

# **Methods of Gas Phase Capture of Iodine from Fuel Reprocessing Off-Gas: A Literature Survey**

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February 2007



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**February 2007**

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## **SUMMARY**

A literature survey was conducted to collect information and summarize the methods available to capture iodine from fuel reprocessing off-gases. Techniques were categorized as either wet scrubbing or solid adsorbent methods, and each method was generally described as it might be used under reprocessing conditions. Decontamination factors are quoted only to give a rough indication of the effectiveness of the method. No attempt is made to identify a preferred capture method at this time, although activities are proposed that would provide a consistent baseline that would aid in evaluating candidate materials and technologies.



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## ACRONYMS/ABBREVIATIONS

AgA	Silver impregnated alumina
AgX	Silver exchanged faujasite
AgZ	Silver exchanged mordenite
Ag°Z	Silver exchanged mordenite (silver reduced to metallic state)
BET	Brunauer, Emmett, and Teller
DF	Decontamination factor
DOG	Dissolver off-gas
LMFBR	Liquid metal fast breeder reactor
PbX	Lead exchanged faujasite
VOG	Vessel off-gas

# Methods of Gas Phase Capture of Iodine from Fuel Reprocessing Off-Gas: A Literature Survey

## 1. OBJECTIVE

The objective of this report is to discuss technologies for removing gas phase iodine from process effluent streams as it pertains to nuclear fuel reprocessing. The primary isotope of interest is I-129 due to its long half-life, toxicity, and persistence in the environment. However, the techniques may be used for any of the iodine isotopes, and furthermore, may be applied to any operation (not just fuel reprocessing) where iodine exists as an air pollutant.

## 2. BACKGROUND

### 2.1 Iodine occurrence

Iodine-129 is one of several radioactive iodine isotopes formed as a fission product in nuclear fuel. It has a very long half-life of  $15.7 \times 10^6$  years, and undergoes beta decay and emission of gamma rays before forming stable Xe-129. Iodine is a volatile material, but is effectively retained within the fuel matrix and by the containment provided by the fuel cladding - very little is normally emitted. Only during an off-normal condition, damaged cladding for example, or during fuel reprocessing would iodine be liberated. Because of its long half-life, I-129 persists in the environment and is one of the radioactive gases targeted for capture during fuel reprocessing.

During reprocessing, I-129 may partition between several different streams and in various proportions depending on the specific process scheme. For example, if the fuel undergoes an initial sizing and thermal conditioning step (voloxidation), a significant fraction may be released to the voloxidation off-gas. The rest would be released during acid dissolution of the fuel, with smaller amounts carried downstream to the solvent extraction operations or released as a precipitate with other undissolved solids. If voloxidation is omitted, the dissolver off-gas (DOG) would contain most of the released iodine (IAEA 1987). The significance for iodine capture is the carrier gas associated with the process options. The voloxidation off-gas will likely have elevated levels of oxygen or ozone, whereas the dissolver off-gas will have high levels of  $\text{NO}_x$  and be nearly saturated with water.

In addition to I-129, other isotopes of iodine (I-131 to I-135) are produced in nuclear fuel and will contribute much greater activities at shutdown. However, these have relatively short half-lives (I-131 has the longest  $t_{1/2}$  of 8 days) and are only a radiological concern if an accident occurred during operations, or if reprocessing were pursued after a short cooling period (IAEA 1973). The effect of the cooling period on isotope distribution is illustrated in Table 1 for Liquid Metal Fast Breeder Reactor (LMFBR) fuel. As shown in this table, after only one year of cooling, the activity of I-131 becomes insignificant relative to I-129.

The stable isotope I-127 is also formed in reactor fuel, and the ratio of it to I-129 is dependent on the fuel type. After a modest cooling period, about 20 wt% of the iodine is I-127 in thermal fuels, the value is about 25 wt% for fast fuels (McKay 1982). So practically speaking, in fuel reprocessing about 20 to 25% of the iodine is stable-127. This must be accounted for when estimating total loadings or activities associated with iodine on adsorbents, final waste forms, etc.

For example, the specific activity of I-129 is  $1.765 \times 10^{-4}$  Ci/g, but when considering the total iodine deposited on a material, the equivalent is say 75% of this or  $1.32 \times 10^{-4}$  Ci/g (total I).

Table 1. Iodine isotope distributions for various times after discharge from a Liquid Metal Fast Breeder Reactor - based on 1 metric ton of fuel (Trevorrow 1983).

