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Methods to Prevent the Source Term of Methyl Iodide During a Core Melt Accident

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Abstract

The purpose of this literature review is to gather available information of the methods to prevent a source term of methyl iodide during a core melt accident. The most widely studied methods for nuclear power plants include the impregnated carbon filters and alkaline additives and sprays. It is indicated that some deficiencies of these methods may emerge. More reactive impregnants and additives could make a great improvement. As a new method in the field of nuclear applications, the potential of transition metals to decompose methyl iodide, is introduced in this review. This area would require an additional research, which could elucidate the remaining questions of the reactions. The ionization of the gaseous methyl iodide by corona-discharge reactors is also shortly described.

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Abbreviations

a	Surface bound molecule
AC6120	Given only as a catalyst carrier in the referred literature
AES	Auger electron spectrometer
AGR	Advanced Gas Reactor
BWR	Boiling Water Reactor
CRD	Control rod driver
DABCO	Diazabicyclo(2.2.2)octane (=TEDA)
E	Electric field strenght
ECCS	Emergency core coolant system
FTP	Fission product transport
Gy	Gray
ΔH	Net entalphy
KI	Potassiun iodide
LWR	Light Water Reactor
Magnox	Gas Cooled Reactor
MCA	Multi-channel analyzer
NPP	Nuclear power plant
NTP	Normal temperature and pressure
PEI 1000	Polyethyleneimine, a trademark of Dow Chemical Company
PHWR	Pressurised Heavy Water Reactor
PWR	Pressurised Water Reactor
QMS	Quadrupole mass spectrometer
R	Alkyl chain
RBMK	Light Water Graphite Moderated Reactor
RH	Relative humidity
RPV	Reactor pressure vessel
SIMS	Secondary ion mass spectrometer
SPAC	System for Photochemical Abatement in Containment

SPARGE	System for Photochemical Abatement in Gaseous Effluent
TEDA	Triethylene diamine (=DABCO)
TMI	Three Mile Island
TPD	Temperature programmend desorption
TVO	Teollisuuden Voima Oy
UHV	Ultra high vacuum
VVER	Russian Pressurised Water Reactor
X	Chlorine, bromine or iodine
XPS	X-ray photoelectron spectroscopy

1. Introduction

This study is a review of the available methods and new possibilities to cope with organo iodides during a core melt accident in a nuclear power plant. The main focus of this review is on the removal of methyl iodide in light water reactor (LWR) accidents. Nuclear power plants in Finland operate four LWRs. There are two pressurized water reactors (PWR) located in Loviisa and two boiling water reactors (BWR) in Olkiluoto. In 1997, 30% of the electricity in Finland was produced by nuclear energy *[STUK]*.

Radioactive iodine is formed in a nuclear reactor as a fission product of uranium fuel. Some iodine is released from the core during the normal operations. The extent of the release is related to iodine concentration in the reactor coolant. Activated carbon filters are the most common method to remove released iodine species. It is however believed that the filters are exhausted in severe accident conditions, since a large amount of iodine can be released from degraded core during an accident *[Bernero 1987]*. People may be exposed to released radioactive iodine by breathing it or by consuming contaminated milk products. Iodine is biologically active element, which concentrates in the thyroid gland. It may cause thyroid gland cancer to children even in relatively small doses. In high doses radioactive iodine may directly damage the thyroid gland or even cause radioation sickness.

Even though a large number of organic compounds is available in the reactor containment building due to the high irradiation field, two most important organo iodides are believed to be methyl and ethyl iodide. The heavier alkyl iodides have been researched in some earlier studies, since the methods to remove methyl iodide cannot be applied to them *[Bernero 1987, Freeman et al. 1987]*. However, the physical and chemical properties of these compounds, indicate that they do not become airborne *[Weast 1984]*. Therefore, those compounds are not addressed in this work.

Several methods have been described in order to prevent the source term of methyl

iodide. These include commonly used filters and their impregnants. Lot of concentration is also put on the high pH of sump water. The formation of elemental and thus organo iodides is decreased in basic solution. Alkaline sprays and other additives are ready to be used in the case of a core melt accident. In some cases sump water is buffered in hope to maintain high pH.

2. Overview to the Nuclear Power Plants

A number of different reactor types exist around the world. These types are presented in table 1. Behaviour of a reactor in an accident is greatly dependent on its structure and materials. Since all four reactors in Finlad are LWRs, this study is mainly focused on the conditions in them.

Table 1. The number of nuclear reactors around the world in 1997 [Energian-alan Keskusliitto ry Finenergy 1999]

The Reactor Type	*%*
Pressurised Water Reactor (PWR)	47
Boiling Water Reactor (BWR)	21
Russian Pressurised Water Reactor (VVER)	13
Pressurised Heavy Water Reactor (PHWR)	7
Gas Cooled Reactor (Magnox)	4
Light Water Graphite Moderated Reactor (RBMK)	3
Advanced Gas Reactor (AGR)	3
Others	2

2.1 Pressurized Water Reactor (PWR)

In the primary circuit of PWR high pressure (15MPa) is employed to prevent the boiling of water even in temperatures above 300°C. The primary coolant flows through the core and is pumped to the steam generator. Water vaporizes in the secondary side of the steam generator, because the pressure there is significantly lower (7MPa). The steam flows through the turbines in order to generate electricity *[Energian-alan Keskusliitto ry Finenergy 1999]*. A schematic picture of PWR is presented in figure 1.

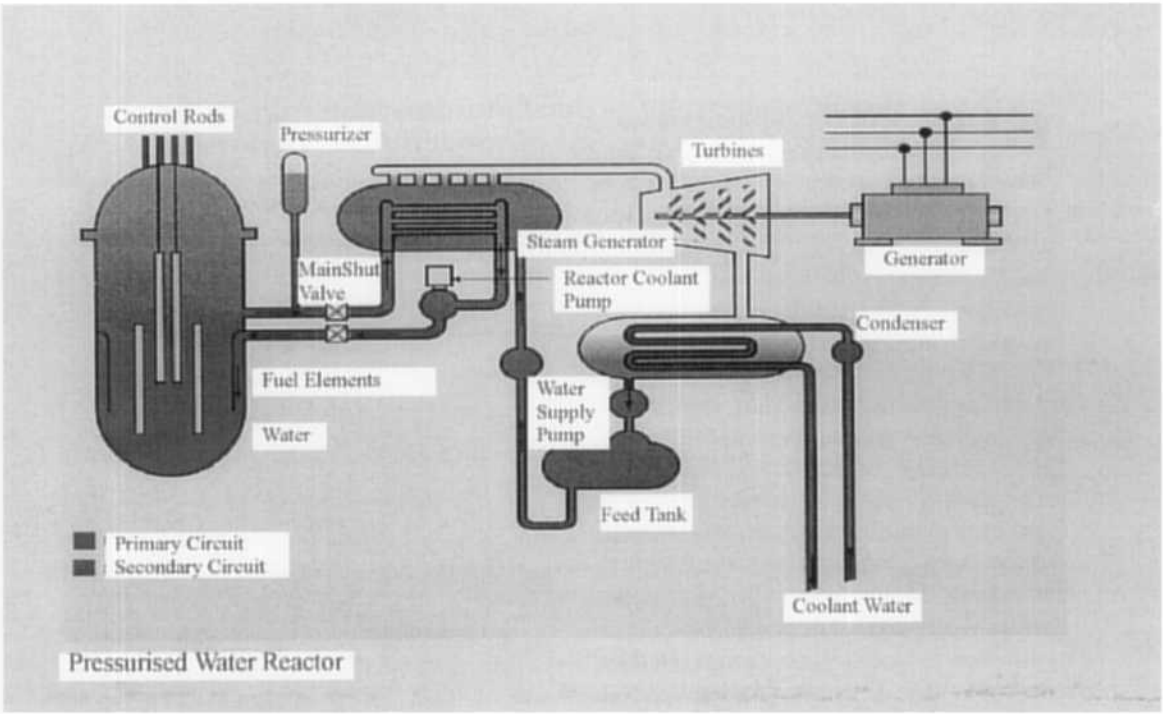


Figure 1. A schematic picture of PWR [Energian-alan Keskusliitto ry Finenergy 1999])

Fortum Power and Heat Ltd. owns the Loviisa nuclear power plant that operates two Russian VVER-440 type PWRs. The power plant is located at Hästholmen near the town of Loviisa in the southern coast of Finland. The reactors possess the net capacity of 488MWe each *[Sjövall et al. 1999]*. The thermal power of units is 1500MWt. The first reactor was built in 1977 and the second one in 1981 *[Energian-alan Keskusliitto ry Finenergy 1999]*.

2.2 Boiling Water Reactor (BWR)

BWR operates only at 7MPa pressure. Water is allowed to boil, when it is flowing through the reactor core. No steam generators are needed in BWR, because the primary coolant circulates directly to the turbines. Hence, the radiation level in turbine building is high during the normal operations *[Energian-alan Keskusliitto ry Finenergy 1999]*.

Two reactors in Olkiluoto nuclear power plant are BWRs build by AB ASEA-ATOM. They are owned by Teollisuuden Voima Ltd. The plant is located 20km north from

Rauma in western coast of Finland. The nuclear power plant were built in 1978 and 1982. The net capacity of each reactor is 840MWe *[Energian-alan Keskusliitto ry Finenergy 1999]*. A schematic picture of BWR is presented in figure 2.

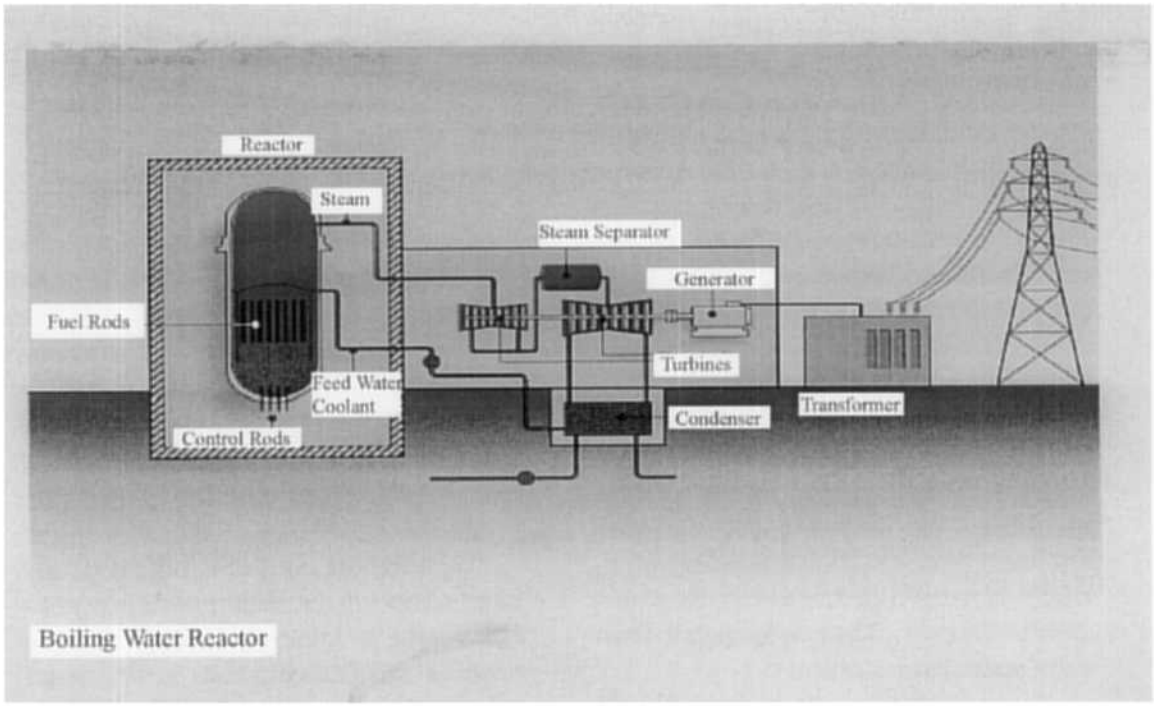


Figure 2. A schematic picture of BWR [Energian-alan Keskusliitto ry Finenergy 1999]

2.3 Comparison of a PWR and a BWR

The accident scenarios for PWR and BWR differ somewhat due to the differences between the structures, materials and size of the core. These difference must be taken into account, when new safety measures are planned for the power plants.

