

# **Iodine Pathways and Off-Gas Stream Characteristics for Aqueous Reprocessing Plants – A Literature Survey and Assessment**

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## **SUMMARY**

Used nuclear fuel is currently being reprocessed in only a few countries, notably France, England, Japan, and Russia. The need to control emissions of the gaseous radionuclides to the air during nuclear fuel reprocessing has already been reported for the entire plant. But since the gaseous radionuclides can partition to various different reprocessing off-gas streams, for example, from the head end, dissolver, vessel, cell, and melter, an understanding of each of these streams is critical. These off-gas streams have different flow rates and compositions and could have different gaseous radionuclide control requirements, depending on how the gaseous radionuclides partition. This report reviews the available literature to summarize specific engineering data on the flow rates, forms of the volatile radionuclides in off-gas streams, distributions of these radionuclides in these streams, and temperatures of these streams. This document contains an extensive bibliography of the information contained in the open literature.

Iodine removal has always been primarily focused on the head-end off-gas operations. But, in light of the estimated iodine emissions control efficiencies of up to 99.9% or higher needed to meet US regulatory requirements, the control of iodine in the dissolver off-gas is insufficient. Operating experience and tests with actual nuclear fuel show that iodine evolution from the dissolver solution into the dissolver off-gas ranges between 95 and 99%. Iodine evolution from the dissolver solution can be improved to >95% with NO<sub>2</sub> sparging, addition of KIO<sub>3</sub> to the dissolver, and addition of iodate. Several studies have shown that much of the residual iodine in the dissolver solution is in the form of colloidal iodine (AgI and PdI<sub>2</sub>); organic iodides formed in the dissolver also factor into the iodine retention. Even if the iodine in the dissolver off-gas is efficiently controlled, the iodine in other reprocessing facility off-gas streams may also need to be controlled.

The flow of the vessel off-gas stream may be on the order of 10 times greater than that of the dissolver off-gas stream. This stream typically contains 40–50% of the iodine that remained in the dissolver solution. The iodine concentration in this stream may be lower by as much as a factor of 10<sup>5</sup> due to the larger gas flow and limited, but not insignificant, quantity of iodine present. A significant fraction of the iodine in the vessel off-gas is organic iodides.

The distribution of the iodine in the solvent extraction system indicates that 40 to 50% of the iodine will transfer to the organic solvent. Caustic washing does not remove significant quantities of this iodine.

A limited amount of information was found on the release of iodine during waste solidification operations. The quantities of release were found to be process specific. The range of release was estimated to be between 0.1 and 1% of the iodine inventory in the plant.

Based on this study, four major iodine release pathways have been identified as requiring treatment to prevent the release of iodine to the stack:

- Dissolver off-gas, including the off-gas from the fuel shearing operation;
- Vessel off-gas, including the vents from the process operations and tanks within the facility;
- Off-gas from liquid waste solidification, including the production of waste forms from the primary off-gas system traps. Vents from the waste storage tanks in this section of the plant must also be connected to iodine-trap system;
- Treatment activities on used solvent and on the solidification of discarded used solvent.

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## ACRONYMS

BWR	boiling water reactor
COG	cell off-gas
DF	decontamination factor
DOG	dissolver off-gas
FCRD	Fuel Cycle Research and Development
GWd	Gigawatt day(s)
GWd/tHM	Gigawatt days per tonne heavy metal
GWd/tiHM	Gigawatt days per tonne initial heavy metal
HOG	head-end off-gas
ICCP	Idaho Chemical Processing Plant
LIRIC	Library of iodine reactions in containment
MEI	maximally exposed individual
MOG	melter off-gas
scfm	standard cubic feet per minute
THORP	Thermal Oxide Reprocessing Plant
TRENDS	Transport and Reaction of Nuclides in Dominant Sequences
UDS	undissolved solids
UNF	used nuclear fuel
VOG	vessel off-gas
WAK	Wiederaufarbeitung von Kernbrennstoffen

# IODINE PATHWAYS AND OFF-GAS STREAM CHARACTERISTICS FOR AQUEOUS REPROCESSING PLANTS – A LITERATURE SURVEY AND ASSESSMENT

## 1. INTRODUCTION

In a previous document, we addressed the needs for treating off-gas streams from the reprocessing of used nuclear fuel (UNF) and the regulations that set the limits for releases from such a facility (Jubin et al. 2012). These regulations ultimately dictate the decontamination factor (DF) that must be met in the facility. Some flexibility exists, however. In the cases we discussed in the “fuel age report” (Jubin et al. 2012), several options for meeting regulations were discussed, including fuel “aging” to allow short-lived radionuclides to decay prior to reprocessing, apportioning environmental releases to different radionuclides, siting of the reprocessing facility, designing equipment to mitigate effects of releases (such as stack height and other parameters that affect air dispersion). This report focused on four radionuclides:  $^3\text{H}$ ,  $^{14}\text{C}$ ,  $^{85}\text{Kr}$ , and  $^{129}\text{I}$ .

We confirmed prior studies that indicated (1) the highest control efficiencies are required for  $^{129}\text{I}$  and (2) the form of the radionuclide, especially  $^{129}\text{I}$ , and its point of release play important roles in the determination of the required control efficiency. For example, iodine could be released in particulate, vapor, or gaseous forms; the particulate form results in a higher dose to the maximum exposed individual (MEI) than the other forms by at least a factor of 100. So not only is the amount of iodine released important but also the chemical and physical form. In another example,  $^3\text{H}$  was found to be very difficult to remove if it cannot be separated from the UNF before the UNF enters the dissolver. At this point, it could form tritiated water ( $^3\text{HHO}$  or  $^3\text{H}_2\text{O}$ ) and mix with the process water and off-gas streams downstream of the dissolver. This could require tritiated water separation processes, if  $^3\text{H}$  emissions need control to meet regulatory requirements (AREVA 2013, Energy Solutions 2013). Carbon-14 required few, if any, controls and is assumed to be released primarily into the dissolver off-gas stream. Krypton is also totally released into the dissolver or head-end off-gas streams. Thus, there is no significant distribution of these latter two radionuclides to other off-gas streams within the plant. For these reasons, it became clear that a document that captured what is known about the fate of  $^{129}\text{I}$  was needed.

Nuclear fuel is currently being reprocessed in only a few countries, notably France, England, Japan, and Russia. Reprocessing was performed in the United States and, while some pertinent information is available from these currently and formerly operating facilities, there is little specific engineering information on the flow rates, forms of the volatile radionuclides in off-gas streams, distributions of these radionuclides in these streams, and temperatures of these streams. Therefore, the information provided in this document relies on published and some anecdotal information. This document contains an extensive bibliography of the information contained in the open literature.

While the need to control air emissions of the gaseous radionuclides during UNF reprocessing has already been covered (Jubin et al. 2012, 2013), the gaseous radionuclides can partition to various reprocessing off-gas streams (head-end off-gas [HOG], dissolver off-gas [DOG], vessel off-gas [VOG], cell off-gas [COG], and melter off-gas [MOG]). These off-gas streams have different flow rates and compositions, and could have different gaseous radionuclide control requirements. Figure 1 shows the relationship and boundaries of the previously reported capture requirements and highlights the focus of the present effort to gather the known information on the relevant streams.

The following sections of this report summarize information on the fate of gaseous radionuclides, especially  $^{129}\text{I}$ , during UNF reprocessing and on the different off-gas streams from UNF reprocessing. This information was obtained from an extensive review of open literature performed during fiscal year 2013. This report includes what is known or hypothesized about the chemistry of iodine during UNF dissolution, since this step initially defines the partitioning of iodine to the DOG, the aqueous nitric acid stream that passes from UNF dissolution to the aqueous separations processes, and undissolved solids (UDS) from the dissolver.