Isotope	$t_{1/2}$	0 days		150 days		365 days	
		Ci	g	Ci	g	Ci	g
I-127	stable	0	74.6	0	77.5	0	78.6
I-129	$1.57 \times 10^7$ yr	$3.90 \times 10^{-2}$	239	$3.94 \times 10^{-2}$	242	$3.94 \times 10^{-2}$	242
I-131	8.04 days	$1.40 \times 10^6$	11.3	3.51	$2.84 \times 10^{-5}$	$3.15 \times 10^{-8}$	$2.54 \times 10^{-15}$

## 2.2 Airborne Speciation of Iodine

There are three potential streams containing airborne iodine in a fuel reprocessing plant: the voloxidation off-gas, the dissolver off-gas, and the combined vessel off-gas. Voloxidation is used if tritium separation is required, otherwise acid dissolution is the initial chemical processing step.

Voloxidation is a process where the fuel is size reduced by chopping or cutting, and then exposed to a high temperature atmosphere containing air, oxygen, ozone, or some combination of these gases. Voloxidation promotes conversion of the  $\text{UO}_2$  to  $\text{U}_3\text{O}_8$  and results in the break down of the lattice structure of the fuel and release of gaseous fission products. Tritium is effectively removed in this manner, but other gases, including I-129, have varying levels of removal based on the particular process conditions (McKay 1982).

The dissolution process involves immersing the fuel in a hot nitric acid solution until the fuel is dissolved. Most of the fission products in the fuel matrix are then either released as a gas or retained as a dissolved species in the acid. Iodine in the fuel element is believed to occur mainly as iodide,  $\text{I}^-$ , however, when contacted with nitric acid, the iodide rapidly oxidizes to elemental  $\text{I}_2$ . Much of the elemental iodine is volatilized to the off-gas, but a portion remains dissolved in solution - this ratio (gas phase/liquid phase) is the distribution coefficient or sometimes expressed as a Henry's Law constant. Further oxidation of the liquid phase iodine results in forming the nonvolatile iodate ion,  $\text{IO}_3^-$ . However, formation of the iodate ion occurs slowly and reduction back to elemental iodine is promoted by nitrous acid, which is present in the dissolver system (McKay 1982). A small fraction of the iodine may remain undissolved and be discharged with the undissolved solids stream. This iodine is likely silver and palladium precipitates and may account for as much as 2.7% of the total iodine (Mineo 2002).

The final source of gas phase iodine is the combined vessel off-gases (VOG) from the other operations in the reprocessing facility. This includes venting from leaching tanks, feed tanks, extraction cells, condensers, and other process overheads.

Although the primary form of gas phase iodine is anticipated to be elemental, the following is a list of the forms identified or postulated in off-gas systems:

- Elemental or diatomic iodine, as I<sub>2</sub>
- Inorganic compounds such as HI and HOI
- ICN
- Adsorbed on particles as elemental iodine or as an iodine compound
- Organic iodine such as methyl iodide (CH<sub>3</sub>I)
- Other alkyl iodides up to octyl iodide

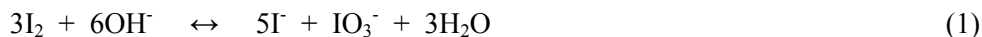
## 2.3 Carrier gas

The carrier gas can be a determining factor in choosing a capture technology and may include material compatibility issues as well as physical chemistry limitations of the system. The dissolver off-gas will likely contain high levels of water vapor and NO/NO<sub>2</sub> gases and any capture system must be tolerant of these. Activated carbon, for example, would not be directly suitable because of its potential to be oxidized by the NO<sub>x</sub>. Similarly, voloxidation can be operated with enhanced levels of oxygen or even ozone, and the potential reactions of these oxidizers on the carbon media must be considered. The combined vessel off-gas is likely to have very low concentrations of iodine so that wet scrubbing might be impractical whereas adsorption on a solid matrix may be more appropriate.

## 3. WET SCRUBBING

### 3.1 Alkaline scrub

Absorption of gas phase constituents by scrubbing with an alkaline solution is a common and relatively simple unit operation. Reprocessing plants that use wet scrubbing typically use a 1 to 2 M NaOH scrub, either alone or in conjunction with a silver-based solid adsorbent (McKay 1982). Under these conditions, I<sub>2</sub> undergoes the following disproportionation reaction:



The captured iodine presumably resides in the scrub as NaI, NaIO<sub>3</sub>, and possibly NaOI. The reported decontamination factors (DFs) vary, but are generally between 10 and 100. The discrepancy may, at least in part, be due to the form of iodine in the gas stream. While the elemental form is effectively removed by caustic scrubbing, the organic forms (methyl iodide for example) are not, and an operation with a significant fraction of organic iodine will have a low removal efficiency.

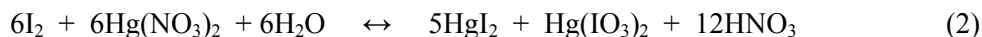
The caustic scrub generates a liquid residue that either requires disposal or conversion to a form suitable for disposal. Direct stabilization in Portland cement is an option, although it has been suggested that a more acceptable approach would be to convert the iodine to a more insoluble form (such as barium iodate) and then solidify the product in cement (Burger 2004).