Since the structures of the primary circuits are dissimilar, as indicated in the figure 1 and 2, the initiating events and the progression of an accident also differ *[Energian-alan Keskusliitto ry Finenergy 1999]*. Besides structural differences there are other factors in the primary circuits that contribute to the behaviour of these plant types in an accident. Firstly the size of the core in BWR is about two times the size of PWR with the equal electrical capacity. The release of the fission products from the BWR core is likely to be

higher than from the PWR *[Wright 1994]*. The calculated inventory of fission products in a PWR and BWR core is presented in table 2. Secondly the control rods in BWR are most commonly boron carbide, which can act as a source of organic compounds during a core melt accident.

Table 2. *The calculated amount of fission products in a core of PWR and BWR [Wright 1994]*

Constituents	*PWR*		*BWR*	
	(mol)	*(kg)*	*(mol)*	*(kg)*
I, Br	146	19, 12	308	39, 25
Cs, Rb	1624	216, 139	3222	428, 275
Te	253	32	533	68
U	$2.95*10^5$	$7*10^4$	$6.22*10^5$	$2*10^5$
Ba, Sr	1279	176, 112	2696	370, 236
Rare earths	4471	-	9421	-
Zr, Nb	2402	219, 223	5060	461, 470
Mo	2179	209	4591	440
Ru	1527	154	3323	336
Pd	914	97	1927	205
Tc	518	-	1091	-
Rh	296	30	624	64
Ag	58	6	122	13

The control rods at PWR are usually composed of In/Cd/Ag alloy. The relative amount of indium, cadmium and silver is 5%, 15% and 80% respectively *[Wright 1994]*. The role of silver will be discussed in detail in the later chapters. In the Loviisa power plant the control rods are made of boric steel, which is typical for Russian PWRs *[STUK 1999]*. Thirdly the water chemistry in the primary circuit is somewhat different in the two plant types. During normal operations about 120 kg (2 kmol) of boric acid is used in coolant water of PWR. If emergency core coolant system (ECCS) is used in an accident, the

amount of boric acid can be increased up to 39 000 kg (630 kmol) *[Wright 1994]*. This may cause the water pools in the containment building to become acidic, and enhance the evolution of elemental iodine *[Sjövall et al. 1999]*. Boric acid may also react with CsI forming HI. Further reactions of HI can lead to the evolution of gaseous iodine in primary circuit *[Wright 1994]*. Boric acid is not used at BWR during the normal operations *[Duberstadt & Hamilton 1976]*. However, in ECCS there is boric acid also in BWR *[STUK 1999]*.

The structure of PWR and BWR containment building differ. A typical BWR containment is small, and it is built to withstand high pressure and temperature. A PWR containment building is large in order to keep the pressure and temperature moderate. The amount of water in a BWR containment building is also usually much greater than in a PWR containment, which leads to the more dilute solutions. The large amount of water ensures a long cooling period in the case of a malfunction in the safety systems delaying the possible core melt. Due to a larger core size, there is also a greater number of contol rods in BWR than in PWR. Therefore there are more cable materials present in BWR containment. Thus, during an accident a greater amount of different organic and chlorine containing compounds can be released from BWR than PWR. This can have a major impact on the chemistry of the sump water in the containment building. In addition to this in BWR a significant number of cables are located directly below the reactor pressure vessel (RPV). The reason for this is that the control rod drives (CRD) must be operated from below the RPV, since the steam separating unit is located above the core. If RPV fails during an accident, the molten fuel may drop onto the cables. Thus the release of the organic materials may be very fast. The situation is different in PWR, where the control rods and their cables are located above the pressure vessel *[STUK 1999]*.

A considerable effort on the iodine management at the nuclear power plants is focused on the maintenance of high pH in water pools of containment. High pH is hoped to prevent the formation of elemental iodine and thus decrease the amount of organo iodide *[Sjövall et al. 1999]*.

In the Loviisa nuclear power plant the focus of the accident management is on the long-term containment cooling. The special feature of Loviisa is the ice condensers that contain a large amount of borax ($Na_2B_4O_7 \bullet 10H_2O$ = sodium tetraborate). Ice melts during a severe accident and suppresses the temperature and pressure. Due to borax, sump water will be alkaline, which should prevent the formation of elemental iodine. In Loviisa power plant hydrazine (N_2H_4) and potassium hydroxide (KOH) are also added to the containment sprays in order to remove volatile iodine species. The filtration system of the plant is not designed for the severe accident conditions. Therefore containment venting should be avoided during an accident *[Sjövall et al. 1999]*.

In the Olkiluoto NPP the filter of the containment venting system is able to capture the particulate and elemental iodine. Thus, iodine should be hold mainly in these two forms to guarantee efficient filtration. The filter is a 20 m^3 tank filled with $Na_2S_2O_3$ (0.2%) and NaOH (0.5%) water solution. A new, large NaOH tank is also going to be installed during 1999. The purpose of this tank is to keep the containment water pools alkaline during a severe accident and thus diminish the formation of volatile iodine species *[Sjövall et al. 1999]*.

2.4 Future Aspects of Nuclear Power in Finland

The discussion about the fifth nuclear reactor has been a long term issue in Finland. Increasing energy consumption, and the demand for cheap energy by the industry, forces the government to consider available energy sources. In order to fulfill the Kioto agreement, Finland has to decrease the consumption of fossil fuels in favor of renewable energy sources and nuclear power. Since the service life of existing NPPs is limited, the discussion for the fifth power plant seems quite urgent. To guarantee the safe use of the existing and prospective nuclear power plants, the continuous research on this area is needed.

3. Physical and Chemical Properties of Iodine and Methyl Iodide

3.1 Elemental Iodine

Elemental iodine (I_2) is a highly volatile compound, which easily escapes to the environment during a core melt accident. The high biological activity of iodine makes it a major concern in the case of a release *[Parsly 1970, Taylor 1959, Petit et al. 1999]*. The most important radioactive iodine isotope is ^{131}I, which has a half-life of 8.05 days *[Thomas et al. 1991]*. The chemical and physical properties of iodine are described in table 3. Iodine is produced commercially by the reduction reaction of the iodates:

$$2IO_3^- + 5HSO_3^- \rightarrow I_2 \downarrow + 5SO_4^{2-} + 3H^+ + H_2O \qquad \textbf{(1)}$$

The oxidation of iodides with the strong oxidizing agents also forms elemental iodine *[Laitinen & Toivonen 1993]*.

Table 3. Chemical and physical properties of iodine, I_2 [Weast 1984]

Constant	*Numerical Value*
M (g/mol)	253.809
ρ (g/cm^3)	4.93
m_p (^{o}C)	113.5
b_p (^{o}C, atm)	184.35
solubility in water (in grams per 100cc)	0.029 (20°C) / 0.078(50°C)

3.1.1 Release and Formation of Elemental Iodine

In a severe accident iodine released from the reactor is likely to be in the form of cesium iodide (CsI). CsI is very soluble in water, and is easily oxidized to volatile iodine, I_2, in aqueous solution at low pH by the radiolytic reactions *[Ashmore et al. 1999, Wren et al. 1999a]*.

$$I^- + \bullet OH \rightarrow I\bullet + OH^- \quad (2)$$

$$I\bullet + I\bullet \rightarrow I_2 \quad (3)$$

The reaction of the iodine species with the •OH-radicals produced by the radiolysis of water may proceed, since the activation energy of the reaction **(2)** is negative *[Wren et al. 1999a]*.

The formation of volatile I_2 is very pH dependent. Caclulations of the effect of pH to I_2 formation are described in figure 3. The reaction of I^- to I_2 is considered to be negligible at pH above 8 *[Beahm et al. 1992]*.

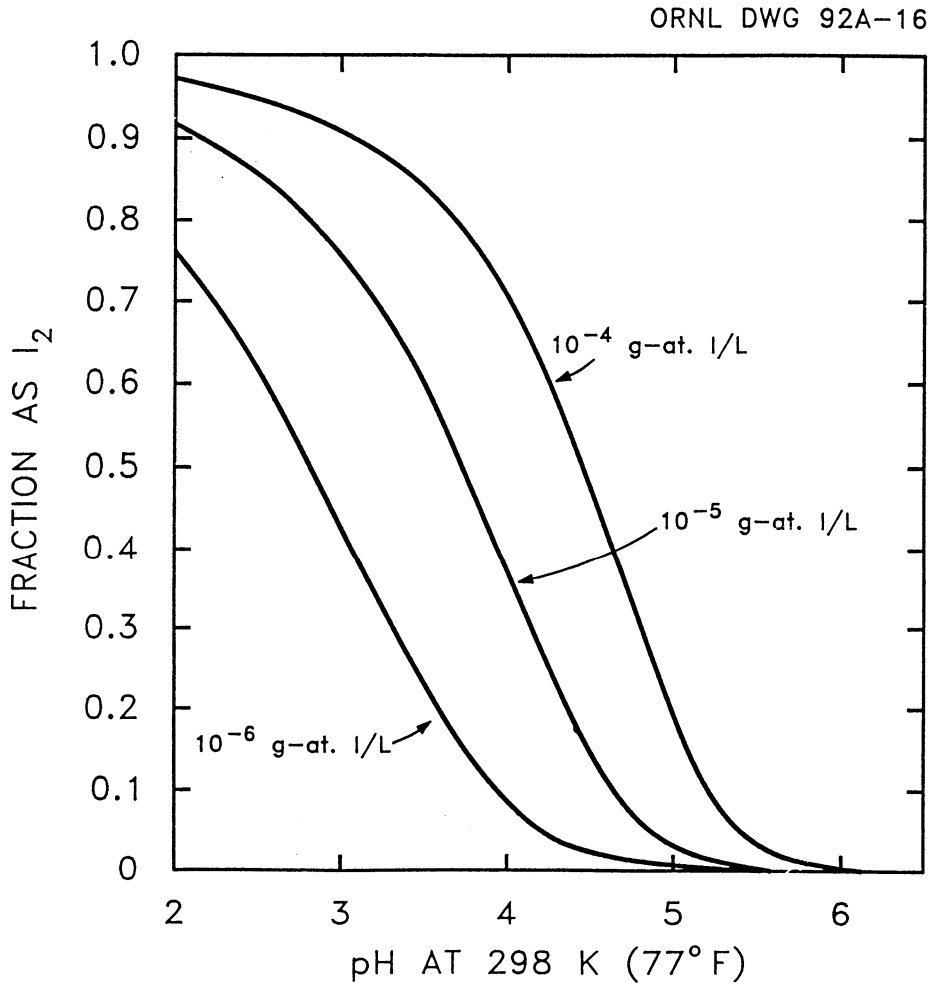


Figure 3. Calculations of the effect of pH to I_2 formation [Beahm et al. 1992].

The concentration of I_2 is known to increase by an order of a magnitude when pH decreases one unit *[Wren et al. 1999a]*. Since the most probable pathway to the formation of organo iodides is via methyl-radicals and elemental iodine, the pH control is considered to be one of the most important tools to diminish the evolution of organo iodides *[Ashmore et al. 1999]*.

3.1.2 Reactions of Elemental Iodine in the Aqueous Phase

The homo- and heterogeneous reactions of iodine in the aqueous phase have been considered to be more important than the gas phase reactions, since they proceed more rapidly. However, there is no agreement, which of the several possible pathways of iodine reactions is the most dominant.

The heterogeneous reactions on the surfaces are assumed to be slow, even though iodine is readily adsorbed to metal surfaces. The surfaces are covered in a thin film of water, which hinders the reactions probably, because the concentration of iodine that reaches the surface is lowered *[Wren et al. 1999a]*. However, there is contradictory evidence of water enhancing the reactions on the zinc primer coated surfaces at the room temperature *[Evans & Bekeris 1996]*. The mechanisms of the surface reactions are still not fully understood and are under ongoing research.

Elemental iodine can undergo either oxidation or reduction the latter being dominating in aqueous conditions. The temperature dependent reactions of aqueous iodine with water or oxygen are following *[Wren et al. 1999a]*:

$$I_2(aq) + H_2O \leftrightarrow HOI + I^- H^+ \quad \textbf{(4)}$$

$$I_2(aq) + O_2^- \leftrightarrow I_2^- + O_2 \quad \textbf{(5)}$$

$$I_2(aq) + H_2O \leftrightarrow 2I^- + 2H^+ + O_2(aq) \quad \textbf{(6)}$$

Especially the reaction **(4)** has been under the interest in several studies, but its thermodynamics has not been clarified. The similarity of the reaction **(4)** with the reaction

of NaOH and elemental chlorine was proposed, and the conclusion was that in the basic solutions some HOI would be present *[Bernero 1987]*. However, the reactions of chlorine should not be compared to the chemistry of iodine. The reaction of iodine in hot, alkaline solution is *[Laitinen & Toivonen 1993]*:

$$3I_2 + 6OH^- \leftrightarrow IO_3^- + 5I^- + 3H_2O \qquad (7)$$

All IO_x^- compounds such as HIO_3, HIO_4, IO_2/I_2O_4 tend to decompose upon heating, indicating that no HOI would be present. This property of iodates is different compared to the oxides of other halogens *[Weast 1984]*. As a conclusion the reaction **(4)** may not be as significant as previously thought.

