, recombiners or powders. The supporting materials for catalytic reactions are often insulators such as SiO₂, Al₂O₃, TiO₂, MgO and different zeolitic frameworks. Ceramic materials such as SiC are also used. Activity of the catalyst is affected by the crystallite morphology, loading, pretreatment and reaction conditions. The support material may also affect the activity, since some carriers such as ZrO₂ are catalytically active [Méthivier *et al.* 1998].

Chamberlain et al. have studied the sorption of iodine to various surfaces. The results of their studies are presented in table 6. The effect of temperature on the iodine sorption is significant only in the surface of copper and silver [Chamberlain et al. 1963]. The properties of copper and silver will be discussed in more detail in this review. Also lead, zinc, cadmium may be considered as an iodine-adsorbing metal. However, silver is the most effective metal. The amount of methyl iodide adsorbed by different metals is shown in table 7. [Kamiya et al. 1980].

Table 6. The sorption of iodine to various surfaces in air at 20 °C and 200 °C. Sorption time was 1 h [Chamberlain et al. 1963].

	Low vapor concentration		High vapor concentration	
	20	200	20	200
Temp. (°C)	20	200	20	200
I ₂ conc. (mg/m ³)	0.73	0.50	46.5	37.2
I ₂ on surface (µg/cm ₂):				
Glass	0.043	0.015	0.45	0.40
Magnesium	0.21	0.031	1.83	1.96
Graphite	0.063	0.075	1.00	1.32
Aluminium	0.107	0.037	1.32	1.15
Mild Steel	0.36	0.50	5.7	1.52
Copper	2.0	0.90	108	17.2
Silver	1.6	0.81	90	40

Table 7. The amount of adsorbed methyl iodide by different metals [*Kamiya et al. 1980*].

Metal in nitrate form on support	Adsorbed CH ₃ I per 1 mol of metal (mmol)
Ag	0.26
Cu	0.16
Pb	0.15
Zn	0.13
Cd	0.12
Ni	0.10
Co	0.08

6.1 Silver Impregnated Filters

Non-carbenous adsorbents for organic halides are typically substrates for silver or lead compounds. These are zeolites, silicas and alumina-silica composites. These are usually more sensitive to water than carbon adsorbents, but they are more stable in high temperatures and in oxidising environment [*Chamberlain et al. 1963*].

6.1.1 Silver Impregnated Alumina

Funabashi et al. have studied the removal of methyl iodide with silver alumina. Silver impregnated alumina was prepared by dipping alumina into a silver nitrate solution under reduced pressure. The chemical form of silver was transformed mainly by soaking AgNO₃ impregnated alumina into a solution of sodium salt. The test facility is shown in figure 1 [*Funabashi et al. 1994*].