If there are significant levels of carbon dioxide in the entering gas stream, sodium carbonate may precipitate. To mitigate this, KOH may be used as an alternative since the solubility of potassium carbonate (111 g/100 g water) is greater than that for the comparable sodium (21.5 g/100 g water) compound (Dean 1999).

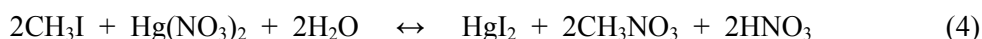
### 3.2 Mercurex process

This process uses a mercuric nitrate-nitric acid solution circulated in a packed or tray column. The raw scrub solution is a combination of 0.4 M  $\text{Hg}(\text{NO}_3)_2$  and up to 14 M  $\text{HNO}_3$ , although other concentrations have been used with varying degrees of effectiveness (IAEA 1987). The process removes elemental and organic iodide, with higher acid concentrations improving the extent of organic iodine removal. The significant chemical reactions are presented below (Trevorrow 1983):

For elemental iodine:



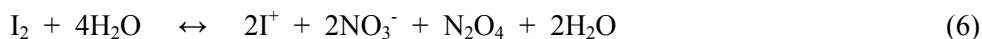
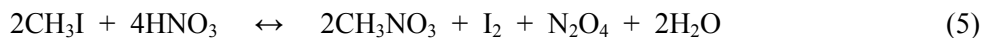
For methyl iodide:



The scrubbed product iodine species includes the mercury compounds  $\text{Hg}(\text{IO}_3)_2$  and  $\text{HgI}_2$ . Tests conducted at Oak Ridge reported DFs of up to  $10^4$  for elemental and organic iodine, while the small Dounreay Plant (shut down) in the United Kingdom claimed a factor of about 150 (Jubin 1988). However, a full-scale operating plant (Allied-General Nuclear Services) was designed based on more modest factors of about 10 to 75 (IAEA 1987). Utilization of this process may be limited due to the use of mercury, which is regulated as a toxic metal. Conversion of the iodine to a non-mercury species with recycle of recovered mercury may lessen the potential environmental concerns with this process. This conversion may entail oxidizing  $\text{HgI}_2$  to form insoluble mercury iodate, separation and subsequent dissolution of the mercury iodate, and ultimately precipitating mercury as insoluble (barium) iodate (Trevorrow 1983).

### 3.3 Iodex process

The Iodex process uses 20-23 M  $\text{HNO}_3$  (hyperazeotropic) scrub solution to solubilize and oxidize both elemental and organic iodine. The process has been demonstrated at Oak Ridge using a 10.2 cm ID Pyrex column, with 8 bubble-cap trays. The feed gas was adjusted to mimic the conditions that could be encountered during reprocessing: iodine (either  $\text{I}_2$  or  $\text{CH}_3\text{I}$ ) ranging from about 20 to 50 ppm,  $\text{NO}_2$  and water at about 2% each, with the balance air. The scrub column was operated at about 40 to 50°C. DFs of greater than  $10^4$  were reported for the demonstration unit. The significant chemical (oxidation) reactions occurring in the Iodex process are the following (Holladay 1979):



The resulting scrubbed species is the iodate ion,  $(\text{IO}_3)^-$ , which requires immobilization in some manner prior to permanent disposal. One route is to form sparingly soluble  $\text{Ba}(\text{IO}_3)_2$ , and encapsulate the ensuing precipitate. Another is to evaporate the nitric acid from the scrub liquid to form the solid iodic acid,  $\text{HI}_3\text{O}_8$ , which may be incorporated in cement or stabilized in some

other manner. Potential unattractive features of the Iodex process are the availability and corrosiveness of hyperazeotropic nitric acid, and the potential to form nitrated organics ( $\text{CH}_3\text{NO}_3$ ) in the system.

### 3.4 Electrolytic scrubbing

Electrolytic scrubbing is a variant of the Iodex process described above. Instead of using hyperazeotropic nitric acid, the scrub is 8 to 12 M nitric acid containing about 0.1 M cobalt. The  $\text{Co}^{+3}$  ion is the oxidant in the system and is continuously generated by electrochemical means. Both elemental and organic iodine are oxidized to the nonvolatile iodate form, which is retained in the scrub solution. Laboratory tests indicate DFs of about 600 for elemental and 100 for methyl iodine. However, tests have also shown that  $\text{NO}_2$  competes with  $\text{I}_2$  and  $\text{CH}_3\text{I}$  for the available  $\text{Co}^{+3}$  oxidant, and the presence of 1%  $\text{NO}_2$  or more will reduce the iodine DF by a factor of 10. Similar to the Iodex process, the resulting scrub solution requires some treatment prior to disposal. Evaporating the nitric acid produces a salt mixture of cobalt nitrate and cobalt periodate. The reported solubility of this residue (assumed as a single compound) in water is 2.2 g/L (Mailen 1975).