3.2 Methyl Iodide

Methyl iodide is chemically relatively inactive and therefore difficult to remove from the gas streams. It is able to penetrate most of the filters in use, even though the removal of other iodine species is quite efficient. The physical and chemical properties of methyl iodide are described in table 4.

Table 4. Physical and chemical properties of methyl iodide, CH_3I [Weast 1984]

Constant	*Numerical Value*
M (g/mol)	141.94
ρ (g/cm^3)	2.279 (20 °C)
m_p (°C)	-66.4
b_p (°C)	42.5
solubility (in grams per 100cc)	alcohols, ethers, acetone

There is an indication that methyl iodide is moderately soluble in water. The partition coefficient is the ratio of the concentration in the liquid phase versus gas phase at equilibrium. According to studies it is 5.2 at 20°C and 1.7 at 100°C for methyl iodide *[Parsly 1970]*. It is thus evident that temperature has a great influence on the methyl

iodide partition. The partition coefficient of methyl iodide vs reciprocal temperature is presented in figure 4. It can be assumed that a very significant fraction of methyl iodide is in the gaseous phase under the accident conditions in a PWR. This might not be the case in some BWRs, where water can occupy almost all of the free space in the containment *[Hasty 1968]*.

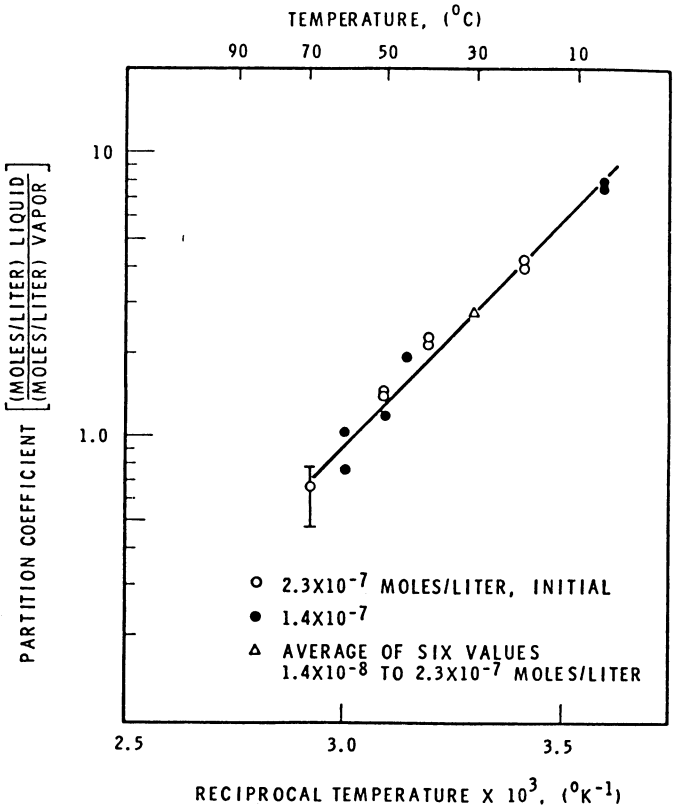


Figure 4. Partition coefficient of methyl iodide versus reciprocal temperature [Hasty 1968].

3.2.1 Formation of Methyl Iodide

There are a lot of organic compounds in the containment building mostly in the form of organic polymers such as the organic paints (vinyl-, polyurethane-, and epoxy-coatings), solvents (toluene, xylene etc.), cable sheathings (polymers), and lubricants (grease and oil). They may degrade in a nuclear accident under the elevated temperature and intense radiation field producing organic radicals *[Wren et al. 1999a]*. In a BWR the control rods

contain boron carbide, which can be added to the sources of organic materials *[Sjövall et al. 1999]*. At high temperature boron carbide decomposes in water *[Beahm et al. 1987]*:

$$B_4C + 7H_2O \leftrightarrow 2B_2O_3 + CO + 7H_2 \quad \textbf{(8)}$$

$$B_4C + 8H_2O \leftrightarrow 2B_2O_3 + CO_2 + 8H_2 \quad \textbf{(9)}$$

$$B_4C + 6H_2O \leftrightarrow 2B_2O_3 + CH_4 + 4H_2 \quad \textbf{(10)}$$

The main products of boron carbide reactions are carbon monoxide, carbon dioxide and boron oxide. They may decrease pH of the sump water by forming carbonic acid. According to calculations some methane may form, if H_2 to steam ratio and pressure are high *[Beahm et al. 1987]*.

The formation of organic radicals (R•) is very similar to the formation of elemental iodine *[Wren et al. 1999a]*:

$$RH(aq) + \bullet OH \rightarrow R\bullet + H_2O \quad \textbf{(11)}$$

Organic radicals can react to yield alcohols, acids, CO_2, and organo iodide. Because the activation energy of the reaction **(11)** is negative, the formation of radicals is likely to proceed *[Wren et al. 1999a]*.

The formation of methyl iodide is most likely to proceed via the reaction of CH_3-radicals with I_2 *[Ashmore 1999]*. The enthalpy (ΔH) of this reaction is -83.7 kJ/mol according to Fessenden & Fessenden, whereas Sykes reported ΔH to be -75 kJ/mol *[Fessenden & Fessenden 1994, Sykes 1986]*.

$I\bullet + CH_4 + 138.2kJ/mol \rightarrow HI + CH_3\bullet$ ($\Delta H = +138.2kJ/mol$) **(12)**

$CH_3\bullet + I_2 \rightarrow MeI + I\bullet + 83.7kJ/mol$ ($\Delta H = -83.7kJ/mol$) **(13)**

$CH_4 + I_2 + 54.5kJ/mol \rightarrow MeI + HI$ ($net\Delta H = 54.5kJ/mol$) **(14)**

[Fessenden & Fessenden 1994)

The presence of chlorine can decrease the reaction rate of iodine and methyl radical, because the entalphy for the reaction between Cl_2 and CH_3-radicals is even smaller. According to Sykes it is -96kJ/mol. The net reaction entalphy for chlorine and methane is -100 kJ/mol *[Sykes 1986]*. The formation of organo iodides is also depended on the ratio of organic material and iodine concentration. The reaction of I^- and CH_4 is considered to be less important than the radical reactions.

There is no agreement, whether the formation of methyl iodide takes place in the aqueous phase, gaseous phase or on the surface of metals *[Ashmore 1999]*. It has been postulated that the formation of organo iodides by the homogeneous pathway will most likely occur in the aqueous phase, since most of the iodine species are expected to be in water after the fission products are released into the containment building *[Wren et al. 1999a, Beahm et al. 1987]*. According to the experiments the amount of methyl iodide in the water phase was also greater than the partition coefficient indicated. The test at pH 6.0 with a $2*10^{-1}$ mol/dm^3 borate solution gave the partition coefficient around 270 to methyl iodide, when according to the calculations it should have been between 2-3. The conversion of I_2 and CH_4 to CH_3I in an irradiated bubbling pool is presented in figure 5 *[Beahm et al. 1987]*. This supports the theory of the formation taking place in the aqueous phase. An experiment performed by bubbling methyl iodide into the reaction solution also supports this theory *[Karjunen et al. 1994]*.

Even though heterogeneous reactions on the metal surfaces (Zn, Al) have been under intensive studies, they are not fully understood *[Wren et al. 1999a]*. The rate of the formation of methyl iodide on the surfaces is depended on elemental iodine

concentration, temperature, irradiation and the state of the surfaces *[Ashmore et al. 1999, Wren et al. 1999a]*. According to the tests, between 30 and 35°C the conversion of iodine to methyl iodides without irradiation is less than $1*10^{-3}$%, while $1*10^{4}$Gy increased the conversion to 20.7% *[Beahm et al. 1987]*. In the absence of irradiation the formation of

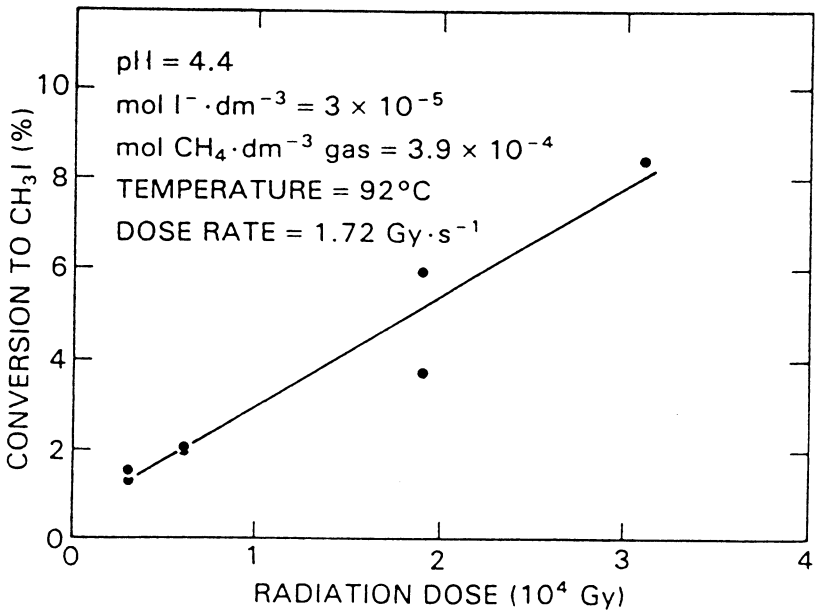


Figure 5. Conversion of I_2 and CH_4 to CH_3I in an irradiated bubbling pool [Beahm et al. 1987].

organo iodides is greatly depended on the temperature, which affects the diffusion rate of iodine and methane in water and the release of organo iodides to the gas phase. The heterogeneous reactions on the painted surfaces are assumed to proceed via the same mechanism as in the aquatic media. The experiment of the formation of methyl iodide on the painted coupons confirmed that methyl iodide is the major product on the surfaces *[Ashmore et al. 1999]*.

One should also bear in mind, that there are competing reactions with the radiolysis products of water and air. They can decrease the rate of formation of methyl iodide on the surfaces as well as in the aqueous phase.

3.2.2 Radiolytic Decomposition of Methyl Iodide

Under the irradiation methyl iodide can decompose producing non-volatile I^- and $\bullet CH_3$

(reaction **(17)**). The hydrolysis of methyl iodide yields also I^- species *[(15-16) Ashmore et al. 1999, (17) Beahm et al. 1987]*.

$$e^-_{aq} + CH_3I \leftrightarrow \bullet CH_3 + I^- \quad \textbf{(15)}$$

$$RI(aq) + H_2O \leftrightarrow I^- + H^+ + ROH(aq) \quad \textbf{(16)}$$

$$RI(aq) + OH^- \leftrightarrow I^- + ROH \quad \textbf{(17)}$$

However, the radiolytic decomposition is likely to be a slower reaction than the formation of methyl iodide. The concentration of organo iodides is determined by a steady state between the formation and decomposition.

3.2.3 Photolytic Decomposition of Methyl Iodide

The photolytic degradation of methyl iodide is known to enhance the decomposition caused by other methods. Organo iodides absorb light between 200 and 300nm, that causes the C-I bonds to cleave *[Vikis et al. 1991]*:

$$RI + h\upsilon \rightarrow R\bullet + I\bullet \quad \textbf{(18)}$$

The conditions in the containment building define the further reactions of the radical species. When air is present and the concentration of organo iodides is low, the oxidation reaction is:

$$R\bullet + O_2 \rightarrow aldehyde / ketone \quad \textbf{(19)}$$

Two procedures that employ only the photolytic dissociation are reported: System for Photochemical Abatement of Radioiodine in Gaseous Effluent (SPARGE) and System for Photochemical Abatement in Containment (SPAC) *[Vikis et al. 1991]*. These procedures could be applied to assist other removal methods.