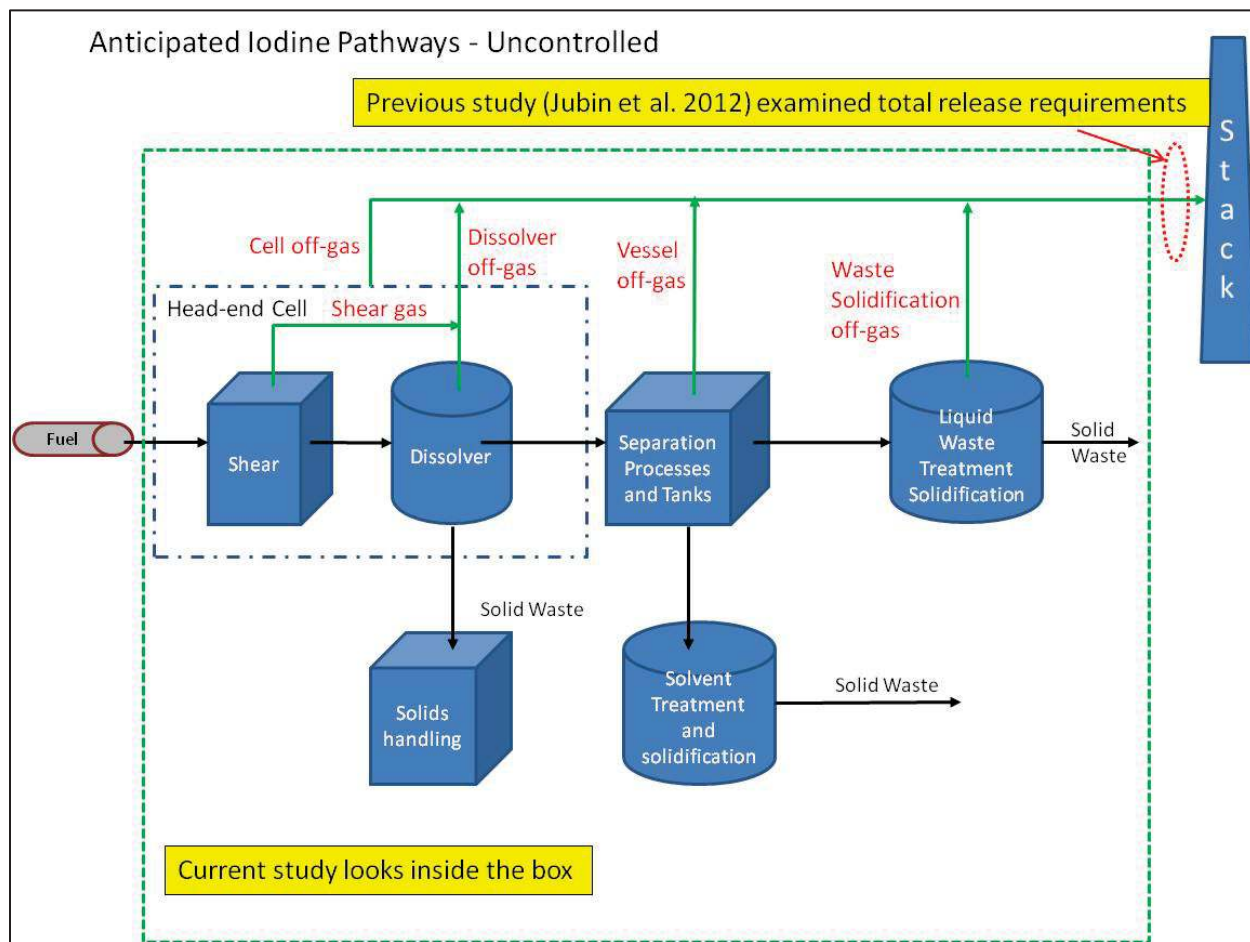


Figure 1. Schematic of typical unit operations for an aqueous-process-based UNF reprocessing plant.

In this report, we do not address the fate of gaseous radionuclides during other separations processes, such as electrochemical or fluoride volatility.

## 2. HEAD-END PROCESSES

The head-end processes for aqueous UNF reprocessing include shearing, dissolution, hull and hardware compaction, dissolver solution clarification, and the DOG. Gaseous radionuclides can volatilize into the

cell atmosphere during shearing or into the DOG during dissolution. Figure 2 illustrates processes typically included in the head end.

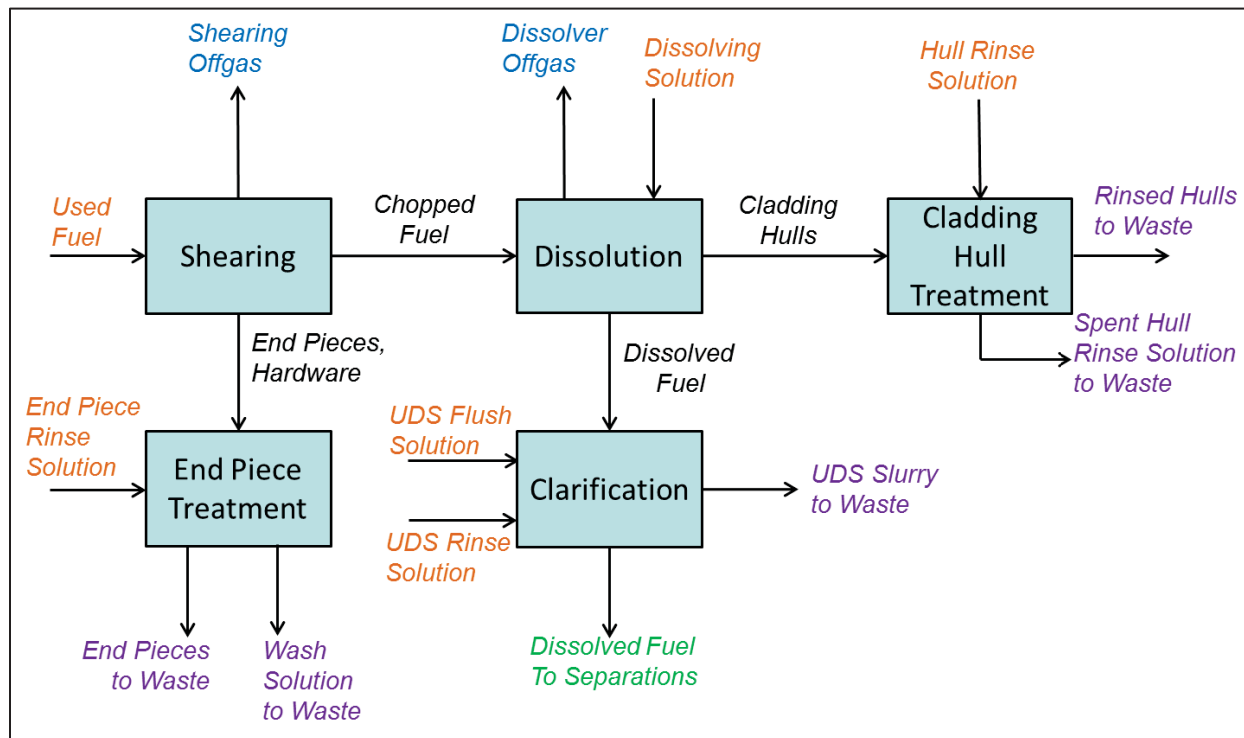


Figure 2. Schematic of typical head-end processes for an aqueous-process-based UNF reprocessing plant.

## 2.1 Shearing Cell Off-gas

The fuel assembly end pieces are sheared from the fuel rods, and the fuel rods are chopped into short segments in a shearing cell. The shearing processes are performed at ambient temperature. The fuel elements may be hotter than the cell ambient temperature, depending on burn-up of the UNF and the aging time after reactor discharge. While the chopping process exposes fuel meat to the cell atmosphere, only small amounts of the gaseous radionuclides are released into the cell atmosphere which is discharged to the shear cell off-gas. This is because the temperatures are moderate and most of the radionuclides remain contained within the fuel matrix. Even for the noble gases, the release is small (<5%) during this operation (Kogai et al. 1988; Hastings et al. 1986; Johnson et al. 2012; Sah et al. 2008; Sato et al. 2011). Often the off-gas from the shearing operation is routed to the dissolver.

The need to capture gaseous radionuclides that could volatilize during shearing depends on the specific control efficiencies needed for each radionuclide and the quantities released during shearing. Estimates for the fraction of gaseous radionuclides released during shearing are shown in Table 1.

Table 1. Iodine radionuclide partitioning during fuel rod shearing

Partitioning to the shearing cell gas (WAK)	Shearing + dissolver cell gas flow rate [m <sup>3</sup> /h (scfm <sup>a</sup> )]	Reference
0.15% of UNF <sup>129</sup> I inventory	7300 (4300)	(Herrmann et al. 1993)
0.3% (3 × 10 <sup>-5</sup> to 18 × 10 <sup>-5</sup> mg/m <sup>3</sup> ; 6–36 µL/L)	–	(Herrmann et al. 1997)

<sup>a</sup> scfm = standard cubic feet per minute

Leudet et al. (1983) discuss a series of tests with UNF. Five rods were chopped and dissolved in nitric acid. The purpose of the tests was to determine the mass balance for the volatile species during head-end operations. During chopping of the fuel rods, 4.4% of the Kr and 3.8% of the Xe collected were released, consistent with the literature discussed in Section 2.1. Iodine release was below the detection limit (10<sup>-4</sup> g) or less than 0.1% of the iodine in a single rod. Less than 1% of the <sup>14</sup>C as CO<sub>2</sub> was released, and <sup>3</sup>H release was between 0.01 and 0.0001% of the inventory.

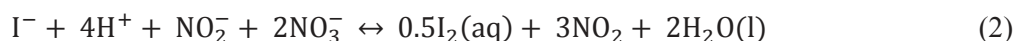
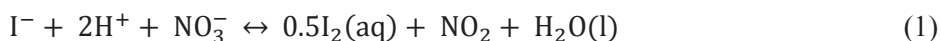
Hudson et al. (1995) indicate that the off-gas from the shearing operation at the THORP facility is combined with the off-gas from the three dissolvers. The total flow of this combined stream is about 400 m<sup>3</sup>/h for a 1200 t/year facility. All of the off-gas streams are routed to a single 125-m stack. Total design flow of the stack is 485,000 m<sup>3</sup>/h. This is made up of the DOG, the central off-gas (vessel off-gas), the cell ventilation, and the building ventilation.

## 2.2 Chemistry and Distribution of Iodine during Spent-Fuel Dissolution

Sakurai et al. (1997) provides a very good discussion on their experiments on the dissolution of spent fuel at the laboratory scale. They describe the distribution of radioiodine into the off-gas fuel solution and the solid residue; the results are summarized below.

### 2.2.1 Volatilization into DOG

Sakurai et al. (1997) report that in their experiments with actual fuel, more than 90% of the iodine was volatilized, indicating that iodine was oxidized by HNO<sub>3</sub> and HNO<sub>2</sub> was observed spectro photometrically to have been produced during fuel dissolution. The proposed oxidation reactions are:



The dissolved iodine, I<sub>2</sub>(aq), is then volatilized as I<sub>2</sub>(g):



A small fraction remains in solution as an iodate:



They indicate that only small quantities of iodine are present in the 3 to 4 M nitric acid dissolver solution. At these molarities the iodate is reduced to I<sub>2</sub> by the NO<sub>x</sub> and HNO<sub>2</sub>.

Sakurai et al. (1997, 1993) indicate that less than 7% of the iodine in the off-gas stream is an organic iodide. They speculate that the organic iodide compounds are formed from organic impurities in the solutions.