### 3.5 Fluorocarbon solvents

Extensive work has been performed at Oak Ridge on a fluorocarbon absorption system for removing radioactive contaminants from reprocessing off-gases. Although primarily targeted for Kr-85 and C-14 removal, tests have shown that other contaminants, including iodine, can be absorbed by a fluorocarbon solvent. Tests at Oak Ridge used dichlorodifluoromethane (called R-12) in a packed column configuration operated at 300 psig and temperatures of -25 to 10°F. DFs of greater than  $10^4$  are claimed for both  $\text{I}_2$  and methyl iodide. The fluorocarbon solvent does not appear to suffer any detrimental effects of contacting  $\text{NO}_2$ , in fact, tests have shown that 97 to 99% of the  $\text{NO}_2$  is retained in the solvent (Stephenson 1976, Vondra 1976).

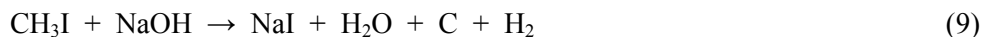
The initial concept was to use fluorocarbon absorption at the end of an off-gas process line to capture Kr-85 and C-14 after other contaminants were removed. However, one design concept placed the absorption system as the primary control unit where iodine and other contaminants (Kr-85, Xe,  $\text{CO}_2$ ,  $\text{NO}_2$ , etc.) would be retained in the solvent. Controlled separation and isolation of contaminants would then be achieved in solvent stripping columns operated at different temperatures or pressures. The design concept would exploit the differences in solubility of the constituents in the fluorocarbon solvent (Stephenson 1976, Toth 1978).

### 3.6 Silicon-Organic (polymethylsiloxane) solvents

Laboratory tests conducted by Russia researchers indicate retention of elemental iodine on a series of polymethylsiloxane liquids. Reported solubilities range up to a maximum value of 4.56 kg/m<sup>3</sup>. Iodine distribution coefficients between air and solvent were reported for several temperatures:  $1.34 \times 10^3$  (at 20°C),  $4.5 \times 10^2$  (at 50°C), and  $2.4 \times 10^2$  (at 70°C). The polymethylsiloxane solvents were also found to be resistant to detrimental effects of  $\text{NO}_2$ . The tests were conducted by passing the target gas through a series of three bubblers. Iodine, as well as  $\text{NO}_2$ , accumulated in the solvent. The researchers indicate that regeneration is accomplished by passing warm air (90°C) through the solvent to remove dissolved nitric oxides and then extracting the iodine to an alkaline solution. DFs of up to 150 for  $\text{I}_2$  are reported. The authors indicate that little, if any, retention of organic iodine is anticipated (Nakhutin 1980).

### 3.7 Molten Hydroxide

Researchers at Oak Ridge have proposed a method using molten hydroxide, NaOH or KOH, to remove iodine (Trowbridge 2003). The process requires mixing the targeted off-gas with a small amount of hydrogen (~ 4%) to maintain a reducing environment, and then contacting this mixture directly with the molten hydroxide. Experiments were conducted by simply bubbling the gas mixture through the melt. The iodine reacts with the alkali metal hydroxide to form the corresponding iodine salts, as shown by the following reactions:



Iodine capture was found to be a function of melt temperature and the contact efficiency between the gas and melt. The maximum  $\text{I}_2$  removal was reported as 96%, although the researchers expect improvements as the technology is developed. No experimental work was reported using organic iodine or  $\text{NO}_x$ , however, thermodynamic calculation favors methyl iodide decomposition according to reaction (9) above. Thermodynamics also suggests that  $\text{NO}_2$  will react and be retained in the melt. Separation of the iodide product (NaI or KI) is achieved by slowly cooling the melt to allow crystallization of the primary iodide phase. The researchers have noted that the iodide product does retain an appreciable amount of hydroxide. This technology has not been developed beyond the initial scoping studies.

### 3.8 Wet Scrubbing Summary

Table 2 summarizes the wet scrubbing techniques available for iodine capture. Mercurex, Iodox, and fluorocarbon absorption have the potential for the highest DFs, and remove elemental as well as organic iodine. All wet scrubbing techniques collect the iodine into a liquid solvent, which must undergo additional processing prior to permanent disposal of the iodine. This could entail one or combinations of several processes including: direct stabilization (grout, low-melting glass, ceramic), chemical conversion of the iodine, or separation and placement on a preferred matrix material. Depending on the preferred final waste form, this may or may not be a significant factor in using a wet scrubbing system.