4. Filtering Systems for Iodine Compounds

The impregnated carbon filters including the charcoal filters are the most commonly used iodine trapping systems in the nuclear power plant. Filters are required to remove low concentrations of different gaseous iodine species from the gas streams. The capacity and efficiency of filtration is dependent on the physical and chemical properties such as the impregnants, temperature, relative humidity, bed depth, flow velocity, properties of the adsorbent, aging and the presence of other compounds *[Freeman & Enneking 1991]*. It is postulated that during a severe accident the efficiency of carbon filters to remove methyl iodide is low, even though their performance under the normal operating conditions is satisfactory *[Bernero 1987]*. Therefore different impregnants and filter materials are being studied in order to improve the properties of the filters.

4.1 Porous Bed Filters

Large surface area, around 1000 m^2/g, can be achieved with microporous bed materials *[Billinge et al. 1984]*. These include for example active carbon, zeolites, silica and alumina. Benefits of porous bed materials are high capacity and efficiency of filtration compared to the size of the filter. However, these materials are sensitive to high relative humidity *[Billinge et al. 1984]*.

4.1.1 Active Carbon Filters

The active carbon filters are commonly used in the nuclear industry to remove radioactive iodine species *[Billinge et al. 1984]*. Carbon for the filters can be received from several sources: coal, coconut and peat *[Deuber et al. 1987a]*. The source of carbon may have an impact on the performance of the filter, since the impurities such as KOH contained in some carbons may enhance the removal of methyl iodide. An indication of the improved efficiency was made for example in the case of potassium iodide (KI) impregnated coal based carbon filter *[Billinge et al. 1984]*.

Methyl iodide is adsorbed to the pure carbon reversibly through physical adsorption. The adsorption capacity is dependent on the concentration of methyl iodide in the gas stream

and the porosity of the bed material *[Nakhutin et al. 1987]*. Under dry conditions the adsorption to the carbon filters is believed to proceed via external mass transfer and pore diffusion. The comparison of the experimental results and calculations indicate that both steps affect the overall adsorption resistance *[Chang & Cho 1985]*. The dynamic capacity of the filters under dry conditions is strongly dependent on the density of carbon, and reaches a maximum when the bulk density is between 560 and 580 kg/m^3. Impregnated carbon has slightly different values than pure carbon *[Nakhutin et al. 1987]*. The capacity of the active carbon filters as the function of the bulk density in both dry and humid conditions is presented in figure 6.

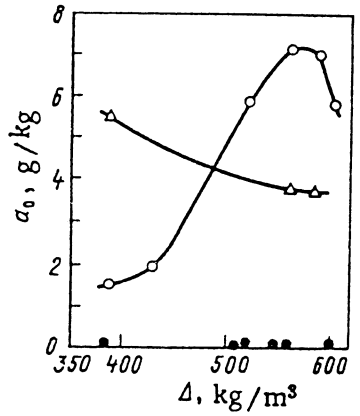


Figure 6. Capacity of the impregnated (Δ) and nonimpregnated (o, •) activated carbons as the function of the bulk density. (o) is in dry and (•, Δ) in humid conditions [Nakhutin et al. 1987].

The size is an important factor affecting the efficiency of the filter. Bed depth and cross sectional area of the filter determines the retention time. It should be long enough to guarantee efficient removal of methyl iodide *[Deitz 1987]*. Less than 1% penetration of methyl iodide through a 2 inches thick charcoal bed was allowed by Nuclear power plant standard specifications in 1986 *[Bernero 1987]*. Largest iodine filters with a residence time in the order of 1 s contain approximately 20000 kg activated carbon *[30] [Deuber & Giraud 1987]*.

High relative humidity, >70%, may clog the pores of the filter *[Billinge et al. 1984, Wren et al. 1999b]*. This is due to capillary condensation of water vapour. The condensation is likely to affect especially the micropores leaving only the meso- and macropores for the adsorption of methyl iodide *[Chang & Cho 1985]*. The blocked micropores decrease the efficiency of the filter, since the residence time and the mass transfer rate of methyl iodide is decreased. The capacity of the filter can diminish even by a factor of 50 to 100 in the humid conditions *[Nakhutin et al. 1987]*. Figure 7 shows the methyl iodide filtration efficiency of dried and undried carbon. The effect of relative humidity to the equilibrium adsorption capacity and to the pore diffusivity of methyl iodide is presented in figure 8.

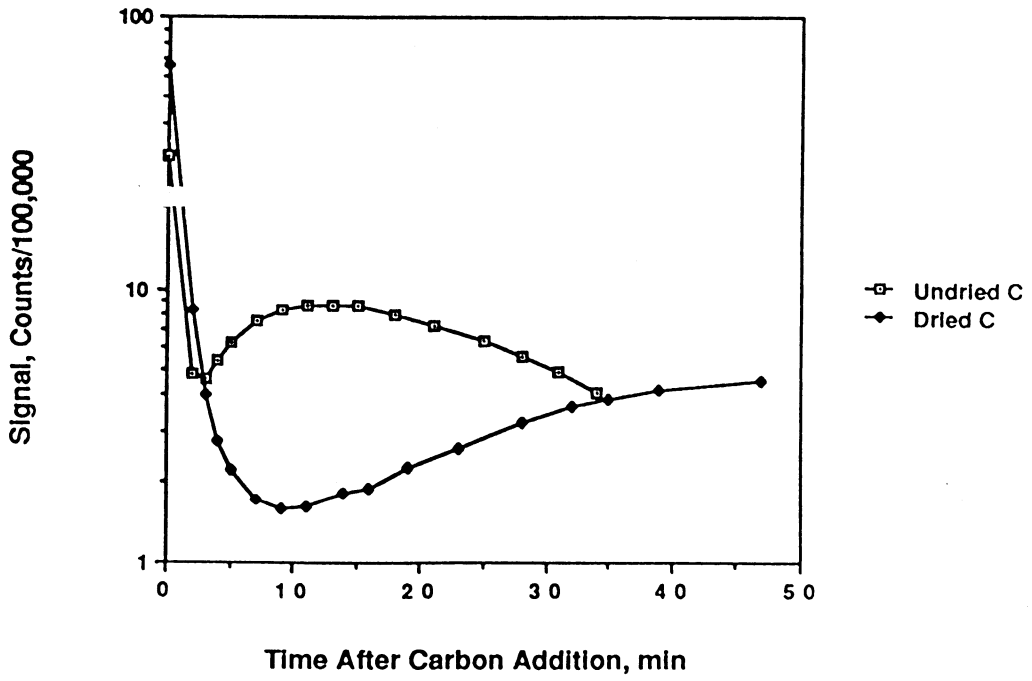


Figure 7. Comparison of dried and undried carbons. Methyl iodide is held more strongly in dried carbon [Hyder & Malmstrom 1991].

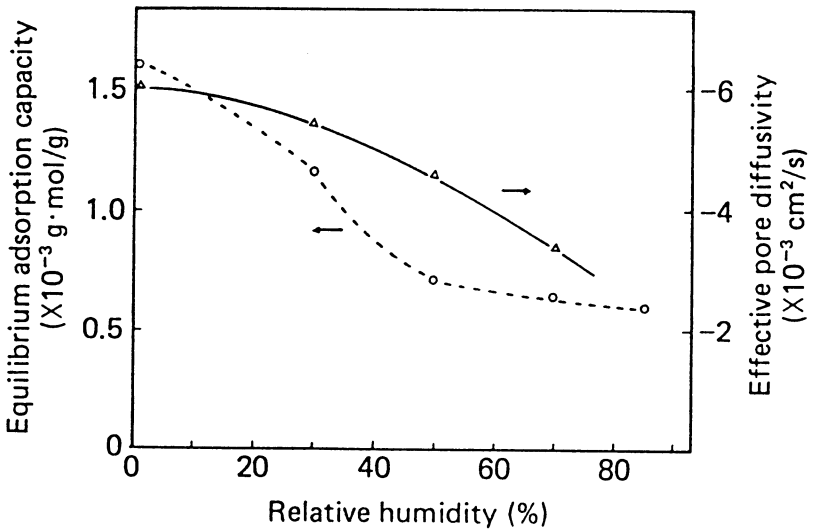


Figure 8. The effect of relative humidity to equilibrium adsorption capacity and to the pore diffusivity of methyl iodide [Chang & Cho 1985].

The carbon filters are known to age relatively fast in the presence of organic and inorganic impurities. The downstream movement of iodine is characteristic to the aged carbon filters, because of the decreased efficiency *[Deitz 1987]*. Several different impregnants are used to improve the capacity of the filters. The most common impregnants currently in use are triethylene diamine (TEDA=1,4-diazabicyclo(2.2.2)octane, also known as DABCO) and potassium iodide (KI).

4.1.2 Zeolite Filters

Zeolites are crystalline alkali-aluminium silicates that have the general formula of $M_{2/n}O \bullet Al_2O_3 \bullet ySiO_2 \bullet wH_2O$, where 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. Zeolites are most commonly used as molecular sieves, filters, adsorbents and catalysts, because of their high sorption capacity and selectivity *[Budavari 1989]*. They are stable under acidic conditions and upon heating. They also show a high affinity toward methyl iodide, which is readily adsorbed to the surface. Thus they can be considered as a highly potential agent to remove methyl iodide. Unlike carbon based filters zeolite filters can also be

regenerated. However, the removal of methyl iodide from the filter may be somewhat problematic, and should be considered only as a secondary options to the replacement *[Fan et al. 1987]*.

Tests carried out using silver free zeolite shows that the presence of NO_2 can accelerate the decomposition of methyl iodide in the filter. The adsorption of methyl iodide to zeolite is likely to occur before the reaction of methyl iodide with NO_2:

$$CH_3I + 2NO_2 \leftrightarrow \tfrac{1}{2} I_2 + CH_3NO_3 + NO \qquad \textbf{(20)}$$

Similar decomposition reaction takes place in the case of ethyl iodide. There is evidence that zeolite efficiently removes also other organo iodides under dry conditions. However, the performance of the zeolite filter drastically decreases in humid conditions as referred in the study of Maeck *et al.* As in the case with active carbon filters, this is due to the coadsorption of water *[Sakurai et al. 1984]*.

Silver zeolites are claimed to be efficient to remove most iodine species. In the experiments by Mandler *et al.* some penetration of iodine compounds was observed. It was postulated to be caused by heavier alkyl iodides. However, additional tests are required to determine the nature of these compounds. Another characteristic of silver zeolite filters that requires further study, is the relatively fast aging. Silver zeolite filters degrade within only a month *[Mandler et al. 1987]*.

There is also another case, when some iodine species were not efficiently trapped by zeolite filters. About 40% of iodine species were not retained into the double zeolite filter during the Phebus FTP-1 experiment. As in the case of silver zeolites this was assumed to be due to some unidentified iodine compounds other than I_2, HI or CH_3I. However, these untraceable species were claimed to be rapidly transformed into compounds, that could be efficiently removed by a zeolite filter located downstream in the facility *[Jacquemain et al. 1999]*. Further studies are needed on the subject though before conclusions can be

made.

4.1.3 Other Materials for the Porous Bed Filters

Some possible materials for the filters are for example silica, alumina and AC6120 catalyst carrier *[Kobayashi et al. 1991]*. Both silica gel and alumina exhibited the same removal capacity, when operated at low (0.4%) relative humidity. However, the performance of silica gel in humid conditions was not encouraging. An experiment with KI impregnated silica gel indicated a low tolerance of silica toward humid conditions. The capacity of a silica gel filter decreased significantly more than capacity of an impregnated carbon filter operated under the same conditions *[Billinge 1984]*.

4.2 Impregnants

When the relative humidity is greater than 50%, only a small fraction of the surface area of a porous bed filter is available. The adsorption in these conditions occur mainly to the meso- and macropores. The addition of an impregnant is essential in order to maintain the capacity of the filter in an acceptable level *[Billinge 1984]*. The reaction of methyl iodide and impregnant is irreversible and consumes the impregnant. A typical level of impregnation is approximately 5% *[Nakhutin 1987]*. Most commonly used impregnants in iodine filtration are TEDA and its derivatives, other amine compounds, KI and silver compounds.

Impregnated carbon as well as plain carbon filters tend to loose their efficiency with time. The same effects are most likely to occur also with other porous materials. The aging is mainly caused by the presence of organic solvents and inorganic compounds like O_2, O_3 SO_2, NO, NO_2. Organic materials can occupy the effective surface area, while inorganic compounds may decrease the retention of methyl iodide by reducing the pH of the filter *[Deuber et al. 1987a]*.