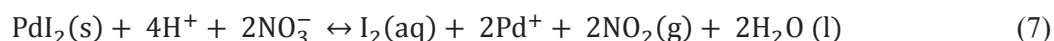
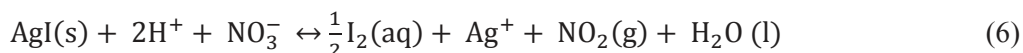
### **2.2.2 Retention of Iodine Species in Spent-Fuel Solutions**

Sakurai et al. (1997) also indicate that colloidal iodine is formed during the dissolution of the UNF. They have proposed the following reaction for the formation of the colloidal iodine:



They note that this reaction competed with Reactions (1) and (2) and indicate that the production of colloids was reduced at high fuel dissolution rates. They state this was true even with high burn-up fuels where higher levels of silver and palladium were present (Sakurai et al. 1995b). High dissolution rates resulted in higher concentrations of NO<sub>x</sub> and HNO<sub>2</sub>.

They also point out that colloidal iodine may decompose to molecular iodine in hot acid solutions by the following two reactions:



Colloidal iodine can also be produced when the concentrations of NO<sub>x</sub> and HNO<sub>2</sub> are too high. The higher concentrations of NO<sub>x</sub> and HNO<sub>2</sub> can reverse the two reactions above and form AgI.

In their experiments with a simulated used fuel solution, they found the following distribution of iodine species: 60% colloidal iodine, 20% I<sub>2</sub>, and 20% iodate.

### **2.2.3 Deposition onto Insoluble Residue or to a Precipitate or Both**

Sakurai et al. (1992) found that ≤3% iodine from UNF dissolution was precipitated as an insoluble residue.

Sakurai et al. report that when the UO<sub>2</sub><sup>2+</sup> concentration in the dissolver solution exceeded 170 g U/L, there was an increase in the precipitation of metal molybdates upon which iodine was deposited (Sakurai et al. 1991a). This work was conducted with simulated fuel, and the causes for the increased precipitation were not determined; they included simulated fission products in their test.

Sakurai et al. (1997) provide the following distribution of iodine around the dissolver: insoluble residue, 0 to 3% as AgI or PdI<sub>2</sub>; colloidal iodine in solution as AgI or PdI<sub>2</sub>, 0 to ~10%; and the balance, to the dissolver off-gas.

## **2.3 Fate of Iodine during UNF Dissolution**

A search through the literature showed that the iodine chemistry in an aqueous-process-based reprocessing plant is complex; the multiple reactions that occur while dissolving UO<sub>2</sub>-based nuclear fuels and the possibility of metallic fuels in the future which complicates the chemistry further. The complexity of iodine chemistry was highlighted in part in containment studies (Beahm et al. 1988a; Beahm et al. 1988b; Chesne et al. 1977; Glowa et al. 2000; Glowa and Wren 2003; Kress et al. 1993; Lemire et al. 1981; Wisbey et al. 1986b; Wisbey et al. 1986a; Wren and Ball 2001; Wren et al. 2000; Yarbrow et al.

1977). These studies are cited here for completeness. These studies point to the importance of the presence of organic contaminants (in recycled nitric acid) and radiation in iodine chemistry.

## 2.4 Plant Experience – Dissolver and Dissolver Off-Gas

Table 2 shows the values for the partitioning of iodine to the DOG as reported by different references, under specific conditions of acid concentration, temperature, dissolver duration, and sparging. We found no references to iodine chemistry or the fate of iodine in the reprocessing plants at the Hanford or Savannah River Plant sites

Table 2. Gaseous <sup>129</sup>I partitioning during UNF dissolution

% Partitioning to:			Comments and references
DOG after condenser	Aqueous dissolved fuel stream	UDS	
99	–	–	Goles et al. (1981)
99	–	–	Leudet et al. (1983)
99	–	–	Such high volatilization was only achieved with NO <sub>x</sub> sparging (Auchapt et al. 1984; Henrich et al. 1989; Leudet et al. 1983)
–	1	–	Herrmann et al. (1988)
–	0.6	–	Before N <sub>2</sub> sparging (Lieser et al. 1989)
–	0.3	–	After N <sub>2</sub> sparging (Lieser et al. 1989)
	0.7		Noukis and Henrich (1991)
Remainder	1–5	2–5	Sakurai et al. (1991a)
–	<1	–	Even after extensive treatment to volatilize iodine Lieser et al. (1989)
≥95	≤5	–	Herrmann et al. (1993); Weinlaender et al. (1991)
	<1		Sakurai et al. (1997)
94	5	1	Required 8 h of boiling plus other measures; actual partitioning in WAK (Herrmann et al. 1997)

Furrer et al. (1979) also state that the iodine released during dissolution of uranium oxide fuel was primarily I<sub>2</sub>. The organic iodides were formed at low concentrations as a result of the recycled and recombined acid. Data from the WAK facility showed that, in the dissolver off-gas, the organic iodide concentration was observed to be <0.05% of the total iodine. The compounds CH<sub>3</sub>I, C<sub>2</sub>H<sub>5</sub>I, and C<sub>4</sub>H<sub>9</sub>I were specifically identified. They also report the temporal release of iodine from the dissolver. The iodine concentration in the dissolver off-gas rose quickly during first hour and then decreased over the remaining 7–8 h of dissolution.

Goles et al. (1981) discuss the off-gas from a nuclear waste vitrification project conducted at the Pacific Northwest Laboratory. This project involved the dissolution of spent uranium fuel followed by the separation of uranium and plutonium from the dissolver solution with solvent extraction. Under the

conditions of the test, the volatilization of iodine and  $^3\text{H}$  was maximized; 99% of the iodine was volatilized. They did not analyze for  $^3\text{H}$  in the dissolver solution.

The early work by McManus et al. (1983) at the Idaho Chemical Processing Plant (ICPP), while mostly a statistical study, indicates that only 2–5% of the  $^{129}\text{I}$  in the fuel was expected to be released to the DOG, which was much lower than the 95% or higher values reported by other researchers. This large difference might be due to variety and types of different fuels reprocessed at the ICPP. The ICPP has processed aluminum-clad fuels, Zr-clad or alloyed fuels, stainless steel-clad fuels, and graphite fuels (Pace et al. 2006). The dissolution conditions for these various types of fuels could cause different iodine partitioning conditions during dissolution.

Dissolution of nuclear fuel involves the following kinds of reactions of iodine (Lieser et al. 1989):

1. In the first step iodine is dissolved from the UNF into the nitric acid solution in form of  $\text{I}^-$ ,  $\text{I}^0$  (atomic), or  $\text{I}_2$  with a rate proportional to the rate of fuel dissolution.
2. These primary species may react with other compounds in the medium or with each other, and volatile reaction products, such as  $\text{I}_2$  or organic iodides ( $\text{R-I}$ , where R stands for carbon chains) with small numbers of carbon atoms, escape continuously.

In the experiments reported by Lieser et al. (1989), iodine was initially at relatively high concentrations that decreased with experimental time. During these experiments, no equilibrium state was ever achieved. During dissolution of nuclear fuel, nitrogen oxides were produced that may have reacted with the primary or secondary iodine species and that may have acted as carriers for volatile iodine-bearing compounds. The distribution of iodine species depended on the total concentration of iodine (Richard and Gaona 2011; Schmitz 2004; Sebok-Nagy and Kortvelyesi 2004). Because of the concentrations used in their experiments, the effect of the total iodine concentration needed to be taken into account when interpreting the results from Lieser et al.

Nevertheless, it is interesting to note that in 3 M  $\text{HNO}_3$  of highest purity, ~0.6% of the  $^{129}\text{I}$  in the input fuel was dissolved (before nitrogen sparging); ~0.3% remained dissolved after nitrogen sparging. The initial iodine concentration was  $\sim 2 \times 10^{-3}$  mM, similar to the results observed in dissolution of nuclear fuel (Henrich et al. 1988). This indicated that  $\text{HNO}_3$  itself and the impurities contained therein played an important role in the course of the chemical reactions of iodine.

To remove iodine from the dissolver solutions, sparging with  $\text{NO}_2$  at elevated temperatures has been recommended for iodate removal by conversion to  $\text{I}_2$  that is subsequently volatilized (Boukis and Henrich 1991a; Henrich et al. 1981; Lieser et al. 1989; Morgan and Holland 1980; Sakurai et al. 1996b). More than 99% of input iodine was volatilized to the DOG in both laboratory- and plant-scale experiments (Henrich et al. 1989; Auchapt et al. 1984; Leudet et al. 1983). According to the reports from an actual reprocessing plant, however, considerable amounts of iodine (up to 5%) remained in spent-fuel solutions and migrated to the separations process (Herrmann et al. 1993; Weinlaender et al. 1991). Although the causes were not discussed, this finding suggests the presence of other iodine species in spent-fuel solutions or the presence of some factors that influence the behavior of iodine between laboratory-scale experiments and actual reprocessing plants. Iodine solids and organic iodides have also been implicated (see discussion below).

The Rokkasho Reprocessing Plant is a commercial 800 t/d reprocessing plant in Japan. Since the release of  $^{129}\text{I}$  into the environment is strictly regulated, studies were performed to evaluate the iodine species in spent fuel solutions and the methods of expelling this iodine to the DOG, where it could be captured, and so it would not contaminate the downstream processes (Sakurai et al. 1987; Sakurai et al. 1989; Sakurai et al. 1996a; Sakurai et al. 1991b, 1992; Sakurai et al. 1996b; Takeshita and Azegami 2004; Tanigaki et al.