Table 2. Summary of wet scrubbing methods for I-129 capture.

Process	Scrub solution	Decontamination factor for I <sub>2</sub>	Decontamination factor for organic iodine	State of Development	Comments
Caustic scrub	1 to 2 M NaOH	10 to 100	~1	Deployed at full scale	Essentially no organic iodine is retained, KOH may be used if carbonate precipitation is problematic
Mercurex	0.2 to 0.4 M Hg(NO <sub>3</sub> ) <sub>2</sub> 14 M HNO <sub>3</sub>	10 <sup>2</sup> to 10 <sup>4</sup>	10 <sup>2</sup> to 10 <sup>4</sup>	Pilot scale	Mercurex process was designed for NFS West Valley but was never implemented
Iodox	20 to 23 M HNO <sub>3</sub>	>10 <sup>4</sup>	>10 <sup>4</sup>	Pilot scale	Application limited to laboratory and engineering scale
Electrolytic scrubbing	8 to 12 M HNO <sub>3</sub> 0.1 M Co <sup>+3</sup>	600	100	Lab scale	Presence of 1% NO <sub>2</sub> will reduce DF by a factor of 10
Fluorocarbon	CCl <sub>2</sub> F <sub>2</sub> (Freon R-12)	10 <sup>4</sup>	10 <sup>4</sup>	Pilot scale	Absorption operated at 300 psig, -25 to +10°F
Silicon-organic liquid	Polymethylsiloxane	150	~1	Lab scale	Iodine retained in elemental form, organic iodine not absorbed
Molten hydroxide	NaOH or KOH	~25	-	Lab scale	Only initial testing has been done



## **4. SOLID ADSORBENTS**

From an engineering perspective, the removal of gaseous iodine compounds via adsorption onto a solid adsorbent has many advantages over traditional liquid scrubbing methods. Adsorption column operations are generally more simplistic in design, resulting in a more reliable system with lower maintenance costs. A properly designed adsorbent system should also yield higher iodine removal efficiencies and does not require the highly corrosive liquids typically associated with liquid scrubbers. The majority of the full-scale, first generation, metal/metal-oxide fuel reprocessing plants were designed with liquid scrubbing systems for iodine removal, and consequently there is a very sparse amount of data available regarding the performance of solid adsorbents in actual fuel reprocessing applications. However, significant data have been obtained from various investigations performed with bench-scale and pilot-scale systems. The primary adsorbent materials tested include activated charcoal, various forms of metal loaded alumina silicates and macroreticular resins.

### **4.1 Activated Carbon**

Activated carbon is widely used for removing iodine from relatively benign gaseous streams, e.g. impregnated activated carbon is used almost exclusively for gaseous radioiodine removal at nuclear power plants (Jubin 1988). Activated charcoal performs very well in these applications, but it is not usually considered an option for iodine removal in fuel reprocessing plants because it exhibits poor iodine retention at high temperatures, has a relatively low ignition point, and the presence of nitrogen oxides in the gas stream adversely affects the media performance. Nitrogen oxides may also form unstable or explosive compounds in the carbon bed (Pence 1972).

### **4.2 Macroreticular resins**

Macroreticular resins (such as the Amberlite XAD series) are generally functionalized acrylic esters or polystyrene with di-vinyl benzene cross-linking. In the gas phase, these resins are thought to attract molecular species due to their relative hydrophobicity or hydrophilicity. Therefore, this media functions primarily as a non-ionic adsorber and shows a strong attraction for uncharged species such as elemental or organic iodine (Moore 1970, 1971). The very limited amount of data presented in the literature indicate that the acrylic esters have the highest iodine capacity and show good resistance to radiation damage. The resins are also quite porous and acid resistant, so they would be expected to facilitate rapid mass transfer and be reasonably stable in feed streams containing  $\text{NO}_x$ . However, published data indicate that the iodine removal efficiency of these resins is greatly reduced at temperatures above 50°C.

### 4.3 Silver-Based Adsorbents

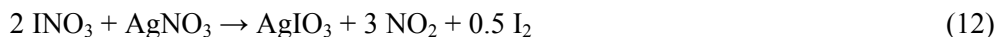
Solid adsorbents containing metals in various forms have been the most widely studied solid media for iodine removal. The vast majority of these use silver as the active phase due to the well-known affinity of silver for iodine. The silver loaded adsorbents are primarily silver-exchanged or silver-impregnated zeolites, silica, or alumina based materials. The silver-based media all exhibit the following key characteristics (IAEA 1987):

- Effective retention of both elemental and organic iodine (provided operating temperatures are high enough to ensure reaction of organic iodides)
- High loading capacity and removal efficiencies
- The media are non-flammable