In table 5 the efficiency of typical impregnated carbon filters to remove organo iodides is compared. In all experiments impregnated filters show low removal rates for ethyl iodide. This is due the properties of ethyl iodide. The isotopic exchange rate of ethyl iodide is so

much slower than with methyl iodide, that it cannot be compensated by the faster physical adsorption *[Freeman et al. 1987]*.

Table 5. The efficiency (%) of impregnated carbons to remove organo iodides [Freeman et al. 1987]

Impregnant	CH_3I	CH_3CH_2I	$CH_3\ CH_2\ CH_2I$
TEDA	98.82	95.31	99.60
KI	97.89	91.70	97.59
TEDA/KI	99.19	93.25	99.11

4.2.1 Triethylenediamine

Triethylene diamine (TEDA), also known as DABCO (diazabicyclo[2.2.2]octane), is the most commonly used impregnant in activated carbon filters. TEDA impregnated filters are known to remove organo iodides with high efficiency. The reference to a study of Dietz and Jonas indicates, that the removal of methyl iodide by TEDA filter is a first order catalytic reaction. Solid diffusion is considered to have a minor impact on the retention *[Chang & Cho 1985]*. However, a contradictory statement is presented by Fessenden & Fessenden. The reactions of alkyl halides with amines are typically S_n2 reactions, which proceed well with methyl halides. The general reaction mechanism for the primary organo halides and tertiary amines is *[Fessenden & Fessenden 1994]*:

$$CH_3I + R_3N \leftrightarrow CH_3N^+R_3X^- \qquad \textbf{(21)}$$

The removal mechanism of a TEDA impregnated filter is assumed to have two stages: a physical adsorption followed by a chemisorption. The final reaction of methyl iodide is proposed to be the decomposition of the quaternary ammoniun salts (TEDA-CH_3I). The activation energy of the chemical adsorption of methyl iodide is 35±5 kJ/mol *[Wren et al. 1999b]*.

Relatively low temperatures and dry conditions are required for TEDA filters to maintain their capacity *[Deuber et al. 1987]*. TEDA has a low ignition temperature, melting point (mp=158°C) and boiling point (bp=174°C). Its crystals are also very hygroscopic, which may have an impact to the retention of methyl iodide.*[Budavari 1989]*. In humid conditions all tertiary amines, such as TEDA, are able to react with water producing hydroxide ions. Since water is present in the containment building in much larger amounts than methyl iodide, the reaction of TEDA and water is likely to occur *[Fessenden & Fessenden 1994]*.

$$R_3N + H - OH \leftrightarrow R_3N^+H + {}^- OH \qquad \textbf{(22)}$$

The efficiency of the carbon filters impregnated by TEDA was assumed to diminish in relatively humid conditions, since water vapour may block the pores of the filter and reduce the amount of TEDA available *[Billinge et al. 1984, Wren et al. 1999b]*. However,

Table 6. The laboratory test of carbon adsorbent with CH_3I in air at 25°C, and 95% relative humidity (except the sample 1, RH 100%) [Slade & Philippi 1987]

Number of Filter	*Retention and Accuracy (%)*
1	97.23±0.05
2	98.42±0.04
3	98.88±0.04
4	98.31±0.06
5	98.16±0.04
6	98.92±0.02
7	99.31±0.02
Carbon Manufacturer's rating	99.00 minimum

the reaction of methyl iodide in humid conditions may proceed via $^-$OH-ions instead of TEDA. TEDA filters have shown to keep their removal efficiency of methyl iodide even at 95% relative humidity (RH). The retention according to the experiments was around

97-99% at 25°C as shown in table 6.

4.2.2 Potassium Iodide (KI) Impregnation

The removal of radioactive compounds by the KI impregnated filters is based on the isotopic exchange. The isotopic exchange is much slower than the addition reaction taking place in the TEDA filter. For heavier organo iodides the reaction in the KI filter is even slower than that for methyl iodide *[Freeman et al. 1987]*.

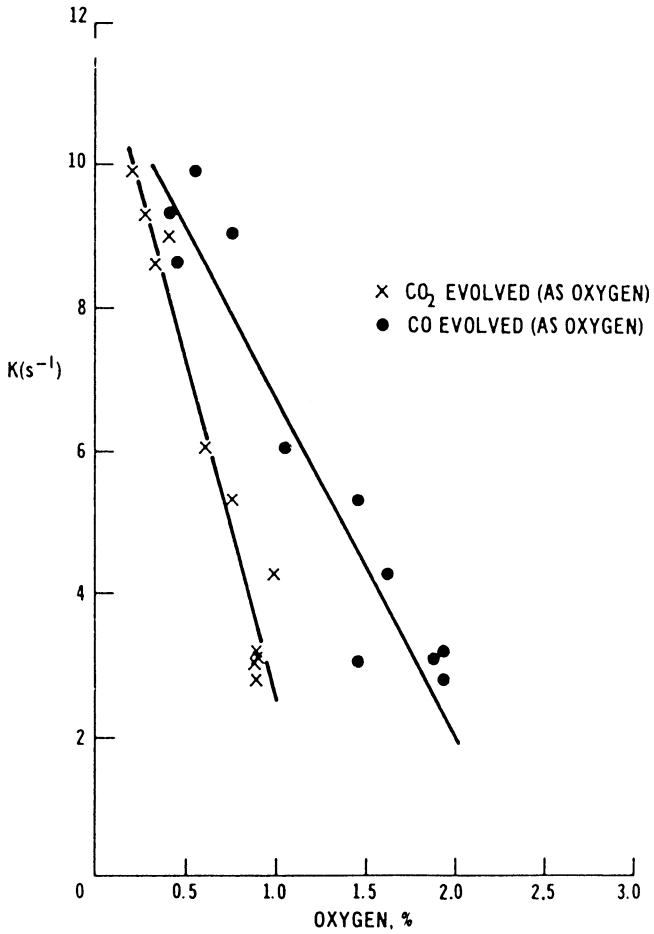


Figure 9. The effect of oxygen concentration to the adsorption efficiency of KI impregnated carbon [Billinge et al 1984].

Another problem of the KI impregnated carbon filters is their relatively fast exhaustion. In experiments performed with KI filters a significant decrease in the capacity took place

already during the 14 days operational period. This decrease can be partly attributed to high humidity, low operating temperature and nitrogen oxides present in the gas streams during the tests *[Billinge et al. 1984, Amend et al. 1991]*. In the presence of oxidizing agents such as nitrogen oxides, the isotope exchange of KI impregnated filter may be stopped completely *[Deitz 1987]*. The effect of oxygen concentration to the adsorption efficiency of KI impregnated carbon is shown in figure 9.

4.2.3 Derivatives of TEDA

The need to find more reactive and stable impregnants, that would perform well under severe accident conditions, has lead to studies of TEDA/KI impregnation and TEDA derivatives. All these compounds take advantage of both addition and exchange reactions. The amount of impregnant determines, which one of the reactions will dominate *[Kim 1991]*. A higher level of impregnation favours the exchange reaction, whereas with the smaller percentage of impregnat the addition is the primary reaction. The properties of activated carbon filters impregnated by a TEDA derivative and TEDA/KI are presented in table 7.

Table 7. The properties of activated carbon filters impregnated by a TEDA derivative and TEDA/KI [Kim 1991].

Compound	$N(CH_2CH_2)_3N^+CH_3I^-$	$N(CH_2CH_2)_3N$/KI
m_p(°C)	211	170
Amount of Isotope exchange (%)	81.86	TEDA: 78.85, KI:66.12
Level of Impregnation (wt%)	4.43	TEDA:2.14, KI:1.70
Deterioration at 80°C, rh 90%, 15h	none	TEDA: ~20%
Penetration (%)	0.08	0.08

There is evidence of the improved properties of the TEDA/KI impregnated filter. For example its ignition point is higher than that of pure TEDA. In an experiment the TEDA/KI filter was able to maintain its capacity even up to 180°C *[Deuber et al. 1987a]*. However, as stated before, a major problem of the impregnated carbon filters is aging.

With TEDA/KI impregnated filters the aging seems to be even faster than with pure TEDA filters. The penetration of methyl iodide through TEDA/KI impregnated filter was around 10% over the period of 9 to 27 months, when tested at 30°C and at 95% relative humidity *[Deitz 1987]*. The decrease in the capacity can be partly explained by the less efficient isotope exchange, and partly by the lower rates of the adsorption and chemical reactions.

TEDA derivatives include for example monoalkyl iodides of TEDA. Their behaviour resembles the TEDA/KI impregnation. There is an evidence, that methyl iodide reacts relatively fast with monoalkyl iodides. The reactions of methyl iodide and monoalkyl iodides of cyclic amines proceed via addition and exchange reactions. One isotopic exchange and two addition reactions are believed to occur. However, the actual pathway of the reaction is greatly depended on the level of impregnation as pointed out before. Two different derivatives, methyl and ethyl iodide of TEDA, have been examined with a purpose to improve the properties of the filter. Filter impregnated with monoethyl iodide of TEDA could tolerate humid conditions for a longer period of time than TEDA filters at the operational temperature of 80°C. The ethyl iodide derivatives were observed to be more reactive than the methyl iodide derivatives investigated in these experiments. The difference in the efficiency can probably be attributed to the better electron donating properties of the ethyl-group *[Kim 1991]*.

4.2.4 Other Amine Compounds

Two different amine derivatives, methyl and ethyl iodide of 1,4-dimethylpiperazine, have been examined for organo iodide filtration. With these impregnant the isotopic exchange seems to be the dominating reaction. The removal rates of methyl iodide were observed to be slower than with TEDA derivatives *[Kim 1991]*.

More data of the amine compounds is needed for a further evaluation of their properties. This could prove to be an interesting area of research, if impregnants capable of effective organo iodide filtration in humid conditions and at elevated temperatures are desired.

4.2.5 Silver Compounds

Some transition metals seems to possess suitable properties to decompose methyl iodide. The most widely studied transition metal in nuclear applications is silver and its compounds. The focus here is in the properties of silver nitrate ($AgNO_3$) as an impregnant of silica, alumina or AC6120 catalyst carrier. A schematic picture of $AgNO_3$ impregnated AC6120 filter is presented in figured 10. The catalytic properties of silver are introduced in chapter 6.2.5.

The reaction of organo iodides, particularly methyl iodide and silver nitrate produces yellow, insoluble AgI *[Sakurai and Takahashi 1994, Herrmann et al. 1991]*.

$$AgNO_3(s) + CH_3I(g) \leftrightarrow AgI(s) + CH_3NO_3(g) \qquad \textbf{(23)}$$

AgI is a very stable compound, although it is known to decompose to Ag and I_2, when exposed to sun light. There is no agreement, whether AgI is stable in the intense radiation field of a severe accident. The possible decomposition of AgI seems to depend on the type of radiation *[Cripps et al. 1999, Dickinson et al. 1999]*.

Silver nitrate ($AgNO_3$) impregnated filters have shown promising results in the iodine and organo iodide filtration in the several studies *[Furrer et al. 1991]*. $AgNO_3$ impregnated AC6120 filters have already replaced KI-filters in some reprocessing plants due to their more effective performance. According to the reports the filters have maintained their ability to remove I-129 even after 10 to 15 weeks operational periods. The performance of both silica and alumina filters impregnated with $AgNO_3$ is greatly dependent on temperature, concentration of iodine species and relative humidity. A good efficiency in organo and inorgano iodide removal has been reported also for these filters *[Amend 1991]*. Like the zeolite filters $AgNO_3$ impregnated filters can also be regenerated in the presence of nitrogen oxides *[Amend 1991]*. However, methyl iodide is more difficult to remove from the filters than heavier organo iodides *[Kobayashi 1991]*. The feasibility of regeneration should thus be considered carefully.

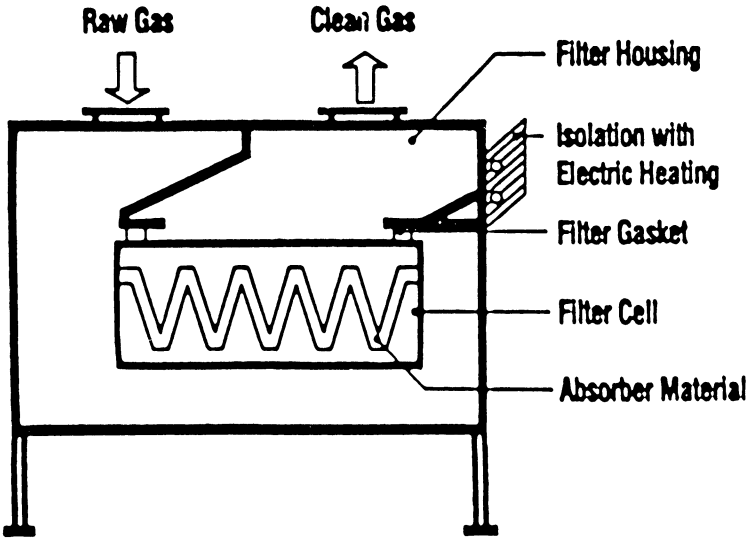


Figure 10. A schematic picture of $AgNO_3$ impregnated AC6120 filter including an electric heater [Amend 1991].