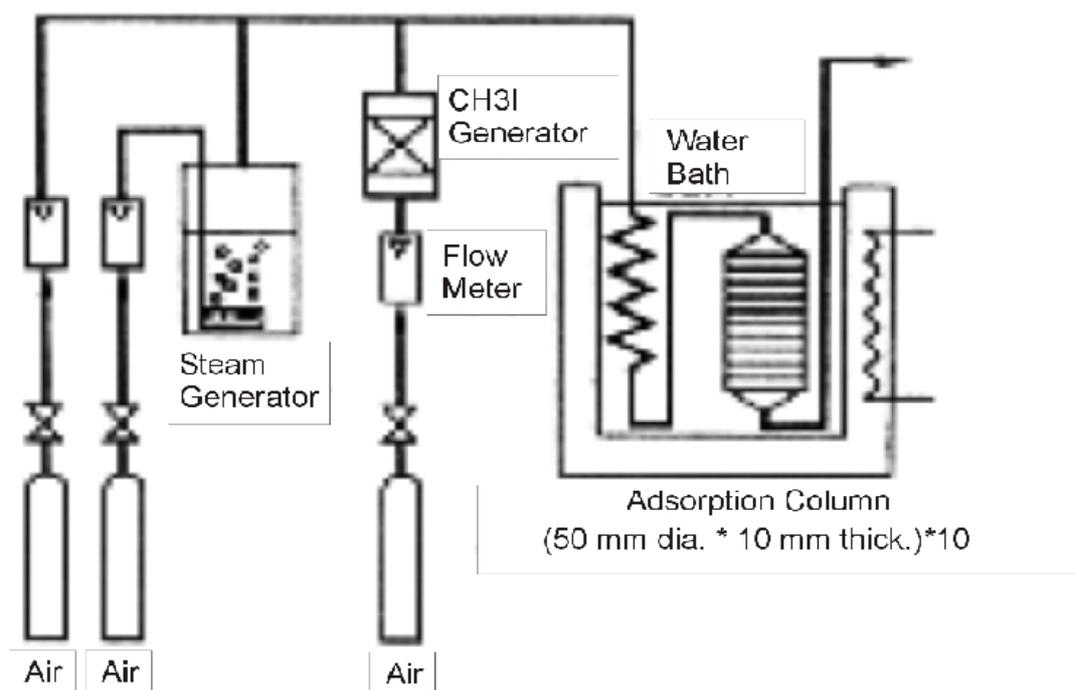


Figure 1. A schematic picture of the test facility to study the removal of methyl iodide by silver impregnated alumina [Funabashi et al. 1994].

The efficiency of the filter was determined by measuring the decontamination factor (DF), which can be derived from an equation [Funabashi et al. 1994]:

$$DF_x = Q_T / Q_{n+10} \quad (17)$$

Where x = bed depth

N = bed number from the column inlet

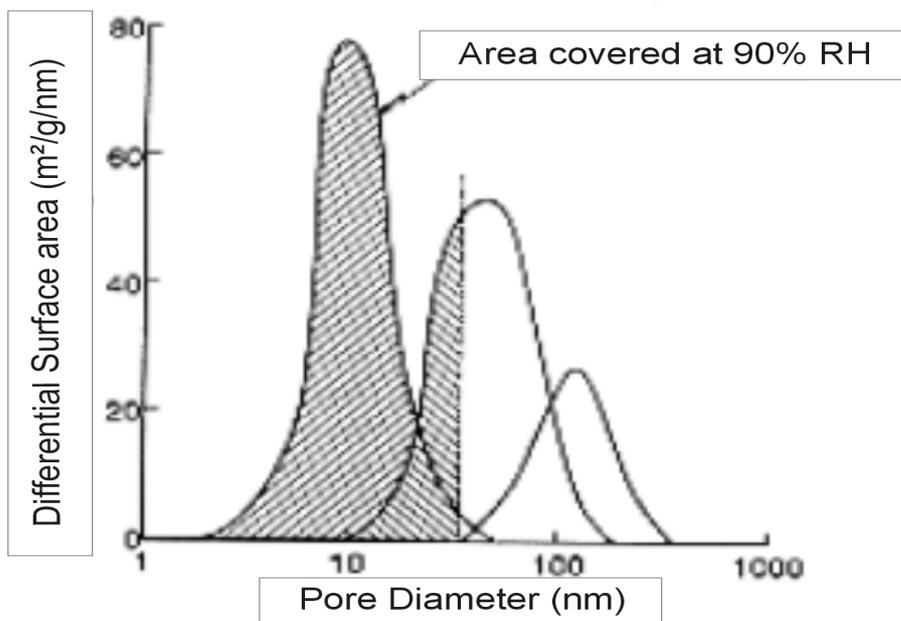
Q_T = CH_3I amount adsorbed in all (1 to 10) sections of the column

Q_T = CH_3I amount adsorbed in $n+1$ to 10 sections of the column.

The pore diameter of three filters was determined. The distribution of pore sizes is shown in figure 2. In 90% relative humidity, the micropores are affected more than meso- and macropores, which can be seen in figure 2. This is due to the condensation of water vapor to smaller pores, which leads to decrease in the surface area available for the reaction. The optimum pore size for alumina carrier was estimated to be around 60 nm. With a

pore diameter of 60 nm, most of the surface was free of water and available for the reaction to take place [Funabashi et al. 1994].

Figure 2. The distribution of pore diameters in different alumina carriers. The



comparison of the effect of high relative humidity to different pore size [Funabashi et al. 1994].