1992; Tsukaue et al. 1994; Tsukaue et al. 1995). From this work, it was determined that colloids of silver iodide ( $\text{AgI}$ ) and palladium iodide ( $\text{PdI}_2$ ) played an important role in the behavior of iodine in the dissolution stage (Sakurai et al. 1989, 1995a; Sakurai et al. 1996a; Sakurai et al. 1991b, 1992, 1993; Sakurai et al. 1996b). Although not specifically discussed in these studies, these low-solubility iodides would either partition to the UDS or to the aqueous dissolved fuel stream, if not efficiently separated from the aqueous phase. If the UDS is vitrified into a glass waste form or melted into a metal waste form (Crum et al. 2013), these halides that partition to the UDS are expected to thermally decompose, yielding  $\text{I}_2$  in the melter off-gas. Any amounts of colloidal iodides or dissolved iodine species that remain with the aqueous dissolved fuel stream would pass into the downstream separations processes and could contaminate downstream product and waste streams. Iodine that partitions with the fission products to a glass melter could volatilize during vitrification. Iodine that remains with waste solvent could volatilize during waste solvent pyrolysis.

Work in Germany (Boukis and Henrich 1991a, b; Lieser et al. 1989) and Japan (Nakamura et al. 1973; Nakashima et al. 1981; Numakura et al. 1973; Saeki et al. 1974; Tachikawa et al. 1971) identifies the presence of organics in  $\text{HNO}_3$  as one source of organic iodides. Some of these organic iodides persist despite efforts to remove them from the dissolver solution (Boukis and Henrich 1991a, b). These organic iodides remain dissolved or entrained with the aqueous dissolved fuel stream and enter the downstream separations processes, where they follow either the aqueous or organic streams. If they follow the aqueous streams, they could ultimately become part of the melter feed and would thermally decompose to form  $\text{I}_2$  in the melter off-gas. If they follow the organic solvent streams, they become part of the organic waste and could volatilize during waste solvent pyrolysis. A portion of these organic iodides could also be recycled back to the dissolver in recycled nitric acid or be recycled back to the separations processes in recycled solvent.

Residual iodine concentrations of 1  $\mu\text{molal}$  in dissolver solutions were routinely obtained in WAK (Henrich et al. 1980). Henrich et al. (1980) found that, to achieve adequate removal of iodine from the dissolver solutions, lower boiling temperatures plus  $\text{KIO}_3$  additions were needed. Even with extensive treatment, <1% of the iodine remained with the recycled acid because it was removed during  $\text{HNO}_3$  decomposition. Similarly, Herrmann et al. (1988) found that 1% of the iodine remaining in the dissolver solution was transported into the solvent extraction process.

Herrmann et al. (1997) determined that the amount of residual iodine in the dissolver solution is independent of burn-up. Therefore, the *relative* amount of iodine retained was higher for low burn-up fuel than for high burn-up fuel. The residual contents depended strongly on the quality of the starting acid, with the trace organics playing an important role in how much was retained. About 94% of the iodine reported to the DOG; the remainder went into the rest of the process. To achieve 94% volatilization of the iodine inventory, 8 h of boiling was required plus other measures. To further facilitate removal of the iodine from the dissolver to the Ag reactors used for iodine capture, nonradioactive iodine must be added. Iodine downstream of the Ag reactors decreased with time, dropping over 3 orders of magnitude over the span of a year. Sampling errors played a big role in estimates of the iodine releases and of the amount of iodine detected at various locations.

During industrial operations at La Hague reprocessing plant, the essential part of the iodine inventory of the spent fuel is oxidized into the  $\text{I}(0)$  form, which is transferred as molecular iodine,  $\text{I}_2$ , to the dissolver off-gas (Madic et al. 2002). Iodine is then trapped (as a mixture of iodide,  $\text{I}^-$  and iodate, and  $\text{IO}_3^-$  ions) from the dissolver off-gases by washing them with an aqueous soda solution. The iodine so recovered is actually discharged into the sea. Very low fractions of the iodine inventory are either trapped into solid iodine filters (initially loaded with silver nitrate) or released into the atmosphere.

So, the research carried out presently at the CEA consists of defining processes for the recovery of iodine from the Ag solid filters present in various areas within the plant in order to increase the iodine recovery yield to ~99%. Then, the recovered iodine could be precipitated for instance as  $PbI_2$ .

Silver-loaded adsorbents were studied for the removal of iodine from the process off-gas (Takeshita and Nakano 2001). A mathematical model to predict the breakthrough curve of  $I_2$  on the adsorbent bed was proposed. This model consisted of the mass balance equation of  $I_2$  on the adsorbent bed, the mass transfer equation of  $I_2$  through the boundary layer surrounding the adsorbent particle, the intra-particle diffusion of  $I_2$ , and the kinetic equation for the gas–solid reaction between  $I_2$  and the  $Ag^0$  on the sorbent. Two unknown parameters in the model, the intra-particle diffusivity,  $D_e$ , and the apparent rate constant for the gas-solid reaction,  $k_r$ , were determined simultaneously from the adsorption data. The breakthrough curves calculated with the model containing these parameters were in good agreement with the experimental breakthrough curves. The rate-determining step of iodine adsorption was estimated to be the reaction of iodine with  $Ag^0$  and the concentration gradient of iodine in the adsorbent particles.

Wilhelm and Schuettelkopf (1973) report on the development of an inorganic iodine absorber material based on  $AgNO_3$ -impregnated amorphous silicic acid. This material, initially called Ag-KTB, later became known as AC-6120 (originally Bayer, Leverkusen, Germany; later Sud-Chemie, Munich, Germany; no longer available); a material called KTC was also tested, the principal difference being the surface area. The KTB material was tested in the laboratory with  $CH_3I$  and in a bypass line in a PUREX-based reprocessing plant in Germany. The sampling in the reprocessing plant was after the water wash column for the dissolver off-gas and on the off-gas line from the solvent and waste tanks. Both off-gas sample streams were HEPA filtered before reaching the Ag-KTB samplers.

Hudson et al. (1995) discuss the behavior of  $^{14}C$  and  $NO_x$  in the dissolver off-gas. The THORP facility removes iodine,  $NO_x$ , and  $CO_2$  from the dissolver off-gas using a combination of acid and caustic scrubbing.  $NO_x$  is scrubbed with 6 M nitric acid. Following the acid scrubber, a delay tank or “noxidiser” provides approximately a 2 minute delay for the oxidation of  $NO$  to  $NO_2$ . This is followed by a caustic scrubber to remove iodine and  $CO_2$ . The  $NO_x$  concentration is reduced to below 1000 ppm. Iodine and  $^{14}C$  are reduced by factors of 100 and 70 respectively. Pilot-scale tests were conducted to confirm that the 1% to 2%  $NO_x$  would not adversely affect the  $CO_2$  removal efficiency. They point out that a small fraction of the  $^{14}C$  is released from the dissolver as  $CO$  rather than  $CO_2$ . They have also confirmed that the small fraction (<1%) of  $CO$  would not preclude their ability to reduce  $^{14}C$  levels by a factor of 70.

## 2.5 Studies with Simulated Spent-Fuel Solutions

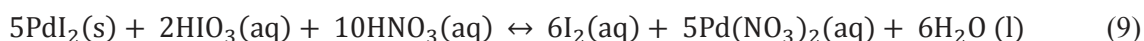
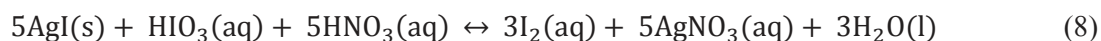
Sakurai et al. (1997) conducted dissolution tests with nonradioactive surrogates. Stable elements were added to simulate the fission products that would be found in UNF with a burn-up of 40 GWd/t (Sakurai et al. 1989; Sakurai et al. 1993). Varying amounts of  $K^{131}I$  were added to these solutions, and the iodine species produced were analyzed for  $I_2(aq)$ ,  $I^-$ ,  $IO_3^-$ , and organic iodine with the remaining iodine relative to the total considered to be non-ionic submicrometer particles (Castleman et al. 1968). The following results were obtained:

1. The main iodine species found in the simulated spent-fuel solution was submicrometer particles; iodate was the main species in uranium nitric acid solution.
2. The quantity of iodine in the submicrometer particles increased with increasing concentrations of  $Ag^+$  and  $Pd^{2+}$ . When heated in 3 to 4 M  $HNO_3$ , the submicrometer particles released molecular iodine ( $I_2$ ).

3. The  $^{131}\text{I}$  activity supernatant portion of simulated spent-fuel solution could be reduced by ultracentrifugation. This was attributed to the removal of undissolved particles by ultracentrifugation.

They concluded that iodate could not be the main iodine species based on thermochemical calculations. Calculations indicated that it should have been reduced to  $\text{I}_2$  by the  $\text{NO}_x$  produced during dissolution (Sakurai, Takahashi et al. 1993).

Sakurai et al. (1997) concluded that the submicrometer particles were colloids of  $\text{AgI}$  and  $\text{PdI}_2$ . They determined that the colloidal iodine, immediately after its formation, was unstable in hot nitric acid solution and decomposed into molecular iodine according to reactions (6) and (7). Colloidal iodine that was not decomposed ages in the dissolver and incorporates iodine into the solid particles. They found that excess iodate (e.g.,  $\text{HIO}_3$ ) was effective in the decomposition of the colloids. The decomposition occurs according to the following two reactions:



Sakurai et al. (1997) proposed the following two-step process to enhance the volatilization of iodine remaining in dissolver solutions (Sakurai et al. 1992; Sakurai et al. 1995b).

1. Heat the dissolver solution without supplying  $\text{NO}_x$  to decompose the colloidal iodine. Allow the aging of colloidal iodine after dissolution, then add an excess amount of iodate.
2. Sparge (bubble)  $\text{NO}_2$  through the dissolver solution while heating to reduce the iodate. This will result the formation of volatile  $\text{I}_2$ .