The removal of elemental iodine by the $AgNO_3$ filters is not thermodynamically favorable. A pure Ag-filter should be employed instead, when the removal of I_2 is desired *[Herrmann et al. 1991]*. The slow reaction rate of $AgNO_3$ and I_2 is probably due to the decomposition of $AgNO_3$, which is assumed to take place before the reaction with I_2. $AgNO_3$ decomposes probably forming Ag(s), NO_2(g) and $1/2O_2$. The evolution of metallic Ag allows further reaction with I_2 to proceed. A number of studies indicate that the reaction of silver and iodine occurs in acidic conditions. In alkaline solution this reaction is insignificant probably due to the oxidation of the Ag surface. However, the formation of elemental iodine and therefore organo iodides is negligible in basic conditions. Thus only acidic conditions are considered to be problematic *[Dickinson et al. 1999]*. Information on the reaction of Ag and methyl iodide could not be found. They should be studied in detail though, because these reactions could be efficient in organo iodide mitigation.

5. Chemical Reactions of Methyl Iodide and pH Control

As has been pointed out in chapter 3.1.1, it is beneficial to keep pH of the containment water pools as high as possible, because alkaline environment hinders the formation of elemental and organo iodides. When no pH control chemicals are present in sump water, pH during a severe accident is dependent on the nature and amount of compounds released to the containment. The most important bases released include fission product compounds such as CsOH, CsI and $Cs_2B_4O_7$, and basic oxides from core concrete interaction. Acidic compounds include pyrolysis and radiolysis products from organic materials, boric acid from ECCS and atmospheric species such as HNO_3 and CO_2. When no pH control is applied, the water pools in the containment will become eventually acidic *[Beahm et al. 1987]*.

The pH control chemicals are basic compounds like NaOH, KOH and LiOH. Usually they are stored in separate units, from which they will be pumped to the water pools in a case of a severe accident. For example in Olkiluoto NPP a large amount of NaOH is readily available for the pH control. Another method to maintain alkaline pH is to buffer water in suppression pools with borate or phosphate buffer. The buffering range for borate is around pH 9 and for phosphate around pH 7 *[Budavari 1989]*. Alkaline chemicals may also be added to the containment sprays, which are designed primarily to remove heat and airborne fission products during a core melt accident *[Parsly 1970]*. For example the sprays in Loviisa NPP contain hydrazine and KOH. In addition to this ice condensers in Loviisa contain a large amount of borax ($Na_2B_4O_7 \cdot H_2O$) *[Sjövall et al. 1999]*.

5.1 Typical Reactions of Primary Alkyl Halides

In this chapter some of the typical reactions of primary alkyl halides are described. The main emphasis is on the chemistry of hydroxides, thiosulfates and nitrogen compounds, such as amines, with methyl iodide. The reactions of methyl iodide with carboxylate and cyanide ions are only shortly covered, since no information is available on their behaviour in severe accident conditions. In addition, some of the compounds introduced here exhibit unwanted properties, such as toxicity, which limits their usability for the removal of

methyl iodide.

5.1.1 Reactions of Methyl Iodide with Hydroxide and Carboxylate Ions

Alkaline compounds are mainly applied in maintaining high pH in the containment building. If methyl iodide already exists in the sump water, its reaction with hydroxyl ions proceeds well.

$$CH_3I + OH^- \leftrightarrow CH_3OH + I^- \qquad \textbf{(24)}$$

However, the experiments performed by Parsly using a water solution of boric acid and sodium hydroxide (**solution 1**),

Solution 1: $H_3BO_3(0.28M) + NaOH(0.17M)$

gave slower reaction rate than expected *[Parsly 1970]*. Boric acid was used in the solution in order to simulate the water chemistry during a severe accident.

Primary alkyl halides react also with carboxylate ions producing esters and halide ions,

$$1^o RX + {}^- OC(=O)R' \leftrightarrow ROC(=O)R' + X^- \qquad \textbf{(25)}$$

where 1^oRX is a primary alkyl halide, R is an alkyl chain and X is Cl, Br or I *[Fessenden & Fessenden 1994]*. Carboxylate ions are not studied in severe accident conditions. It might act as a source of organic material, which may prove to be a disadvantage in an accident.

5.1.2 Reactions of Thiosulfates and Methyl Iodide

The reaction of thiosulfate with elemental iodine produces iodide ions:

$$I_2 + 2S_2O_3^{2-} \leftrightarrow 2I^- + S_4O_6^{2-} \qquad \textbf{(26)}$$

Thiosulfates have also been studied for the removal of methyl iodide. Parsly performed similar experiments with them as with hydroxides adding sodium thiosulfate to the solution *[Parsly 1970]*.

Solution 2: $H_3BO_3(0.28M) + NaOH(0.17M) + Na_2S_2O_3(0.063M)$

Even though the reaction of thiosulfate ions with methyl iodide was reported to be 500 times faster than the reaction with hydroxyl ions, elevated temperatures were required to achieve a good removal efficiency *[Parsly 1970]*. $Na_2S_2O_3$ solution is used in Olkiluoto NPP together with NaOH as mentioned in chapter 2.3.

It has been reported that elemental iodine reacts with sulfite ion analogously to reaction **(26)** *[Laitinen and Toivonen 1993]*. Thus, it is very likely that the following reaction would proceed also with methyl iodide.

$$SO_3^{2-} + H_2O + I_2 \leftrightarrow SO_4^{2-} + 2H^+ + 2I^- \qquad \textbf{(27)}$$

In the reaction elemental iodine is reduced to iodide ions and sulfuric acid is produced. Thus, it might not be as advantageous as reaction **(26)**.

5.1.3 Reactions of Methyl Iodide with Hydrogen Sulfide Ions and Thiols

The reaction of methyl iodide with hydrogen sulfide ions proceeds well, when there is an excess of HS^-. The reaction produces thiols and iodide ions:

$$CH_3I + {}^-SH \rightarrow CH_3SH + I^- \qquad \textbf{(28)}$$

Hydrogen sulfide (H_2S) is a volatile compound, which readily decomposes in water producing ^-SH ions. The acidity of this compound might not be a tempting property. It is also a toxic compound that should be handeled with care *[Fessenden & Fessenden 1994]*.

As in reaction **(28)** primary alkyl halides react with thiols producing sulfides and halide ions.

$$1^{o} RX + {}^{-} SR' \leftrightarrow RSR' + X^{-} \qquad \textbf{(29)}$$

Thiols produced in the reaction **(28)** are also able to react further with mild oxidizing agents such as I_2. In oxidative conditions reaction produces disulfides and in reductive conditions it is reversed *[Fessenden & Fessenden 1994]*.

$$2CH_3SH \underset{[H]}{\overset{[O]}{\longleftrightarrow}} CH_3S - SCH_3 \qquad \textbf{(30)}$$

5.1.4 Nitrogen Compounds

The reactions of primary alkyl halides, such as methyl iodide, with tertiary amines were described already in chapter 4. It proceeds as presented in equation **(21)**. The reaction with cyanide ion is only shortly covered here, because of the toxicity of this compound.

$$1^{o} RX + {}^{-} CN \leftrightarrow RCN + X^{-} \qquad \textbf{(31)}$$

There is also a report of the reaction between hydorxylamine and iodine. It is smooth and rapid in alkaline media *[Cau dit Coumes et al. 1996]*:

$$2NH_2OH + 2I_2 \leftrightarrow N_2O + 4I^{-} + H_2O + 4H^{+} \qquad \textbf{(32)}$$

However, hydroxylamine is a difficult compound to handle, because it detonates when heated with a flame *[Budavari 1989]*.

There are also some commercially available nitrogen compounds, such as PEI 1000 (polyethyleneimine, a trademark of Dow Chemical Company) and cetyl

trimethylammonium bromide, for the removal of organo iodides. Parsly have carried out some experiments with PEI similar to those with hydroxides and thiosulfates. The results showed that PEI accelerated the removal rate of methyl iodide. The reaction was almost four times faster, when compared to **solution 1**. The use of PEI together with **solution 2** reduced the half-life of methyl iodide about 20%. Even though the addition of PEI increased the reaction rate, a still faster reaction is desired. The experiments of cetyl trimethylammonium bromide with methyl iodide proved that this compound reacts fast only up to room temperature. At higher temperatures its impact is less significant *[Parsly 1970]*.

6. Potential of Surface Catalysts to Decompose Methyl Iodide

Transition metals as well as silicon from the carbon group are widely used as surface catalysts, since they provide a reaction pathway with a lower activation energy for example in a methanation reaction. The activity of a catalyst is depended on the strength of adsorption to its surface, because the surface of a catalyst should be covered extensively by the adsorbate *[Atkins 1990]*. The studies introduced here are focused on the stability of methyl radicals on surfaces and on the catalytic methanation reactions. Reaction kinetics are not described. The properties of the transition metals vary greatly. Some physical and chemical characteristics of surface catalysts are presented in table 5. It should be noted that also gold is likely to exhibit similar properties than other elements in group 11. It is not included in this literature review though, since studies on its behaviour could not be found.

The potential of transition metals or silicon to decompose methyl iodide has not been studied in nuclear applications. Nevertheless they could provide an efficient way to remove organo iodides. A large amount of some of these metals, for example nickel, copper and silver, are already present in a nuclear power plant.

Table 8. Physical and chemical properties of the surface catalysts [Weast 1984].

Group	*Element*	*M*	m_p	b_p	*Solubility*		
		(g/mol)	(°C)	(°C)	*insoluble*	*slightly soluble*	*soluble*
6	Tungsten (W)	183.85	3410±20	5660	water, HF, KOH	HNO_3, H_2SO_4, aqua regia	HNO_3+HF, fused $NaOH+NaNO_3$
10	Nickel (Ni)	58.69	1455	2730	water, NH_3	HCl, H_2SO_4	dilute HNO_3
	Palladium (Pd)	106.42	1554	2970	water	HCl	hot HNO_3, H_2SO_4
	Platinum (Pt)	195.08	1772	3827±100	water	-	aqua regia, dilute acid, fused alkali
11	Copper (Cu)	63.55	1063±0.2	2567	water, NH_3	HCl, NH_4OH	HNO_3, hot H_2SO_4
	Silver (Ag)	107.87	961.93	2212	water	-	HNO_3, hot H_2SO_4, KCN
12	Zinc (Zn)	65.38	419.58	907	water	-	acids, acetic acid, alkali
14	Silicon (Si)	28.09	1410	2355	water, HF	-	HF+HNO_3

6.1 Introduction to the Experimental Arrangement

Organo halides are known to contain a fragile carbon-halogen bond that can easily be dissociated on the surface of a catalyst *[Zhou et al. 1988b]* The dissociation reactions on the surfaces are either thermodynamic or photolytic *[Chiang et al. 1992, Chen & Winograd 1994]*. In most experiments methyl iodide is the source of alkyl radicals *[Chiang et al. 1992, Zaera 1992, French & Harrison 1995, Colaianni et al. 1992]*. It is strongly bonded to the surface via a halogen atom. Unlike other alkyl halides, methyl iodide does not easily desorb from the surface and therefore undergoes the decomposition reaction *[Zhou et al. 1989]*.

In the experiments the catalyst samples are exposed to a gaseous organo halide for a set time in a constant pressure. During this period the gas molecules are adsorbed to the surface of the catalyst. Most experiments are carried out at very low temperatures (around 100K), since both chemi- and physisorption of molecules are temperature depended reactions. When temperature increases gas molecules are able to rebound from the surface, because of their higher kinetic energy. Even at normal temperatures the measurements would be difficult to perform, because the amount of adsorbed compounds would be too small. This situation is made worse by the fact that in most studies also the surface area of the adsorbent is very small. Another reason to use low temperature is the instable nature of methyl radical. *[Adamson 1990]*.