The primary disadvantage of these materials is the high cost of silver, which has prompted studies to determine the efficacy of some of the more abundant, cheaper metals in hopes of finding a viable alternative to silver adsorbents for iodine removal in dissolver off-gas (DOG) streams. Lead-, copper-, cadmium-, manganese-, palladium-, thallium-, mercury-, and copper-exchanged zeolites have been evaluated as possible alternatives to silver based adsorbents. Although some showed promise for removing elemental iodine, all were shown to have unsatisfactory removal efficiencies and/or low loading capacity for methyl iodide (Pence 1970, Maeck 1970, Ackley 1973, Gal 1974, Pence 1972a). Results obtained by Thomas et al. were so poor that they completely abandoned their search for an alternative to silver-exchanged zeolites (Thomas 1977). It has been surmised that most metals that can be exchanged for sodium onto zeolites assume an oxide-like bonding in the substrate. With the exception of silver, these oxide forms are more thermodynamically stable than the corresponding metal iodide, thus direct conversion to the less stable metal iodide is not favored (Thomas 1977). However, tests performed under a very strong reducing atmosphere have demonstrated the potential for using lead-exchanged zeolite as a secondary adsorbent following the regeneration of the primary silver adsorbent.

#### 4.3.1 Silver Nitrate Impregnated Substrates

Solid adsorbents containing silver in the form of silver nitrate have been demonstrated, both in Europe and Japan, to successfully remove elemental iodine and alkyl iodides (primarily methyl iodide) from fuel reprocessing streams. The silver nitrate reacts with elemental iodine to form stable silver iodide or silver iodate according to the following reactions (Wilhelm 1977):



Alkyl iodide, e.g.  $\text{CH}_3\text{I}$  also reacts with silver nitrate by the reaction:



The two primary substrates that have been used to bind the silver nitrate are compounds of silica and alumina. The West German iodine removal process has been developed around a non regenerable process using silver nitrate impregnated amorphous silicic acid known as Ag-KTC and Ag-KTB. The Ag-KTB is the more mechanically stable of the two and has been marketed

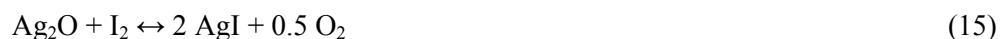
commercially as AC-6120. The material has a nominal BET surface area in the range of 65 - 110 m<sup>2</sup>/g, a pore volume distribution of 20 – 40 nm, grain size of 1 – 2 mm, a pore volume of ~ 0.6 ml/g, and a total silver content of 8 – 12% by mass. Early laboratory testing indicated that water vapor had a deleterious effect on performance and that 150 °C was the optimum operating temperature for iodine removal (Wilhelm 1972). Laboratory tests performed with simulated DOG all showed iodine removal efficiencies of greater than 99.99% using a bed depth of 10 cm, superficial velocity of 25 cm/s, and NO<sub>2</sub> concentrations ranging from 1 to 5%. The AC-6120 adsorbent was used to treat the DOG and vessel off-gas (VOG) from the WAK reprocessing demonstration-scale plant in Karlsruhe Germany from 1975 until the plant was shut down in 1992. The plant processed 207 metric tones of oxide fuel during this period with average I-129 values in the DOG on the order of 1 to 5 mg/m<sup>3</sup>. The AC-6120 provided overall removal efficiencies of 99.8% and 99.0% for the DOG and VOG streams respectively (Herrmann 1996).

A silver nitrate impregnated alumina (AgA) has been developed and tested by Japanese researchers (Fukasawa 1996, IAEA 1987). This adsorbent material contains 24 wt. % silver and was developed for treating off-gas streams at the Tokai fuel reprocessing plant. This material was tested for both methyl iodide and elemental iodine removal at 150 °C and a superficial velocity of 20 cm/s. Reported decontamination factors achieved with the AGA are approximately 250, which equates to a removal efficiency of 99.6%.

The silver nitrate impregnated adsorbents provide high decontamination factors for elemental and organic iodides at elevated temperature (150 °C) and provide a high-percentage utilization of the silver. The adsorbent exhibits high resistance to NO<sub>x</sub>, and moderate concentrations of NO<sub>2</sub> (1 to 10%) actually appear to enhance the performance by preventing the silver from being reduced to the elemental state. However, large amounts of organic contaminants can adversely affect the adsorbent performance in the absence of sufficient NO<sub>2</sub> and removal efficiency is significantly reduced by high humidity, i.e. dew-point temperature excursions. The cost of the silver nitrate adsorbents is reported to be 3 to 10 times less than silver zeolites (IAEA 1987).