The studies Kamiya et al. of silver-alumina adsorbent also showed that the efficiency of this particular adsorbent remains almost constant even in higher RH, when its mean pore size is around 20-200 Å and the pore volume at least 0.1 cc/g. This is different from the conventional silver-zeolite adsorbents. The comparison between silver-alumina and silver-zeolite adsorbents is shown in figure 3. [Kamiya et al. 1980].

Funabashi et al. studied also the effect of different precursors for impregnated silver. The efficiency of the precursor was determined using DF. The studied silver compounds were Ag, Ag₂O, Ag₂SO₄, AgClO₃ and AgNO₃. The silver content in the filter was 10 wt%. No differences between different silver compounds were observed in low RH. In 0% RH the DFs were less than 500 for all silver precursors. At low RH methyl iodide reacts directly

with the silver compound via a gas-solid reaction. The DFs at different RH as a function of the solubility in water are shown in figure 4. [Funabashi et al. 1994].

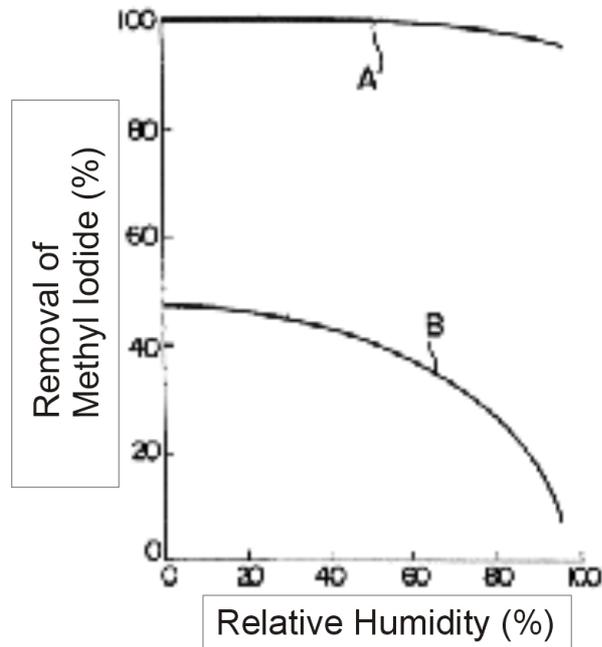


Figure 3. The comparison of silver/alumina filter (A) with a mean pore size between 20-200 Å to conventional silver/zeolite filter (B) [Kamiya et al. 1980].

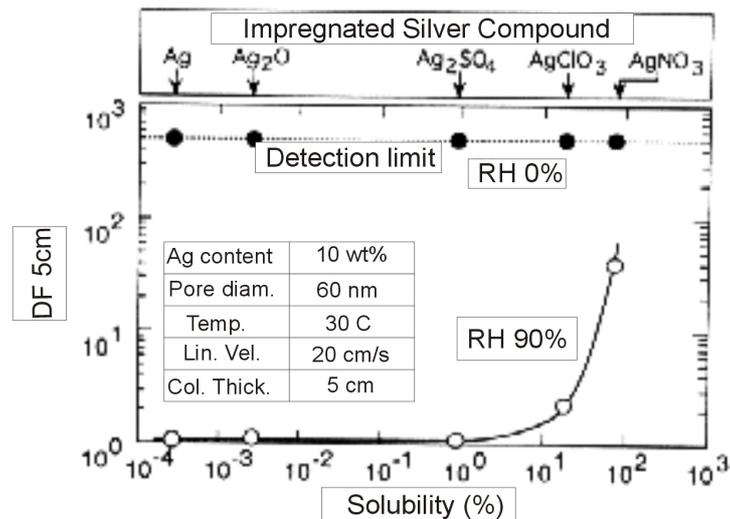


Figure 4. The efficiency of different silver compounds presented as DF compared to the solubility [Funabashi et al. 1994].

The decontamination factor is affected by the solubility of the impregnant in high relative humidity as seen in figure 4. AgNO₃ exhibited the highest DF in 90% RH of the studied compounds. It is believed that water adsorbed into the micropore forms a water layer on the impregnated silver compound. The water layer decreases the reaction rate between methyl iodide and insoluble silver compounds. On the other hand soluble silver compounds form Ag⁺ ions in the water layer, which enhances methyl iodide adsorption by water surface ionic reaction [Funabashi et al. 1994].