After the exposure period the catalyst samples are placed into an ultra high vacuum chamber (UHV). There the samples are heated with a constant heating ramp and the desorption of compounds is measured using spectrometric equipment such as XPS, AES, SIMS or QMS. The metal crystals were always cleaned before their use. The size of the crystals was not determined in some studies. Thus it is difficult to predict the reaction rates and the ratio of methyl iodide versus the metal *[Zhou et al. 1988b, Chiang et al. 1992, Chen & Winograd 1994, Zhou et al. 1989, Zaera 1992, French & Harrison 1995, Colaianni et al. 1992, Solymosi & Révolész 1993, Zhou & White 1987, Zhou & White 1988, Henderson et al. 1987, Gutleben et al. 1991]*.

The experiments can give an insight to the properties of the transition metals. However, their behaviour in severe accident conditions is still largely unknown. For example, there might be some other compounds present in a containment building, that might poison the catalysts *[Dewit et al. 1996]*. Also the effect of higher temperatures and larger ratio of adsorbent vs adsorbate is not known. Thus, during an accident, the chemical reaction of the metals may become more important than the pure catalytic reaction. Further studies are needed to resolve the effect of these factors.

6.1.1 Metallic Nickel (Ni)

In experiments performed by Zhou and White, clean Ni(100) crystals were exposed to methyl iodide at the temperature of 100 K. The gas molecules were observed to adsorb dissociatively to the surface of the catalyst. The adsorption to the clean surface took place by chemisorption, in which both iodide and surface methyl groups, $CH_3(a)$, were attached to the Ni(100) crystal. The cleavage of the C-I bond was due to the low bond energy. The bond dissociation energy in the gas phase was estimated to be 222 kJ/mol and was reduced on Ni(100) surface to 15 kJ/mol. When the same experiment was conducted using methyl chloride, no dissociation was detected. The energy of C-Cl bond was calculated to be 351 kJ/mol in the gas phase. Ni(100) surface was more active for breaking carbon-halogen bonds than Pt(111), Al(111), Mg(0001) or Fe(100). When the exposure of Ni(100) crystal to methyl iodide was increased, also the physisorption of gas molecules was observed *[Zhou & White 1987, Zhou and White 1988]*

When the samples were heated, only a tiny amount of molecular CH_3I desorbed from chemisorbed monolayers of CH_3I at 169 K. However, physisorbed methyl iodide was easily desorbed already at 135 K. Elemental iodine did not start to desorb until the temperature reached 800K. Upon heating, low coverages of $CH_3(a)$ decomposed completely to H(a) and C(a). For higher coverages of $CH_3(a)$, also methane was desorbed from the surface. On deuterium precovered Ni(100) surface, methane formation was enhanced *[Zhou & White 1987, Zhou and White 1988]*. It should be noted though, that $CH_3(a)$ has been observed to behave differently on Ni(111) and on polycrystalline Ni

surfaces *[Zhou and White 1988 Lee et al. 1986, Steinbach et al. 1985]*. The catalytic properties of Ni are interesting, since a large amount of it is in the steel structures of a nuclear power plant.

6.1.2 Metallic Palladium (Pd)

Two sets of experiments were reported, where the reactions of methyl iodide with Pd(100) and Pd{111} crystals were studied. The Pd(100) crystals were exposed to methyl iodide at 85 K and Pd{111} at 100 K. At low temperatures methyl iodide had a high sticking coefficient to the Pd-surfaces, which means that almost all incident molecules adsorbed to the surface. It was reported that methyl iodide adsorbed dissociatively to clean Pd(100) surface whereas on Pd{111} the C-I bond cleavage occurred between 175 K and 200 K *[Solymosi & Révolész 1987, Chen & Winograd 1994]*. It is obvious that the C-I bond breaking is easier on the more open surface of Pd(100). The C-I bond cleavage seemed to require a direct contact of iodide with the Pd surface. When similar experiments were carried out with iodine precovered Pd{111}, the molecular desorption of methyl iodide was observed *[Chen & Winograd 1994]*. The chemisorption of methyl iodide could also be prevented by carbon monoxide saturation *[Chen & Winograd 1994]*.

Some experiments with Pd(100) have been performed at higher temperatures. It was reported that even with a high dose of methyl iodide in temperatures between 300 and 425K, it was almost completely dissociated to C(a) or CH(a) fragments and I(a). No desorption of molecular methyl iodide occurred *[Solymosi & Révolész 1987]*.

No molecular desorption of methyl iodide from the clean Pd(100) surface could be detected at low exposures at 85 K. At higher exposures a single desorption peak developed at 129 K. Methane was the main decomposition product desorbed from Pd(100). The peak of the desorption was at 170 K. Other hydrocarbons could be detected only in trace amounts. Iodine atoms remained on the Pd(100) surface up to 700K *[Solymosi & Révolész 1987]*. Some methyl iodide was desorbed from Pd{111} at 150 K. Above 190 K no significant CH_3I desorption was found. After the decomposition of CH_3I, surface methyl group was hydrogenated forming methane. Methane desorbed

instantly from the Pd{111} surface. Surface iodine remained on the Pd{111} up to 850 K and was completely desorbed at 1100 K *[Chen & Winograd 1994]*.

In nuclear power plants palladium is present in passive hydrogen recombiners as a surface catalysts *[Rohde et al. 1996]*. Thus the possible capability of Pd to decompose methyl iodide would be a further benefit of these equipment. Also inorganic Pd membrane reactors, used for hydrogen separation, could be investigated for the removal of methyl iodide. These dense membrane reactors provide high selectivity and thermal stability under high fluxes *[Ma 1999]*.

6.1.3 Metallic Platinum (Pt)

The thermal dissociation of methyl iodide on the Pt(111) surface has been studied by several groups. Methyl iodide adsorbed molecularly to the Pt(111) surface, when it was exposed to CH_3I at 25, 100 and 105 K. Methyl iodide was bonded to the surface via iodine *[Henderson et al. 1987, Zaera 1992, French & Harrison 1995]*. It was observed to thermally dissociate over the temperature range from 190 to 215 K forming surface bound methyl radicals and iodine. The activation barrier of the dissociation was approximately 48±3 kJ/mol *[French & Harrison 1995]*.

Only a small amount methyl iodide desorbed at low surface coverages. Methyl iodide desorption peak was centered at 225 K. As the coverage increased the desorption peak was substantially broadened toward lower temperatures. At saturation monolayer coverage desorption temperature ranged from 130 to 255 K *[French & Harrison 1995]*. The coadsorption of hydrogen also weakened the binding of methyl iodide to the Pt(111) surface. Thus the amount of desorbed methyl iodide was increased and the phenomenon was observed to take place at lower temperatures *[Zaera 1992]*. When only a small amount of methyl iodide was adsorbed, complete thermal decomposition of surface methyl-group took place and no desorption of methane could be detected. At higher exposures methane desorbed around 275 and 300 K. When methyl iodide was coadsorbed with molecular hydrogen, the decomposition of surface methyl-groups was inhibited. This lead to enhanced formation of methane, which desorbed at 275 K. The desorption of

hydrogen took place at 345 and 550 K. The hydrogen peak at 550 K was due to the decomposition of CH_2 surface fragments *[Zaera 1992]*. The desorption of iodine was observed as a broad peak between 500 and 800 K *[Henderson et al. 1987]*.

6.1.4 Metallic Copper (Cu)

The Cu(110) crystals were exposed to methyl iodide at 120 K. It was reported to dissociate on the surface below 200 K. At low exposures the dissociation probability of methyl iodide was assumed to be unity *[Chiang et al. 1992]*.

Molecular desorption of methyl iodide could be detected only at very high exposures at 135 K and it was attributed to the formation of multilayers. The gas phase products were coverage dependent. At low exposures both methane and ethene were formed. The formation of these compounds followed first order reaction kinetics. The peak of the desorption for both compounds was centered at 470 K. An additional peak at 340 K for methane was also observed. It was probably due to a reaction of surface methyl groups with hydrogen impurity. Also the formation of ethane was observed at high exposures around 400 K. Ethane was produced by the recombination of methyl groups, which was the rate determining step. The formation followed second order kinetics. Besides the overall surface coverage, the amount of iodine might have increased the formation of ethane and decreased ethene. Iodine was desorbed from the surface only, when it was briefly annealed up to 980 K. It was assumed to desorb as CuI molecules *[Chiang et al. 1992]*.

There is a large amount of copper in the cables of a nuclear power plant. During a severe accident copper may be uncovered under the rubber insulation. Further investigations are needed to determine the reactions between copper and organo iodide.

6.1.5 Metallic Silver (Ag)

Both thermal and photolytical decomposition of methyl iodide has been studied on the Ag(111) surface. The clean Ag(111) crystals were exposed to methyl iodide at 100 K. Methyl iodide adsorbed molecularly to the surface with a high sticking coefficient that

remained constant even at high surface coverages. According to the results, the reaction of iodine compounds with silver surface was mass-transfer limited *[Zhou et al. 1989]*. Methyl iodide formed a strong bond between the surface and iodide *[Zhou and White 1991]*. A large amount of the adsorbed methyl iodide decomposed between 135 K and 190 K producing surface methyl- and iodide-groups *[Zhou et al. 1989]*.

While methyl iodide did not thermally dissociate on the Ag(111) surface at 100 K, it could readily be photolyzed to CH_3(a) and I(a). This experiment was carried out using high pressure Hg arc lamp to produce UV irradiation. The maximum rate of photolysis was about $(9\pm1)*10^{11}$ molecules / (cm^2*s). The effective photolysis rate was higher for multilayer than for monolayer of methyl iodide on Ag(111). The threshold of methyl iodide photodissociation on the Ag(111) surface was measured using cutoff filters. It was observed to be 480 nm. In the gas phase the threshold was 340 nm. The decomposition of gaseous methyl iodide was due to the dissociative electron attachment *[Zhou and White 1991]*.

Methyl iodide may undergo a chemical reaction with silver producing AgI. This is analogous to the reaction **(23)** of $AgNO_3$ and CH_3I *[Herrmann et al. 1991]*.

$$Ag(s) + CH_3I(g) \leftrightarrow AgI(s) + \tfrac{1}{2} C_2H_6 \qquad \textbf{(33)}$$

Molecular desorption of methyl iodide could only be observed at high coverages from the Ag(111) surface between 188 K and 225 K *[Zhou and White 1991]*. The desorption energies were very close to the heats of sublimation that is 37 kJ/mol for methyl iodide No methane or hydrogen desorption from the surface could be detected, since the recombination of CH_3-species to C_2H_6 was faster than dehydrogenation. This was due to the catalytic properties of silver. Ethane was desorbed above 200 K with peak centered at 257 K. No desorption of silver iodide or elemental iodide was observed. Thus it was concluded that iodine desorbed as atoms between 700 K and 920 K *[Zhou et al. 1989]*. The products of photolysed methyl iodide desorbed analogously to the thermally

dissociated molecules. However, most CH_3 fragments desorbed already during the UV irradiation. The remained surface methyl groups formed ethane as was the case with thermal dissociation products *[Zhou and White 1991]*.

Silver is one of the component of Ag-In-Cd control rods used in most PWRs. There is approximately 2260 kg of Ag readily available in a typical 1000 MWe PWR core. A small amount, around 58 mol, of Ag is also in the fuel as a fission product of uranium *[Wright 1994]*. Silver is most likely released from the control rods during a core melt accident. It enters the containment building in an aerosol form. In a humid atmosphere it settles rapidly into the sump water, where it is likely to exist either in colloidal or soluble form. The solubility of Ag is an important factor, since most of the reactions take place in the aqueous phase. According to the reports the reaction of iodine with silver is fast and most likely irreversible *[Dickinson et al. 1999]*. Thus it can be considered as an iodine sink. However, the stability of AgI is not fully agreed. The radiolytic and photolytic decomposition of AgI was discussed in chapter 4.2.5.

6.1.6 Metallic Tungsten (W)

The W(100) crystals were exposed to methyl chloride, bromide and iodide at 140 K. The sticking coefficient for methyl iodide remained constant even at high surface coverages, which was different than reported for other halides. All methyl halides were decomposed to some extent, which was due to a strong bonding between W(100) and CH_3X molecules (X= Cl, Br, I). The decomposition was directly related to the bond strength of C-X. Thus methyl iodide decomposed more easily than other halides. The decomposition of methyl iodide produced surface methyl- and iodide-groups. It was postulated that CH_3(a) reacted further forming H(a), C(a) and CH(a) below the room temperature. No methane formation could be detected. However, the actual reaction mechanism is not known *[Zhou et al. 1988b]*.