#### 4.3.2 Silver Zeolites

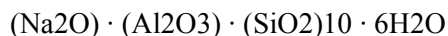
The silver nitrate based adsorbents have received attention in Europe and Japan, but most work in the U.S. has been focused on the development of various types of silver zeolites for iodine removal. The silver zeolites are produced by exchanging a portion of the sodium in the zeolite compound with silver and are usually abbreviated as AgX. An example of AgX is silver-exchanged faujasite, which is available commercially. Different types of zeolites have varying physical properties but arguably the most important is the SiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub> ratio. The zeolite generally becomes harder and more acid resistant as this ratio increases, but a high ratio is inversely related to the ion exchange capacity, i.e. a fewer number of sodium atoms can be replaced by silver atoms. Some combination of physisorption and chemisorption, varying with the type of zeolite, is thought to be responsible for iodine sorption but the exact mechanism has not yet been elucidated. A proposed reaction for iodine in typical silver exchanged Linde molecular sieve zeolites is (Herrmann 1996):



where it is assumed that silver directly replaces a portion of the sodium in the xNa<sub>2</sub>O·yAl<sub>2</sub>O<sub>3</sub>·zSiO<sub>2</sub> zeolite structure. Many researchers in the U.S. have studied the performance of AgX using simulated feed gases to approximate actual process conditions in DOG and/or VOG streams, or by pulling slipstreams from actual processes (Murphy 1977, Holladay 1979, Brown 1983). The

published data from the various tests do not agree in all respects, but general performance trends are evident. The AgX adsorbents do show high decontamination factors for both elemental and organic iodides, typically ranging from  $10^3$  to  $10^5$ , under the right operating conditions. High humidity appears to have a slight negative effect on the uptake of elemental iodine, but can decrease the decontamination factor for methyl iodide by orders of magnitude. This problem is overcome by increasing operating temperatures to 150 °C or greater in order to keep the relative humidity low. The increased temperature causes a very minimal reduction in elemental iodine capacity, but allows high decontamination factors to be achieved for organic iodides. There does not seem to be a consensus among researchers regarding the exact mechanism for this behavior but some combination of organic oxidation and faster sorption kinetics is likely. The removal of elemental iodine is not seriously affected by most contaminants but the uptake of methyl iodide is significantly decreased by high concentrations of  $\text{NO}_2$  (>2%), as well as residual hydrocarbons that are usually associated with the use of recycled acid in the dissolver. The standard AgX adsorbents are not acid resistant and are not applicable to off-gases containing high amounts of water vapor and  $\text{NO}_x$ . Thus the application of AgX in a DOG system would be limited to secondary treatment downstream of an alkaline scrubbing system.

Mordenites (zeolons) are a class of natural and synthetic zeolites that have a significantly higher Si:Al ratio than the faujasite class of zeolites, and hence a much higher chemical stability. The synthetic mordenites typically have a Si:Al ratio of 10 and have the chemical form:



The synthetic forms are also made with a very narrow pore size distribution, high specific surface area, and may include a binder depending on the application. The high chemical stability of the mordenites gives them a high acid resistance and thus the silver-exchanged form, AgZ, has been extensively studied for primary iodine treatment applications in DOG streams. Commercial forms are typically 15 wt.% silver with specific surface areas of approximately 400  $\text{m}^2/\text{g}$  and thermal stability in temperatures up to 500 °C. Some researchers have noted that silver-exchanged mordenite containing silver in the metallic state appears to have a higher capacity than the ionic form for the chemisorption of elemental iodine (Thomas 1977, Staples 1976). Consequently, AgZ is often pretreated with hydrogen gas at 500°C prior to service in order to reduce silver to the metallic state, i.e. to form  $\text{Ag}^\circ\text{Z}$ . It is difficult to quantify what performance advantage, if any, is gained with  $\text{Ag}^\circ\text{Z}$ . The published data are ambiguous in this respect since a number of the experiments showing high equilibrium loadings of elemental iodine in  $\text{Ag}^\circ\text{Z}$  were performed with much higher iodine concentrations in the feed stream than those reported for AgZ. The higher concentrations in the feed stream would be expected to result in higher equilibrium loadings regardless of the sorption mechanism. However, a high concentration of  $\text{NO}_2$  in the absence of NO did result in lower iodine loadings, i.e. it is speculated that  $\text{NO}_2$  oxidized a portion of the metallic silver and reduced the adsorbent's capacity. Experiments conducted with AgZ and  $\text{Ag}^\circ\text{Z}$  have shown both forms to be much more acid resistant than AgX, while average removal efficiencies for both elemental iodine and methyl iodide are within the same order of magnitude of those obtained with AgX under similar conditions (Holladay 1979). Average iodine loadings were approximately half of theoretical capacity which is also very similar to loadings obtained with AgX tested using similar feed stream concentrations.