6.1.2 Silver Impregnated Zeolite

Zeolites are aluminosilicates with a following structure:



M is an element either from group 1 or 2, n is the cation valence, y equals at least 2 and w is the number of water molecules. Suitable molecular sieves are for example sodium aluminosilicates with a structure of faujasite type [Lothar & Jurgen 1990]:



In the impregnation of the filter with silver, the sodium ions are exchanged to silver ions. The sorbent particles are loosely packed granules such as beads, rodlets, grains or chips. They are few millimeters in diameter, which comprises 80 to 90% zeolite X and 10 to 20% zeolite A. With silver-exchanged zeolite filter high degrees of separation of methyl iodide and elemental iodine from the gas streams are achieved. The filter maintains its high efficiency even at high RHs according to Lothar & Jurgen. They have also reported that silver-exchanged molecular sieve zeolites can tolerate superheated steam. Unlike in impregnated silica gel filters the impregnant is not washed out from the zeolite filters in superheated conditions [Lothar & Jurgen 1990]. According to Kamiya et al. the silver-zeolite filter has one disadvantage, when compared to active carbon filter. Since the pore size of zeolite is as small as 10 Å, water vapor is easily condensed in these pores

inhibiting the reaction of iodine with the impregnant. Thus, the pore size of the zeolite filter plays an important role [Kamiya et al. 1980].

6.1.3 Other Silver Impregnated Adsorbent Materials

Some adsorbers may be used to separate iodine under precisely defined conditions. These are for example silver impregnated ceramics (Berl saddles), silver coated copper chips and silver impregnated silica gel. However, these are insufficiently effective or totally ineffective for removing methyl iodide. They also lose their efficiency, when superheated steam is passed through. Impregnated silica gel takes up water easily, which causes a decrease in efficiency. There has been a report on an amorphous silica, which is capable in removing various iodine compounds. It also tolerates superheated steam, but the salt impregnation may be washed out under superheated conditions at 150 °C [Lothar & Jurgen 1990].

6.2 Metallic Silver

Silver is relatively inert to variety of chemicals. It is also thermally stable. Under normal conditions, silver is attacked only by cyanide solutions, nitric and sulfuric acids. Therefore, it is used in membrane filters. Silver membrane filters provide an excellent filtration from cryogenic temperatures up to 550 °C [SPI 2000]. Tachikawa et al. have studied the properties of granulated silver (7/20 mesh) to remove radioiodine compounds in a gas phase with a success [Tachikawa 1975]. In addition, the studies of Dickinson et al. with a silver mesh in a solution showed that the reaction of iodine with excess of silver reduces the volatility of iodine. Silver has a large effect especially in the acidic pH of the sump water and high ratio of Ag and I. The reaction kinetics gave a pseudo-first order rate constants. Stirring had a great impact to the reaction rate, which indicates that the reaction is mass-transfer limited. It was also proved that silver iodide was stable to irradiation at the dose rates used in these studies. The model based on these studies show that reaction of iodine and silver has a great potential to trap iodine during severe accident [Dickinson et al. 1999a].

The studies of Dai et al. show that methyl iodide reacts well with silver surfaces. The reaction is dependent on the reaction conditions. The interaction of methyl iodide and silver results morphological changes to the surface. The changes on the surface with different loadings of methyl iodide in an aqueous methanol are shown in figure 5. It can be seen from the figure that small holes in the branches of silver are formed. This is explained by the corrosion of methyl iodide [Dai et al. 1998]:



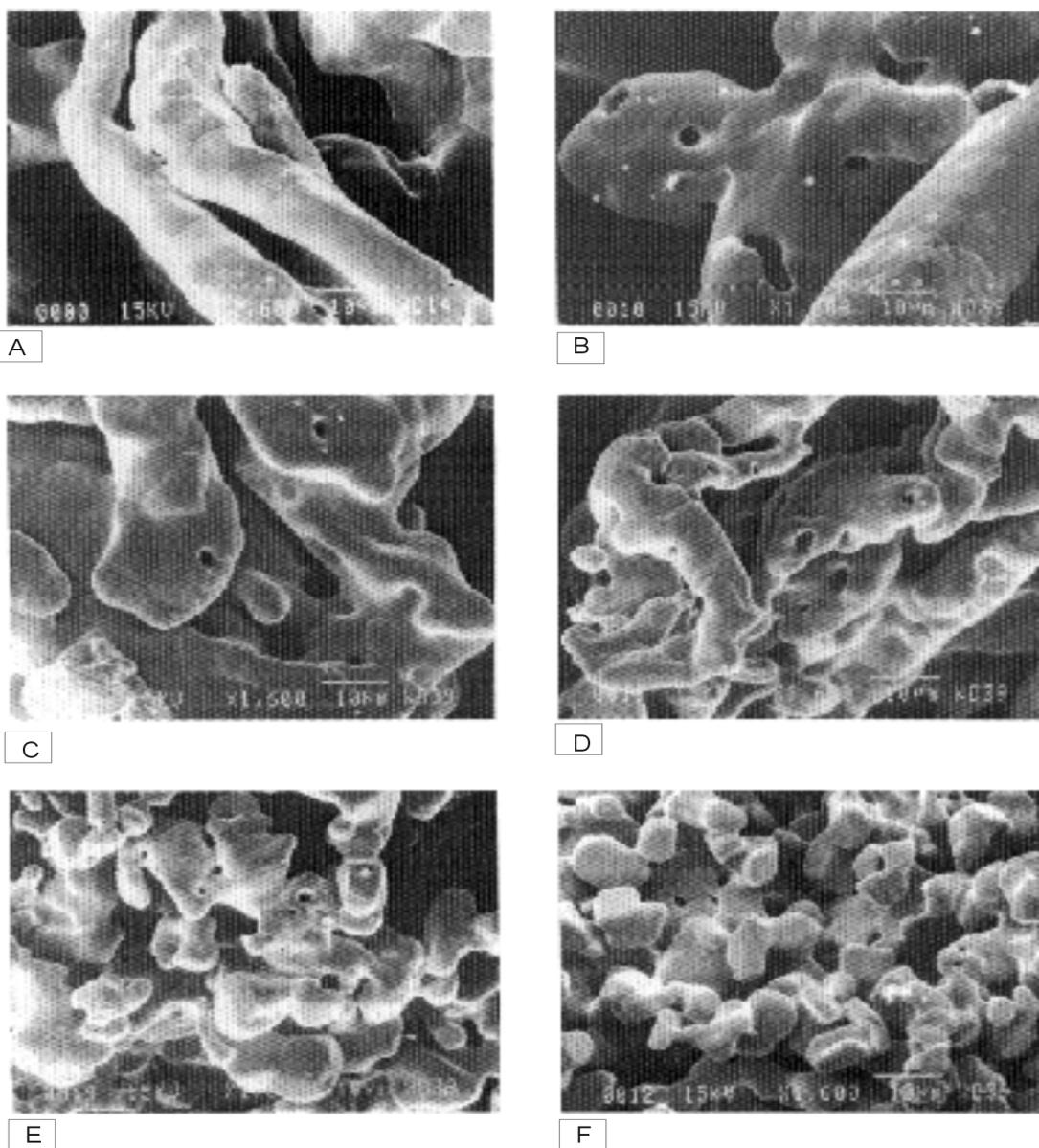
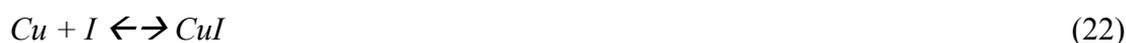


Figure 5. SEM photographs on the effect of different methyl iodide concentrations in a 60% aqueous solution of methanol to 3 g of electrolytic silver surface: a) electrolytic silver; b) 10 ppm; c) 30 ppm; d) 100 ppm; e) 300 ppm; f) 1000 ppm. Reaction temperature was $\sim 620\text{ }^{\circ}\text{C}$, space velocity $\sim 1.2 \times 10^5\text{ h}^{-1}$, pre-reaction time $\sim 2\text{ h}$ [Dai *et al.* 1998].