Boukis and Henrich (1991a) proposed a similar process for decomposition of non-volatile organic iodides formed from organic impurities in nitric acid fed to the dissolver.

Mineo et al. (2000) describe the behavior of  $^{129}\text{I}$  and  $^{14}\text{C}$  during the dissolution of spent fuel and the off-gas treatment process; simulants were also used. An  $^{131}\text{I}$  tracer was used. The dissolution system included a dissolver, an iodine stripping tank, a dissolver solution filter, an extraction feed tank, a condenser, a scrubber, iodine and carbon adsorbent columns, and a blower.

The tests with simulated fuel used unirradiated  $\text{UO}_2$  pellets that included the nonradioactive fission product elements Sr, Zr, Mo, Ru, Rh, Ba, La, Ce, Pr, Nd, and Sm. Cesium and Tc were not included. Silver and Pd were added to the simulated fuel, since these two elements influenced the behavior of iodine.

The dissolution of both unirradiated  $\text{UO}_2$  pellets and actual UNF was done with 4 to 5.5  $M$   $\text{HNO}_3$ . For tests involving simulated fuel, all of the dissolver solution was transferred to the iodine stripping vessel, where it was sparged with  $\text{NO}_2$  gas at 363 K. After the sparging step, the dissolver solution was filtered to remove particulates and the solution was adjusted to 3  $M$   $\text{HNO}_3$  and 250 g/L uranium. This was used as the extraction feed solution.

## 2.6 Experimental Dissolutions with Actual Spent-Fuel Solutions

As noted above, Leudet et al. (1983) discussed a series of tests with UNF. Five rods were chopped and dissolved in nitric acid. The purpose of the tests was to determine the mass balance for the volatile species during head-end operations. During the dissolution process, there was no sparge of nitrogen oxides. The balance of the volatile radionuclides was released. At the end of the dissolution and “gas release,” the

dissolver solution was boiled for 4 h to maximize the iodine release. Recycled nitrogen oxides were bubbled through the solution to limit the oxidation of I<sub>2</sub> by nitric acid that would have resulted in the formation of nonvolatile iodine species, such as IO<sub>3</sub><sup>-</sup>.

Leudet et al. (1983) report that they were able to volatilize >99% of the iodine from the dissolver solution. Despite their control of the experimental conditions to avoid retention of I<sub>2</sub> in the dissolver solution, they indicated that less-than-100% volatilization may have been caused by:

- Insufficient oxidation of the iodides because of the low nitrous acid concentrations. Nitrous acid is the result of NO<sub>2</sub> absorption and has limited stability in a boiling solution.
- Insufficient carrier gas to move I<sub>2</sub> into the off-gas stream.
- Formation of nonvolatile compounds such as HIO<sub>3</sub>, which is the result of oxidation in boiling concentrated nitric acid. They speculate that these compounds would be reduced to the elementary form by nitrous acid.

Subsequent analyses for <sup>129</sup>I in the fuel solution showed <1% residual iodine. They were unable to evaluate the quantity of organic iodides formed, but state that the formation of organic iodides seemed to be related to the presence of organic impurities in liquid or gaseous reagents, even though they used high-purity reagents in these tests.

More than 99.5% of the <sup>3</sup>H inventory remained in the dissolver solution, and 0.2 to 0.4% was found as gaseous HT in the off-gas.

Sakurai et al. 1991a discuss the dissolution of fuel in 4.1 M HNO<sub>3</sub>. This resulted in 2 to 5% of the iodine precipitating as an insoluble residue (8 ± 1 mg), 1 to 5% remaining in solution, and the balance volatilizing. Iodine was incorporated as PdI<sub>2</sub> and AgI. The quantity of iodine in the residue averaged 1.1 ± 0.5 µg/mg. The PdI<sub>2</sub> and AgI in the residue were in equilibrium with Pd<sup>2+</sup>, Ag<sup>+</sup>, and I<sup>-</sup> in the solution. The I<sup>-</sup> could have been oxidized into I<sub>2</sub> and volatilized from a hot nitric acid solution bubbled with NO<sub>2</sub>. A process consisting of heating the concentrated HNO<sub>3</sub> to 100 °C, adding KIO<sub>3</sub>, and then bubbling NO gas through the solution transferred 50 to 90% of the iodine in the residue to the off-gas. The remaining iodine was probably inside the residue particles (sub-surface) as it was difficult to remove.

Sakurai et al. (1993) presented thermochemical calculations and experimental results for distribution of NO<sub>x</sub> and iodine species during the dissolution of spent fuels. The dissolution of a spent PWR-fuel specimen in 3.5 M HNO<sub>3</sub> at 100 °C was calculated to yield a partial pressure of 7 × 10<sup>-2</sup> atmospheres of NO<sub>2</sub>, which was 80% of the NO<sub>x</sub> in the dissolver. This NO<sub>x</sub> fraction was much higher than experimental values of <15%. The high NO<sub>2</sub> fraction suppressed the formation of iodate (IO<sub>3</sub><sup>-</sup>) in the dissolution. From the calculations, no IO<sub>3</sub><sup>-</sup> should have formed. Results indicated that the iodine was colloidal and not IO<sub>3</sub><sup>-</sup>, which earlier workers had postulated. These experimental results were consistent with the thermochemical predictions. For the decomposition of the colloidal iodine, NO<sub>2</sub> sparging had a negative effect because an increase in NO<sub>2</sub> pressure promoted the formation of colloidal AgI.

Sakurai et al. (1997) also conducted dissolution tests with actual UNF. Pressurized water reactor fuels with burn-ups of 21 to 39 GWd/t were used. Two procedures were used and the efficiencies to remove iodine were compared. The first used an NO<sub>2</sub> sparge of the dissolver solution to reduce iodate to volatile iodine (I<sub>2</sub>). This reaction is:



The second procedure was based on the addition of iodate to decompose colloidal iodine as shown in Reactions (8) and (9). This procedure also used NO<sub>x</sub> sparging. The amount of iodine remaining after NO<sub>x</sub> sparging was also determined.

Their results show that 27.4 to 45.7% of the initial iodine in the solutions remained after NO<sub>x</sub> sparging alone. Tests with the second procedure indicated that the iodine was completely removed by the addition of iodate. From this they concluded that the main iodine species in actual dissolver solutions was colloidal iodine and not iodate.

Mineo et al. (2000) also conducted experiments with spent fuel. The dissolution was conducted in the same manner as for unirradiated UO<sub>2</sub> pellets described above. Iodine stripping was carried out in two steps. In the first step, KIO<sub>3</sub> was added to all dissolver solutions. These were heated to 373 K. In the second step, an equivolume gas mixture of NO<sub>2</sub> and N<sub>2</sub> was introduced. Mineo et al. (2000) report that the first step of this method decomposed the AgI and PdI<sub>2</sub> particulates according to the same reactions, (8) and (9), as reported by Sakurai (1997):

After these treatments, 5.06% of the total iodine remained in solution. The HNO<sub>2</sub> concentration was high (0.001 M) because of the NO<sub>2</sub> sparging of the solution. After this final step, 0.37% of the total iodine remained.

The iodine collected in the off-gas train showed that 74.06% of the total iodine in the fuel was on the silver-impregnated silica material in the sorption columns, the HEPA filter contained 11.33%, and the scrubber 0.10%. The iodine that adhered to the surfaces of the pipes was estimated to be 1.58% from analyses of the stainless steel test pieces. Of the total iodine from the fuel, 87.07% was accounted for.

Of the iodine that was not transferred to the off-gas, 0.37% remained in the dissolver solution, 1.49% transferred to the undissolved solids, 0.57% adhered to the dissolver vessel walls, and 0.05% adhered to the dissolution bucket and hulls surfaces. The precipitation product from the dissolver was determined to be zirconium molybdate [ZrMO<sub>2</sub>O<sub>7</sub>(OH)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] with X-ray diffractometry. AgI and PdI<sub>2</sub> appeared to be incorporated into this precipitation product. The precipitation was also found on the dissolution bucket and hulls surfaces.

The residual iodine in the dissolver solution following the NO<sub>2</sub> sparge was found to be in the form of IO<sub>3</sub><sup>-</sup>. As reported by Sakurai et al. (1989), this appeared to decrease with the NO<sub>2</sub> sparge. After stripping, IO<sub>3</sub><sup>-</sup> was no longer the primary form of iodine. Other unspecified forms, possibly colloidal iodine, were reported to dominate. Mineo et al. (2000) also state that this was consistent with observations of (Sakurai et al. 1991b, 1992).

Mineo et al. (2000) used UNF with burn-ups of 8, 29, and 44 GWd/t in tests involving the dissolution of actual UNF. Between 62% and 72% of the total amount of <sup>129</sup>I estimated from an ORIGEN II calculation was captured on the iodine sorption beds.

Mineo et al. (2000) used two methods for iodine stripping. A method using NO<sub>2</sub> gas at 363 K volatilized <sup>129</sup>I. This method resulted in 9.1% of the total <sup>129</sup>I estimated with ORIGEN-II calculations being evolved. The two-step process, previously described for the simulant tests, allowed them to remove additional <sup>129</sup>I into off-gas, which accounted for about 2.1 %. This fraction was believed to be representative of the fraction of <sup>129</sup>I that existed as precipitates. The fraction of iodine evolved was comparable to the iodine found in the precipitates from the simulant test (1.49%). These results are comparable to those reported Sakurai et al. (1992). Analysis of the dissolver solution during both phases of the two-step process showed <sup>129</sup>I concentrations as high as 0.45 Bq/mL decreasing and leveling off at about 0.2 Bq/mL. The species <sup>129</sup>IO<sub>3</sub><sup>-</sup> was detected only once.