One of the primary advantages of silver-loaded zeolites is that they can be regenerated, whereas a regenerable form of the silver nitrate impregnated adsorbents has not been demonstrated. This is important since a technique for regenerating the spent silver adsorbents and transferring the iodine onto cheaper substrates may improve the economic feasibility of the technology. Researchers have shown that iodine can be stripped from spent AgZ and AgX by

passing a pure stream of hydrogen through the bed at 500 °C. The iodine was desorbed as hydrogen iodide and then chemisorbed on a lead-exchanged zeolite (PbX) bed located downstream and held at a temperature of 150 °C (Staples 1976, Murphy 1978). Iodine loading on the PbX bed was approximately 400 mg of I<sub>2</sub> or 90% of the theoretical capacity. The AgX showed a 50% reduction in capacity after 5 regeneration cycles while the AgZ showed only a 20% reduction after 13 cycles. Later work performed by a different team of researchers indicated a much higher reduction in AgZ capacity after only a few regeneration cycles, but these investigators used a dilute hydrogen stream (4.5%) as well as a metal housing to contain the adsorbent material. It is likely that the dilute hydrogen stream reacted with the metal housing making the results suspect (Jubin 1981). The eventual loss in regeneration efficiency for each adsorbent is attributed to the gradual collapse of the pore walls, which restricts hydrogen diffusion and subsequent reaction with silver atoms. However, the superior mechanical strength of the AgZ should allow for up to 3 times more regeneration cycles than the less stable AgX matrix (IAEA 1987).

#### **4.4 Solid Adsorbents Summary**

Table 3 summarizes the solid adsorbents available for iodine capture. The silver-based alumina, silica, and mordenite adsorbents have comparable characteristics and are the currently preferred sorbents. An advantage of the mordenite is that regeneration of the sorbent is possible, thereby utilizing the silver over the course of several cycles. The stripped iodine is then available for sorption using a cheaper metal or conversion to a waste form preferred for long-term storage. Although data is limited, macroreticular resins have shown similar, or even better, capacities and DFs as the silver-based adsorbents. However, the effects of water vapor and other constituents (CO<sub>2</sub>, krypton, etc.) have not been thoroughly evaluated. These also appear to be more sensitive to operating temperature than silver-based adsorbents.

### **5. FUTURE ACTIVITIES**

Future plans under the Aqueous Separations Group at the Idaho National Laboratory call for evaluating the most promising iodine capture technologies in support of fuel reprocessing. Initial efforts will focus on several commercially available silver-based adsorbents. These will undergo laboratory testing under a consistent set of experiments conditions so that direct comparisons between sorbents can be made. Among the test parameters of interest are iodine concentrations (elemental and organic), and the effects of constituents such as NO<sub>x</sub>, water vapor, and CO<sub>2</sub>. Performance at various temperatures is also a key parameter. Finally, cycling of the adsorbent and the effect on sorption capacity and kinetics will be evaluated. Completion of these will form a baseline against which other technologies can be evaluated.

Depending on time and future funding levels, evaluation of other promising adsorbents (macroreticular resins, non-silver-based adsorbents, etc.) and liquid scrub systems may be undertaken. The test platform developed for the initial adsorbent evaluations can then be used to assess these alternate technologies.

Table 3. Summary of solid adsorbents for I-129 capture.

<b>Adsorbent</b>	<b>Temperature (°C)</b>	<b>Adsorbent Capacity (mg I<sub>2</sub>/g)</b>	<b>Decontamination Factor</b>	<b>NO<sub>x</sub> Resistance</b>	<b>Comments</b>
Activated carbon	< 120		10 to 10 <sup>3</sup>	unsuitable	
Macroreticular resins	< 50	200 - 1000	10 <sup>3</sup> - 10 <sup>4</sup>	high	Organic iodine capacities are lower by a factor of 10, high humidity may adversely affect performance
AgA - silver impregnated alumina	~ 150	100 - 235	10 <sup>2</sup> - 10 <sup>3</sup>	high	
AC-6120 – silver impregnated silica gel	~ 130	~ 135	10 <sup>2</sup> - 10 <sup>5</sup>	high	Used at the WAK plant Germany (now shutdown), sorbent was not regenerated
AgX – silver exchanged faujasite	~ 150	80 - 200	10 <sup>2</sup> - 10 <sup>5</sup>	low	Presence of hydrocarbons and NO <sub>x</sub> adversely affects performance
AgZ – silver exchanged mordenite	~ 150	~ 170	10 <sup>2</sup> - 10 <sup>5</sup>	high	Thermally stable to 500°C, can be regenerated
Ag°Z – silver exchanged mordenite	~ 150	~ 170	10 <sup>2</sup> - 10 <sup>5</sup>	high	Silver reduced to metallic state by conditioning with hydrogen

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