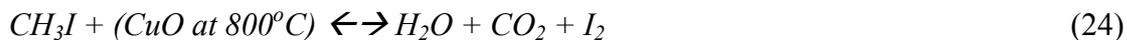
It is obvious from the figure 5. that methyl iodide reacts intensively with silver. A high concentration of methyl iodide causes defects to the surface. In the concentrations over 100 ppm of methyl iodide in methanol, the particular surface started to collapse. The long branches of silver disappeared and broken species of silver were formed. The reaction of methyl iodide with silver surface produced ethane at 300 °C, when a vapor flow of CH₃I was introduced onto the surface. It was the only carbon compound detected. Iodine was observed to accumulate to the surface during the reaction. A yellow AgI layer was formed on the surface. Iodine was released from the surface, when the sample was heated to 600 °C [Dai et al. 1998].

6.3 Metallic Copper

Copper is known as a good trapping material for radioiodine. Certain iodine compounds react with copper producing copper iodide. Copper iodide can be reduced back to copper with hydrogen at high temperatures. Hydrogen iodide is also formed in this reaction. The reaction proceeds most likely by the direct reaction of CuI with H₂ rather than by the thermal decomposition of CuI [Tachikawa 1975]:



Tachikawa et al. have studied the reactions of copper and copper oxide with I₂, HI and CH₃I. The test facility for the experiments of I₂ and HI consisted of a copper column and charcoal column. The copper column was placed inside a furnace, which could be heated up to 900 °C. The removal of iodine in the copper and charcoal columns was followed using a NaI scintillation counter. About 99% of iodine was trapped into the copper column. However, the experiments with methyl iodide showed that essentially all of CH₃I passed through the Cu column. It was concluded that in order to remove methyl iodide, it must be first converted to an inorganic form. Thus, a two step reaction was invented, where methyl iodide was converted to elemental iodide with the following reaction before final removal [Tachikawa 1975]:



The test facility for the studies of removal of CH_3I is shown in figure 6. It consisted of one CuO and one Cu column. The Cu column was used to remove I_2 , which is produced in the reaction (24).

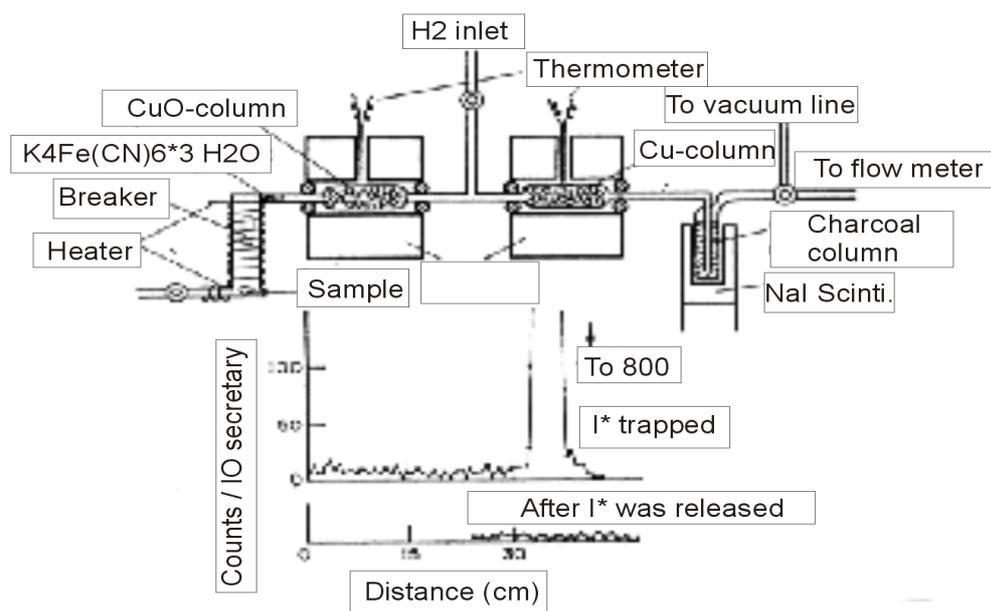


Figure 6. A schematic picture of the test facility to study the removal of methyl iodide using copper- and copper oxide-columns [Tachikawa 1975].

The copper column can be easily regenerated in reducing conditions at high temperatures. The use of copper is limited, because it is easily oxidised under atmospheric conditions [Tachikawa 1975].