### 3. IODINE IN VESSEL OFF-GAS

Once iodine enters the separations processes downstream of the dissolver, the chemistry becomes even more complex than in the dissolver because of the tributyl phosphate (TBP) extractant and kerosene

diluent mixture, and the complex chemistry that results from continued radiolysis. More complexity is added when one considers the radiolytic decomposition products of the organic extractants and diluents used in aqueous separations.

Vessel, evaporator/condenser systems, and other subsystems that have expectedly low off-gas flow rates typically vent to the VOG system. Some of the gaseous radionuclides that pass into the separations processes downstream of the dissolver can eventually volatilize into the VOG system. These volatilized radionuclides in the VOG may require emissions control, depending on the amounts of these volatilized radionuclides and their respective control efficiency requirements for the entire reprocessing facility.

Table 3 summarizes available information from open literature about VOG flow rates and compositions.

Table 3. Vessel off-gas flow rates and compositions

<b>Flow rate [m<sup>3</sup>/h (scfm)]<sup>a</sup></b>	<b>Total iodine (mg/m<sup>3</sup>)</b>	<b>Partitioning of iodine to VOG</b>	<b>Plant or plant scale (t/year)</b>	<b>Reference</b>
Approximate flow rate ratios, DOG/VOG/COG, are 1:10:100	–	–	General range	Herrmann et al. (1980)
350 (206)	–	–	WAK	Herrmann et al. (1993)
270–330 (160–190)	0.002–0.006 (in VOG from HLW tanks); 0.01 (in MAW storage tanks); 8–18 (in VOG)	50% of the iodine in the dissolver solution	WAK	Herrmann et al. (1997)

<sup>a</sup> scfm = standard cubic feet per minute.

McManus et al. (1983) at the Idaho Chemical Processing Plant (ICPP), while mostly a statistical study, found that iodine in the organic extractant was not easily removed, consistent with the studies cited elsewhere in this document. They concluded that the iodine concentration in the organic solvent continued to increase until an equilibrium amount was attained. After 5 to 10 recycles and achieving equilibrium, 80–90% of the <sup>129</sup>I entering the extraction column exits with the raffinate and the remaining <sup>129</sup>I is partitioned to the waste solvent stream. Distribution in the first cycle extraction process was expected to have a distribution coefficient between the organic and the aqueous phases from 8.6 for the reduced chemical forms of iodine to 0.83 for the oxidized forms.

Efforts to wash organic iodides from the organic solvent were unsuccessful (Boukis and Henrich 1991a, b). However, Kindel et al. (1993) found that iodododecane could be removed quantitatively from n-dodecane by absorption on AgNO<sub>3</sub>-impregnated material or on activated charcoal that was impregnated with potassium thiocyanate or 1,4-diazabicyclo-2,2,2-octane. These results were confirmed when organic iodides were quantitatively removed from the kerosene used in the WAK.

Reed and coworkers (2002) were able to obtain the iodine spectra from a spent solvent sample from nuclear fuel reprocessing that contained iodine at 40 mg/L and found iodine in oxidation states from I(II)

to I(VII). While inconclusive, they found the iodine spectrum of the solvent sample to be consistent with an organic iodide species; however, molecular iodine could not be excluded.

Hasty (1968) studied the behavior of  $\text{CH}_3\text{I}$  (often used as a surrogate for the organic iodides in the system) with temperature. At 30 to 50 °C and chemical equilibrium, there was 2 to 3 times more  $\text{CH}_3\text{I}$  in the aqueous phase than in the vapor. Depending on the actual composition of the organic iodide, efforts to remove it at the dissolver may have limited success. These organics would then be transferred to the solvent extraction processes.

Wilhelm et al. (1976) also found that a fraction of the residual iodine contained in the fuel solution was found in the VOG. A number of organic compounds could have resulted from the radiochemical reactions of tributyl phosphate, its decay products, and dodecane. These, in turn, could have reacted with the iodine. Thus, they expected a high fraction of organic iodide in the vessel off-gas.

Work by Thomas et al. (1977) indicated that the use of  $\text{NO}_2$  would be expected to reduce the loading capacity of iodine on materials, such as silver substituted zeolites. They recommended that TBP be removed prior to the iodine removal steps to avoid capacity loss.

Parker and Schwendiman (1979) at Pacific Northwest laboratory evaluated the removal of tributyl phosphate (TBP) vapors from fuel reprocessing off-gas streams. They discuss the results from German laboratory studies (Wilhem and Schuettelkopf 1973) in which the airborne TBP concentrations used were about  $6 \times 10^{-3}$  g/L. These concentrations significantly reduced the iodine sorption capacity of AC 6120. It was found the removal efficiency could be restored by adding  $\text{NO}_2$  to the air stream. Parker and Schwendiman did not find dodecane as having similar deleterious effects.

Henrich et al. (1980) report that the presence of organic iodides in the dissolver solution can result in volatilization of these iodine species into the downstream VOG. For the VOG, the iodine filters showed reduced DFs after about 40 d. This was attributed to the presence of organics in the VOG. From the gas chromatographic analyses, they found iodated dodecane as the dominant organic iodide. They also found straight chain alkane iodines from C-1 to C-11. These organic compounds were retained on the iodine sorption materials that were investigated.

Herrmann et al. (1980) discuss the production of aerosols at various points in the processing plant.

- Aerosols were formed on the surface of the liquid when air and steam bubbles traveled through the liquid and burst; the aerosols were carried along with the gas stream. The aerosol droplets contained the same specific activity as the agitated solution. It was shown that an aerosol content in the gas stream of  $10 \text{ mg/m}^3$  could be assumed. This applied to the dissolution, evaporation, stirring, and air assisted liquid transfer processes.
- It was assumed that the aerosol content of the gas was  $0.1\text{--}1 \text{ mg/m}^3$  for processes in which the gas does not flow through but flows over the solution or in which the liquid surface moves only slightly (e.g., in the cases of scavenging and pulsing air).

Herrmann provided the estimates shown in Table 4 for the aerosol content of various streams.

Stirring and transfer operations dominated in terms of aerosol generation. Typically about  $20 \text{ m}^3/\text{h}$  per square meter of liquid surface was required to mix a solution in a vessel. Nominally the vessels were homogenized for about 20 minutes.

Table 4. Estimates of the aerosol content of various air streams in the WAK

Aerosol Sources	Air (m <sup>3</sup> /h)	Aerosol Loading (mg/m <sup>3</sup> air)
Stirring air	440–3000	10
Transfer air (airlift)	160–200	10
Pulse air	600	0.1
Scavenging air	150	0.1–1

The main organic iodide species has been postulated to be methyl iodide (CH<sub>3</sub>I). In the work published by Sakurai et al. (1983b), they checked the behavior of CH<sub>3</sub>I adsorption from a gas stream onto a column of zeolite 13X. Two experiments were performed, one with and one without NO<sub>2</sub> in the gas stream. In both cases, iodine (<sup>131</sup>I in this case) was sorbed on the columns. In the case where NO<sub>2</sub> was included, color changes suggested to them that a decomposition of the CH<sub>3</sub>I occurred according to the reaction



where  $x$  and  $y$  were to be determined in later experiments. When the column was heated, crystalline I<sub>2</sub> was found on the tubing leading from the column; NO<sub>2</sub> was desorbed before the I<sub>2</sub>. It was also determined that NO<sub>2</sub> and CH<sub>3</sub>I were sorbed at different times, leading to a chromatographic separation of the two gases with NO<sub>2</sub> sorbing media.

Herrmann et al. (1988) reported that the conditions for iodine capture from the vessel off-gas were less favorable than in the dissolver off-gas. The reasons provided were:

- The <sup>129</sup>I concentrations in the vessel off-gas were lower by the factor of 10<sup>5</sup> (10 to 30 Bq/m<sup>3</sup> instead of 10<sup>6</sup> Bq/m<sup>3</sup> in the dissolver off-gas).
- The off-gas stream flow rate was 5 to 20 times higher.
- The vessel off-gas contained organic compounds that may have poisoned the iodine sorbent material (Ag-loaded AC 6120 in this case), for example, dodecane and organic radiolytic products.

Tests were initiated in 1987 with a side stream on the WAK vessel off-gas system. This side stream pulled 10% of the main flow of off-gas. During the first 6 months, the DF was >100 on a Ag-loaded (12 mass %) AC6120 sorption bed. When the DF decreased to 20, the bed was regenerated. Gas chromatographic analyses of traps installed in the system indicated that the predominant iodine-containing organic compound in the VOG was an iodine–dodecane compound. In addition to this compound, all straight chain alkane iodides from C-1 to C-11 were detected.

Experiments were performed with zeolite 5A as an iodine sorbent for treating off-gases and the results indicated that DFs of >1 × 10<sup>6</sup> were obtained from simulated DOG and 0.1 DOG concentrations (Sakurai et al. 1983a). At 200 °C, iodine was not emitted from the column even though it moved. At 265 °C, ~90% of the iodine was removed; up to 10% of the iodine was not removed at temperatures up to 500 °C.

Herrmann et al. (1997) found that not much of the iodine in the organic solvent was removed in the organic wash (Na<sub>2</sub>CO<sub>3</sub> wash) during solvent cleanup. About 50% was released to the VOG. About 2 to 6 µg/m<sup>3</sup> of iodine was found in the vent systems of the high-level waste storage tanks. Caustic scrubbing was ineffective at removing iodine from the DOG—only about 15% was removed. This suggested that much of the iodine in the VOG was in forms, such as organic iodides, that were not highly soluble in



caustic, compared to iodine forms such as  $I_2$  and HI that are quite soluble. The efficiency of the silver-loaded AC 6120 was 99.5 to 99.9%, but decreased to about 90% when the plant was idle. For the VOG, the efficiency was only 90 to 95%. Silver reactors had an efficiency of only 90 to 94% for the HLW tanks. Iodine-131 was continuously produced from the spontaneous fission of  $^{244}\text{Cm}$ .