At low exposures of CH_3X, no molecular desorption could be detected at 140 K. At high exposures both dissociation and desorption of CH_3Cl and CH_3Br took place. Methyl iodide was detected to desorb in TPD spectra at 165 K, 288 K and at very high exposures

at 230 K. No methane or other hydrocarbons desorbed from the surface. Molecular hydrogen desorbed approximately at 335 K with a tail above 500 K. Iodine desorbed as atoms at 1170 K *[Zhou et al. 1988b]*.

6.2.7 Metallic Silicon (Si)

Two sets of experiments were reported, where the reactions of methyl iodide and deuterated methyl iodide on a clean Si(100)-(2x1) surface were studied. The cystals were exposed to methyl iodide at 100 K. At low exposures methyl iodide was reporeted to adsorb dissociatively to Si(100) surface. One methyl iodide molecule was adsorbed per two silicon atoms as shown in figure 11. The multilayer of methyl iodide was decomposed upon heating to 200 K. After that the surface resembeled the low coverage Si(100) surface *[Coloianni et al. 1992]*. Deuterated methyl iodide was dosed to the Si(100) surface at 310 K. It adsorbed with initial sticking coefficient close to unity. The reaction probability was constant up to 70% saturation coverage of the surface *[Gutleben et al. 1991]*.

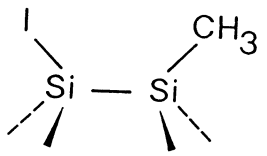


Figure 11. The adsorption of methyl iodide to the Si(100)-(2x1) surface [Gutleben et al. 1991].

No molecular desorption of methyl iodide was detected. Less than 1% of the adsorbed carbon desorbed from the surface saturated with methyl iodide. The main desorption product was ethene, whereas no methane or ethane could be observed *[Gutleben et al. 1991]*. However, it was observed that above 600 K CH_3(a)-groups were decomposed further to CH(a)-groups. According to Gutleben adsorbed carbon began to diffuse to the bulk material above 750 K. Whereas Coloianni reported that CH species remained on the surface up to 775 K *[Coloianni et al. 1992]*. Hydrogen liberated by thermal decomposition of hydrocarbons started to desorb at 700 K *[Gutleben et al. 1991]*. Iodine desorption was observed between 650 K and 850 K *[Coloianni et al. 1992]*. In the

experiments conducted with deuterated methyl iodide, there was evidence also for the formation of DI. However, the production of atomic iodine was much faster than the production of DI. Thus it was concluded that iodine desorbs mainly as atoms *[Gutleben et al. 1991]*.

6.1.8 Zinc (Zn) Surface

Evans and Bekeriss have reported about experiments, where the reactions between inorganic zinc primer coated surfaces and molecular iodine was studied. The mixture of air and iodine was passed through glass tubes coated by zinc paint. The accumulation of iodine to the surface was monitored with 2x2" NaI detector connected to a PC based multi-channel analyzer (MCA). The test parameters were relative humidity, flow rate, iodine concentration and the temperature of the paint. The relative humidity and temperature had a major impact on the reaction rate. The reaction was observed to proceed fast in a relative humidity above 80% and at temperatures below 300 K. At temperatures higher than 363 K, the impact of high relative humidity was less significant. The reaction was also limited by gas phase mass transfer *[Evans & Bekeriss 1996]*.

The deposition of molecular iodide to zinc paint occurred mainly through surface interactions. Iodine was not detected to diffuse throughout the full thickness of the paint. The physical adsorption of iodine was followed by its chemical reaction with zinc coating. The previous studies performed by Kupferschmidt indicated a rapid reduction from molecular iodine to iodide ion on the zinc primer coated surfaces. Iodide ion was then further adsorbed to the surface. According to the results, iodide ion reacted with Zn^{2+} ion producing most likely ZnI_2. However, there are uncertainties in the actual reaction mechanism *[Evans & Bekeriss 1996]*.

The zinc paint was observed to have a vast capacity to adsorb molecular iodide. Thus the surface saturation was not an issue in this study. The desorption of iodine from the zinc coated surface was observed to be slow. The relative humidity of the purging air did not influence the desorption *[Evans & Bekeriss 1996]*. Even though molecular iodine is readily adsorbed on many surface materials present in a nuclear power plant, this might

not be the case with organo iodides. However, zinc primer coated surfaces are reported to have similar properties than silver and should thus be studied further *[Wren et al. 1999a]*.

7. Applying Corona-discharge Reactors to Remove Methyl Iodide and Elemental Iodine

The gas streams can be efficiently purified using electron attachment to decompose halocarbon species. The electrons are produced by a discharge that is generated by directing high voltage through a cathode. The low-energy electrons collide with the gas molecules and produce negative ions. The reaction of methyl iodide is described below:

$$CH_3I + e^- \rightarrow CH_3 + I^- \qquad (34)$$

The negative ions drift toward the anode, where they are collected. *[Sano et al. 1996]*. The ratio of the electric field strength (E) and the gas pressure defines the rate of the reaction *[Tanthapanichakoon et al. 1998]*. In addition, the reaction is dependent on the energy of the electrons, the structure of the gas molecules, and the affinity of the molecules to ionize. In the case of methyl iodide one electron is able to remove approximately three gas molecules. The principle of gas purification by a corona-discharge reactor is shown in figure 12. *[Sano et al. 1996]*.

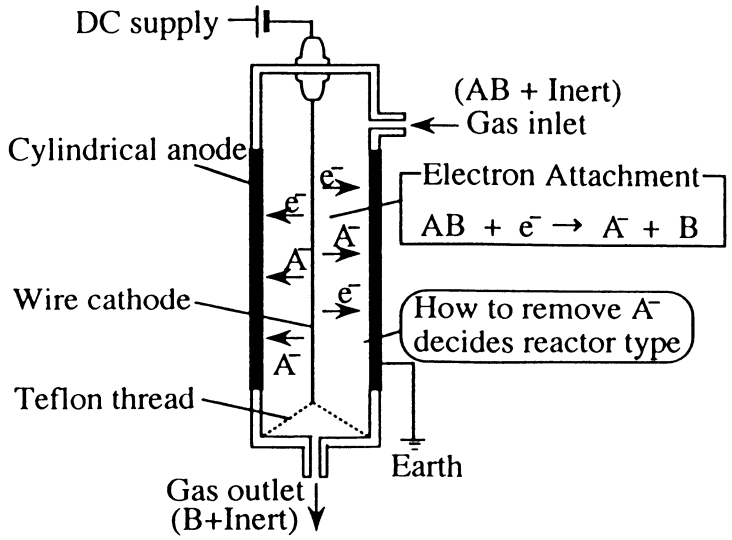


Figure 12. The principle of gas purification by a corona-discharge reactor [Sano et al. 1996].

There are several different types of corona-discharge reactors. In a deposition-type of reactor the negative ions deposit to the surface of the anode, when the gas flows past the anode. In a sweep-out-type of reactor the gas flow is directed trough a porous anode. The weakness of these reactors is that they produce elemental iodine *[Sano et al. 1996]*:

$$I^- \rightarrow I + e^- \quad \textbf{(35)}$$

$$2I \rightarrow I_2 \quad \textbf{(36)}$$

A wetted-wall reactor is a corona-discharge reactor, in which the anode is covered with a thin layer of water. In the wetted-wall reactor the ionized molecules are adsorbed to the liquid film around the anode. Water on the anode enhances the reaction by lowering the concentration of I_2 *[Sano et al. 1996]*. The removal of methyl iodide by deposition-type and wetted-wall reactors is compared in figure 13.

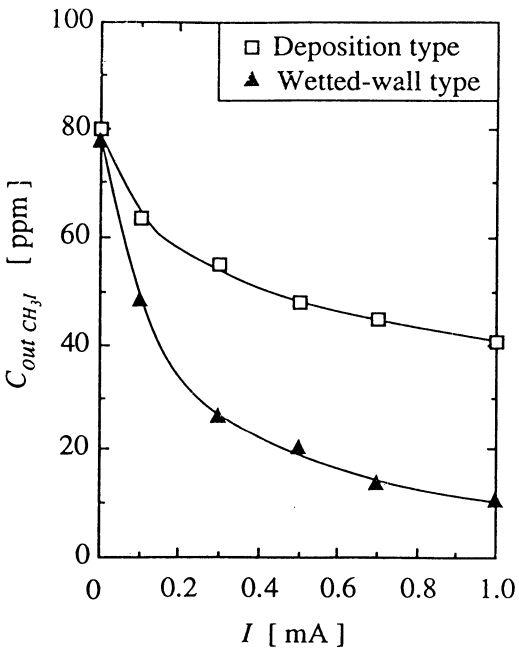


Figure 13. Removal of methyl iodide by deposition-type and wetted-wall reactors with different cathode current [Sano et al. 1996].

The removal of methyl iodide by corona-discharge is reported to be efficient. This

method could be applied under the normal operating conditions of a NPP. However, corona-discharge reactors are not an optimal solution for accident management, because they require an external electricity supply. When considering this aspect the purification by electrodes is not the best option. One should also notice that the presence of O_2 in the reactor may cause the formation of ozone, which may have undesirable effects on the chemistry *[Sano et al. 1997]*.

8. Conclusions

Iodine chemistry during a core melt accident has been under intensive studies, since the accident at TMI-2 NPP. Because of the complex nature of iodine species, the reaction mechanisms and pathways are still somewhat unclear. It has been indicated that whereas the removal of particulate, elemental and ionic iodine species is most likely adequate, this might not be the case with organo iodides. Thus, the evolution of organo iodides during a core melt accident must be kept as low as possible. To achieve this the main method currently in use is pH control. The formation of elemental iodine, that could react further producing organo iodides, is minimal in alkaline solutions. Hence, strong basic chemicals, such as NaOH, KOH and LiOH, are readily available in most nuclear power plants. However, there are several problems associated with strong alkaline compounds. These include the highly corrosive nature of these chemicals, their stability under an intensive radiation and their ability to compensate possibly a very rapid formation of strong acids such as HCl. In addition to the alkaline chemicals, a more effective use of buffers should be established. Two buffer solution, borate and phosphate buffers, are considered as possible candidates for nuclear power plants. However, buffers are not yet considered to be used in a severe accident. If an effective method to use buffers is developed, the maintenance of alkaline pH could be possible for a longer period of time.

Filters are commonly used to remove gaseous iodine species. Most filters are made of porous bed materials, such as activated carbon and zeolite, so that their effective surface is as large as possible. These kind of filters have a high capacity and a good removal efficiency. However, the filtering capacity of porous materials degrade in high relative humidity, since water may condense to the micropores of the filter. This may have a major impact on their ability to remove methyl iodide. One solution to the problem could be the use of improved bed materials in humid conditions. Another solution could be to remove the water vapor before it enters to the filter. A third solution could be a combination of different filter types to guarantee the adequate removal of gaseous iodine species.

Impregnants, such as TEDA and KI, are used to improve the performance of the filters. The reaction of impregnant and methyl iodide is irreversible and can continue only to a certain extent. TEDA has shown a high affinity toward methyl iodide as well as elemental iodine. However, TEDA is not stable in acidic conditions and its ignition temperature is below 200°C. Therefore, there is a need to develop more reactive and stable impregnants. One of these could be $AgNO_3$, which is used in some reprocessing plants to remove methyl iodide. The affinity of $AgNO_3$ to elemental iodine is not as high though. Other possible impregnants could be for example amine and sulfate compounds.

There is also reports on efficient decomposition of methyl iodide by the corona-discharge reactors. It should be noted though, that it is not a passive method. The electrodes are dependent on an outside energy supply, which can cause problems during a severe accident. Also the reliability and maintenance of these equipment may limit their use. Thus, corona-discharge reactors are not considered as potential option in this literature review.

The potential of most transition metals to remove methyl iodide is not investigated in the conditions of a nuclear power plant. The studies conducted with silver and zinc prove that they could decompose methyl iodide in severe accident conditions. The reaction of silver and methyl iodide produces silver iodide, which is known to decompose in light. Currently there is no agreement whether silver iodide is stable in an intense radiation field. Surface catalyst studies report that also other transition metals could be applied to remove organo iodides. Some of these compounds are already present in the containment building. For example passive hydrogen recombiners contain a large amount of palladium. Further studies are needed to determine the behaviour of transition metals during a severe accident.

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