6.4 PVAcetal in Removing Iodine Compounds

Permeable polyvinyl acetyl polymer (PVAcetal) is a porous material, which have shown exceptionally high affinity for iodine. PVAcetal is produced in the reaction of vinyl alcohol with formaldehyde. It is used as sponges in medicine and for various cleaning and processing systems. Iodine is known to bind to PVAcetal in solution. In fact it is used sometimes as and iodine dispersing material. The studies of Shanbrom show that PVAcetal is also an effective trap for gaseous iodine. This also indicates that effective iodine complexing may also occur in the vapor phase. The efficiency of iodine removal is most likely affected by the humidity of air. It was discovered that the efficiency of the filter is increased, when small amounts of humidifying substances such as glyserol and propylene glycol are added. The saturation level of the filter can be seen in the change in the colour. Colourless PVAcetal is readily darkened first to red-brown and finally blue-black colour, when iodine is captured [*Shanbrom 2000*]. No information of the reaction between methyl iodide and PVAcetal is available. The potential of PVAcetal to remove methyl iodide should be investigated.

7 Conclusions

Iodine is one of the most important fission products in the context of reactor safety. Iodine is released from the core most likely as CsI. Volatile elemental iodine is expected to form via radiolytic oxidation of iodide ion. This reaction is strongly dependent on pH and is increased significantly in acidic conditions. Elemental iodine is able to undergo further reactions. Iodine is a free radical scavenger and reacts readily with alkyl radicals. This may lead to the formation of various organic iodides such as methyl iodide. Furthermore, methyl iodide may become a source term during a severe accident, since it is able to penetrate most filters currently in use.

The formation of organic iodides is not fully agreed. However, it is generally accepted that the homogeneous gas phase reactions are of minor importance. The formation proceeds most likely on the surfaces or in the aqueous phase. The radiation is the driving force in the formation of organic iodides. The rate of formation may be decreased by the competitive reactions of organic free radicals with other compounds such as nitrogen oxides. Methyl iodide may also be decomposed thermally below 400 °C or on exposures to light. The volatile iodine compounds will partition between gas and aqueous phase and surfaces. Methyl iodide is more volatile than for example elemental iodine. Thus, the formation of methyl iodide is likely to increase the total iodine concentration in the gas phase.

Since iodine is able to penetrate the current filters in use, more efficient and reactive impregnants and bed materials should be developed. The bed materials have a large impact on the capacity especially in high relative humidity. Water vapor condenses easily in the micropores of the filter and decreases the reactive surface. However, if the pores are too large, there are less active reaction sites and the reaction rate is decreased. In order to develop more stable filters especially in high relative humidity, new carriers should be found. The efficiency of the current filters could also be improved, if one could

control the pore size for example in zeolites during the production. However, the balance between the reaction rate and water condensation should be defined, in order to produce an optimal porous bed material.

The mitigation rate may be increased by using impregnants. Transition metals such as silver and copper may also be used as impregnants besides the conventional compounds like TEDA. Non-carbenous bed materials such as zeolites are typically substrates for silver compounds. Silver is a relatively inert material, which is thermally stable. Iodine and methyl iodide are known to react well with silver. According to the studies, the reaction of methyl iodide with silver surface produces ethane. In fact, ethane was the only carbon compound that could be detected. Iodine was accumulated on the surface. It was released again, when the sample was heated to 600 °C. Copper is also able to react with radioiodine compounds. The reaction produces copper iodide. Even though Cu is effective in removing inorganic iodides like I₂ and HI, organic iodides are able to pass through the copper column. Thus, organic iodides have to be converted to inorganic form prior the actual removal using CuO at 800 °C. Reaction of CH₃I and CuO produces I₂, which can be removed by current filters.

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Title	Gas Phase Chemistry and Removal of CH ₃ I during a Severe Accident
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Abstract	<p>The purpose of this literature review was to gather valuable information on the behavior of methyl iodide on the gas phase during a severe accident. The potential of transition metals, especially silver and copper, to remove organic iodides from the gas streams was also studied. Transition metals are one of the most interesting groups in the context of iodine mitigation. For example silver is known to react intensively with iodine compounds. Silver is also relatively inert material and it is thermally stable. Copper is known to react with some radioiodine species. However, it is not reactive toward methyl iodide. In addition, it is oxidized to copper oxide under atmospheric conditions. This may limit the industrial use of copper.</p>
Key words	Methyl iodide, gas phase, severe accident mitigation