#### 4. STREAM COMPOSITIONS

Herrich et al. (1988) point out that the concentration of organic impurities in fresh nitric acid was in the mg/L range. They also determined that there were mg/L concentrations of iodine in the fresh  $\text{HNO}_3$ . This was an order of magnitude greater than the desired residual iodine content in the dissolver solution (i.e.,  $2 \times 10^{-6} M$ ). Herrich et al. had results comparable to those of Lieser et al. (1989) and (Leudet et al. 1983).

Immediately after fuel dissolution, iodine as a fission product is present mainly in its volatile elementary form (Herrmann et al. 1994). Approximately 5% of the iodine remains in the dissolver solution (feed). This iodine travels with the liquid streams into the WAK Plutonium Uranium Extraction (PUREX) process and into the medium and high activity waste solutions. Part of this iodine volatilized into the PUREX process vessel off-gas, and part of it partitioned to the waste storage systems. Extensive reports were published concerning the distribution of  $^{129}\text{I}$  in WAK (Herrmann et al. 1993; Herrmann et al. 1990; Herrmann et al. 1989).

Herrmann et al. (1997) report that during the 20 years of operation of the WAK plant in Karlsruhe, approximately 207 metric tons of fuel were processed. Most of the iodine was evolved through the dissolver off-gas in a volatile form. The remainder was dispersed across a number of aqueous, organic, and gaseous streams.

Herrmann et al. (1997) indicate, as has been reported elsewhere, that the chemical behavior of iodine in nitric acid is rather complex. This is particularly true at low concentrations where it is dominated by the redox potential in combination with the reactions with organic trace impurities in the solution. The species and the concentration of impurities depend on the supplier of the nitric acid and the overall process details of the flowsheet.

Operating experience at WAK reported by Herrmann et al. (1997) showed that it was difficult to achieve <1% residual iodine (1–4 mg/L) in the dissolver solutions for high burn-up fuels (>30 GWd/tHM). This appeared to be independent of fuel burn-up, indicating that as a fraction of the incoming iodine inventory, a larger fraction of iodine was more difficult to remove for low burn-up fuels. The dissolver operating parameters were >8 h of boiling time with air sparging. Carrier iodine was added during the last 2 h of the dissolution. For low burn-up fuels (7–14 GWd/tHM) the residual iodine content was 4 to 12% (average of 6%), whereas for high-burn-up fuel the residual was 2 to 3%. In all cases the residual iodine concentration was 1 to 4 mg/L. Herrmann et al. indicated that the important parameters for iodine evolution were the quantity of water vapor generated, the formation of nitrous oxides, and the duration of the dissolution process. For standard dissolution, 8 h was required. The off-gas rate through the dissolver and reflux condenser was on the order of 80–120  $\text{m}^3/\text{h}$ . The addition of natural iodine and sparging with  $\text{NO}_2$  during the last hour of dissolution could achieve an average iodine content of about 1% of the total input iodine (1 mg/L concentration in the dissolver solution) for the high burn-up fuels.

Herrmann et al. (1997) report that the bulk of the iodine inventory (94%) in the Karlsruhe reprocessing plant was evolved from the dissolver solution and transported to the dissolver off-gas system. The average values of iodine during the dissolution periods were on the order of 1 to 5  $\text{mg}/\text{m}^3$  though peak values reached 100  $\text{mg}/\text{m}^3$ .

Herrmann et al. (1997) describe the fate of the residual iodine species from the fuel solution. They report that about 1% of the iodine inventory in the fuel was partitioned to the UDS. About 2 to 3% of the iodine inventory was found in the organic solvent with concentrations ranging from 3 to 6 mg/L. The remainder (~2%) of the iodine was spread across the high activity waste streams and different off-gas streams. The organic iodine compounds in the solvent contributed significantly to the iodine emitted to the vessel off-gas system. Only about 0.3% of the iodine was found in the alkaline solvent waste streams. About 50% of the iodine that reached the separation processes was evolved into the vessel off-gas system. The average VOG rate was reported to be 270–330 m<sup>3</sup>/h with an iodine concentration range 0.008–0.018 mg/m<sup>3</sup>. The maximum observed value was about 0.03 mg/m<sup>3</sup>. The iodine concentration in the off-gas from the medium activity waste storage tank was approximately 0.01 mg/m<sup>3</sup>. One year after shutdown of the plant, the iodine concentration was lower by a factor of 10. The off-gas from the high activity liquid waste storage tanks had iodine concentrations between 0.002 and 0.006 mg/m<sup>3</sup>. They note that the activity of <sup>131</sup>I evolved from the high activity waste solution was on the same order of magnitude curie-wise as the <sup>129</sup>I activity. The <sup>131</sup>I was found to come from the spontaneous fission of <sup>244</sup>Cm. The cell ventilation system at WAK during the dissolution periods contained about 0.3% of the <sup>129</sup>I inventory. The iodine concentrations in the cell off-gas were  $3 \times 10^{-5}$  mg/m<sup>3</sup> up to  $18 \times 10^{-5}$  mg/m<sup>3</sup>. Iodine recoveries were 90 to 95% from the vessel off-gas stream.

If cooling times are >1 year, as is the case with commercial reprocessing, practically all of the short-lived <sup>131</sup>I from uranium fission has decayed at the reactor site. However, <sup>131</sup>I from the spontaneous fission of <sup>244</sup>Cm was detected and measured in all steps of the PUREX process: in the dissolver off-gas, in the off-gas of the different process streams, and in the off-gas of the HAW and MAW storage vessels (Herrmann et al. 1994).

The ratios of the dissolver off-gas to vessel off-gas and cell off-gas in a reprocessing facility were approximately 1:10:100 (Herrmann et al. 1980).

Wilhelm and Schuettelkopf (1973) report that the total amount of iodine in the off-gas of the dissolver was higher by a factor of 10 to 1000 compared with the iodine in the tank off-gas. They also state that on a basis of equal iodine loading, the Ag-KTB samplers showed better performance in the dissolver off-gas than in the tank off-gas. Loadings were significantly different for the same time on line. For example, in the third run report which had the highest loadings, 373 mg of <sup>129</sup>I was collected on the dissolver off-gas sampler with about 0.11% iodine penetration through the 7.5-cm-thick bed; for the tank off-gas, 5 mg of <sup>129</sup>I was collected in the same sample period with ~1% iodine penetration through the 7.5-cm-thick sample bed.

## 5. IODINE RELEASES FROM VITRIFICATION AND WASTE PROCESSES

There is limited information on the behavior of iodine during glass melting, and most of the work on the volatilization of halides and iodine in particular appears to be in the geophysical and geochemical literature (Deruelle et al. 1992; Jambon 1994; Kendrick 2012; Kendrick et al. 2012). Two studies in the open literature deal specifically with volatilization of iodine from nuclear waste glass melts (Goles 1996; Hrma 2010). Goles (1996) did laboratory experiments and reported on lab-scale melter tests. The results were that the final concentration in the glass was on the order of 10 mg/kg, with as much iodine being evolved as was being put in with the melter feed. Hrma (2010) determined that the retention of iodine in a dynamic system (continuous feed) was about 20%. Most of the iodine was found to be volatilized as the melter feed was dried, calcined, and melted as the liquid feed transitioned to the melt. Hrma did not give the iodine concentration in the waste in the studies he cited. Many of the references he cited have limited

distribution and, hence, cannot be cited here. On the whole, the two waste-specific studies (Goles 1996; Hrma 2010) and the geologic studies (Deruelle et al. 1992; Jambon 1994; Kendrick 2012; Kendrick et al. 2012) came to the same conclusion; that is, not much of the iodine remains with the melt, and iodine is the most volatile of the four lighter halides.

Goles et al. (1981) discuss the off-gas from a nuclear waste vitrification project conducted at the Pacific Northwest Laboratory in a hot cell. This project involved the dissolution of spent uranium fuel, the separation of uranium and plutonium from the dissolver solution with solvent extraction, and the vitrification of the fission products. The off-gas from the vitrification portion of this demonstration was sampled for  $^3\text{H}$ ,  $^{14}\text{C}$ ,  $^{85}\text{Kr}$ ,  $^{129}\text{I}$ ,  $\text{NO}_x$ , semivolatiles, and particulates. The iodine was sampled in an undiluted process off-gas stream. The  $^{129}\text{I}$  concentrations were found to be  $\sim 1 \text{ nCi/m}^3$  in the process off-gas stream. They did not report the overall material balances. The fraction of iodine released during vitrification was on the order of  $10^{-3}$  of the total emitted in the entire process.

McManus et al. (1983) report that waste solidification was the major atmospheric release point for iodine and that intermediate level waste evaporation was the major liquid release point. They indicate that 14–31% of the  $^{129}\text{I}$  in the UNF was sent to high level waste (HLW) calcination in the blended feed, where it was volatilized and could have been captured on a solid iodine sorbent. Part of the reason for the low release values was because the scrub solutions at the HLW process were expected to capture 45–65% of the volatilized  $^{129}\text{I}$ . However, this collected  $^{129}\text{I}$  would again be volatilized when the scrub solutions are solidified.

More recent estimates of iodine retention in glass, based on a review of a large number of vitrification tests for Hanford waste, are provided in a 2013 limited distribution report that cannot be cited here.

## 6. IDENTIFICATION OF VOLATILE SPECIES FROM RELATED SOURCES

### 6.1 Reactor Containment and Stack Discharge

Keller et al. (1970) discuss the evaluation of various samplers to differentiate the various iodine species that were released from the stacks of nuclear power plants. Sampling studies at operating boiling water reactors (BWRs) indicated that the majority of the iodine being emitted from the stack was not elemental iodine. Previously reported work (Keller et al. 1970) focused on the development of samplers to differentiate particulate, elemental, HOI, and organic species. The monitoring of airborne radioiodine can be quite complex because of the probable existence of several species, including particulate  $\text{I}_2$ , iodine bound to particles, gaseous  $\text{I}_2$ , and gaseous non-elemental compounds (e.g., HI or  $\text{CH}_3\text{I}$ ).

While specifically focused on BWR emissions, it is interesting to note the variations in iodine speciation observed. Two sampling points at an operating BWR were established. One was at the steam jet air ejector, and the other was at the end of the delay line just prior to entry into the plant stack. The results are summarized in Table 5.

Table 5. Results from Keller et al. (1972) on the forms of iodine from an operating BWR

Type	Fraction of Iodine at	
	Steam Ejector	Delay Line
Particulate	ND <sup>a</sup>	ND–0.015
Elemental	0.240–0.350	0.035–0.054
HOI	0.320–0.379	0.196–0.232
Organic	0.271–0.439	0.698–0.767

<sup>a</sup> ND = <0.01.

## 6.2 Nuclear Reactor Accident Radionuclide Containment

Beahm and coworkers investigated the chemistry of iodine with respect to reactor accident containment of fission products and the development of the TRENDS (Transport and Reaction of Nuclides in Dominant Sequences) code (Beahm et al. 1990; Beahm and Shockley 1983; Beahm and Shockley 1984; Beahm et al. 1988a; Beahm et al. 1988b; Weber et al. 1992; Wisbey et al. 1986b; Wisbey et al. 1986a; Wren et al. 2000; Wright et al. 1988). This code was developed to track I<sub>2</sub>, CsI, or I, and HI, CH<sub>3</sub>I, and AgI during accident conditions. However, in the process of this effort, they had to study iodine chemistry and the interaction of iodine with organics, here represented by the organic iodide CH<sub>3</sub>I. They identified the important reactions and the kinetics of those reactions (Buxton and Mulazzani 2007).

In Canada, a code similar to the TRENDS code was developed based on preliminary work by Wren et al. (2000). In their work, they determined that kinetics, not thermodynamics, governs iodine speciation and partitioning under conditions typical of those expected in a reactor containment accident. Iodine volatility was orders of magnitude higher than that expected based on thermodynamic calculations. They determined that the effect on aqueous chemistry of impurities originating from surfaces played a major role in determining iodine volatility. They provided a review and critical evaluation of the data in the context of developing a model for iodine behavior under reactor accident conditions. Later, Wren and Ball (2001) published the “library of iodine reactions in containment” (LIRIC) as a comprehensive mechanistic model for the chemical and mass transport behavior of iodine in containment under nuclear reactor accident conditions. They showed that the LIRIC model could be used to successfully simulate iodine behavior in experiments performed under conditions relevant to post-accident containment.

While not entirely applicable to the scope of the work presented here, Castleman et al. (1968) showed that the species distribution depends on the concentration of iodine and the chemical nature of the environment when irradiated U, UO<sub>2</sub>, and U<sub>3</sub>O<sub>8</sub> are heated to 1000 to 1300 °C. Their results show that the final forms of iodine depended on the chemical nature of the environment, being largely elemental (I<sup>0</sup>) in neutral to oxidizing atmospheres and I<sup>-</sup> in reducing atmospheres. They identified that the reaction I + H<sub>2</sub> = HI + H can account for the extent and rate of formation of HI observed when tracer-level iodine is released into steam containing hydrogen. This may be an important result if dry separations are used in preparing the fuel for dissolution. Methyl iodide was found to be produced in reactions between atomic iodine and impurities in the system.

Strong evidence for the release of <sup>129</sup>I from the West Valley plant in excess of natural or other anthropogenic sources was found by Rao and Fehn (1997). Levels of <sup>129</sup>I in the local surface waters were 10<sup>2</sup> to 10<sup>4</sup> times higher than elsewhere in New York state, including near operating nuclear reactors, while the <sup>36</sup>Cl/Cl and <sup>3</sup>H levels were consistent with modern values.

Wright et al. (1988) discuss the adsorption of iodine species in sampling lines, and they developed a model to calculate the effects of deposition and transport. This was a study mainly of containment and accident conditions, but it indicates some of the errors that can arise from sampling in these complex systems.

While his study was applicable to the operation of a nuclear reactor, Kovach (1999) cited literature to show that iodine released from the fuel during reactor operation was in the inorganic form ( $I_2$  or  $CsI$ ). These were dissolved into the primary and secondary coolants where, even at very low concentrations, the organic content was much higher than the iodine content. This favored the formation of organic iodides. He indicated that longer alkyl chain (ethyl, propyl) iodides, methyl di- and tri- iodides, allene iodide, etc. were likely present in these coolants. The form of the iodine (inorganic or organic) was determined to be very dependent on conditions under which it is released, including the strength of the radiation field.

The works of Schmitz (2004) and Sebok-Nagy and Kortvelyesi (2004) are two of the more recent studies of iodine chemistry. They studied iodine chemistry over different pH ranges. Schmitz (2004) studied the hydrolysis of iodine and its mechanism in acidic to neutral solutions. He recommended values for equilibrium and kinetic constants. He determined the equilibrium constant for the reaction



and found it to be much larger than previously reported. The equilibrium constant decreased slowly with the temperature. They also measured the rate of the reaction



in perchloric acid solutions from  $5 \times 10^{-2} M$  to  $0.5 M$ . It was found to be a second-order reaction with a rate constant nearly independent of the acidity. The value of the rate constant was found to be  $25 \text{ mol}^{-1} \text{ s}^{-1}$  at  $25^\circ \text{C}$  and decreased slightly with increasing temperature, indicating that the disproportionation mechanism was more complicated than originally thought. This result indicated the importance of a dimeric intermediate [Reaction (14)] in the mechanism.



Sebok-Nagy and Kortvelyesi (2004) studied the kinetics of the hydrolytic disproportionation



in buffered solutions in the pH range 8.9 to 10.5 at different initial iodide concentrations. A model was developed and the various rate constants determined.

Organic  $g$  values for methylethylketone (MEK) were found to increase in the presence of  $N_2O$  (Glowa et al. 2000; Driver et al. 2000). They found about 150 reactions for the decomposition of MEK, but none involved iodine. The results from this work, however, show the complexity of the organic constituents that comes about from radiolysis. Other works suggest that there is reaction between these organics and the iodine species (Henrich et al. 1980; Kindel et al. 1993; McManus et al. 1983; Reed et al. 2002; Sakurai et al. 1983b; Wilhelm and Furrer 1977).

## 7. DEPOSITION IN SAMPLE LINES

Evans et al. (1995) discuss the issue of iodine adsorption on sample line surfaces. This can have a significant effect on the reported iodine concentrations in the off-gas lines being sampled. Studies were conducted using short lengths of 316 stainless steel tubing. The gas stream consisted of air and gaseous

elemental iodine with  $^{131}\text{I}$  tracer. The iodine gas concentrations ranged from  $10^{-10}$  to  $10^{-6}$  mol/dm<sup>3</sup>. The relative humidity ranged from 20 to 90%, and the operating temperatures, from 25 to 90 °C.

The rate of iodine deposition was found to be proportional to the gas-phase iodine concentration. The deposition also increased with increasing relative humidity. The deposition rate decreased with increasing temperature. The studies also point out that the chemisorption of iodine occurred primarily in areas of corrosion and depended on the initial surface conditions. They found that pretreating the sample line with nitric acid or electropolishing the surface reduced the retention of iodine.

Iodine deposition on the untreated tubing ranged from 45 ng/cm<sup>2</sup> at iodine gas concentrations of 0.3 nmol/L to 25,400 ng/cm<sup>2</sup> at 20 nmol/L. Electropolished or nitric acid pre-treated surfaces reduced the iodine deposition to 10–50 ng/cm<sup>2</sup> at iodine concentrations ranging from 2 to 8 nmol/L. This compares to iodine deposition of 9500 ng/m<sup>2</sup> at iodine concentrations of 3 nmol/L.

They also found that a large portion of the iodine deposited on the unpolished surfaces could be removed by desorption with air. Analysis of the desorbed iodine indicated predominantly inorganic iodine.

## **8. RECENT WORK ON IODINE AQUEOUS SPECIATION**

Richard and Gaona (2011) give a complete set of thermodynamic constants for the iodine-organic species. This information could be useful when considering what organic iodides could form in the various process streams of a reprocessing plant.

The dominant iodine species at pH  $\leq 8$  is I<sub>2</sub>, but the chemistry becomes much more complex above that pH (Lengyel et al. 1993). Lengyel et al. list a complete set of equilibrium constants and rate constants for the inorganic iodine species.

## **9. DATA GAPS**

While there are considerable data available in the literature to describe the composition of the dissolver off-gas streams, a number of data gaps could not be readily filled from this literature surveyed. Some of these data gaps are understandable as the information may be considered proprietary. Data on flow rates in a reprocessing plant, especially for the vessel and melter off-gas streams, were limited. In addition, very little information was available on cell off-gas rates. Variations in equipment design have significant impacts on in-leakage rates. Plant design also greatly impacts the quantity of air used for fluid transfers.

During the review, it became very apparent that the dissolver conditions were very important to the fraction of iodine volatilized during the dissolution operation. In many cases, the dissolver conditions were not specified. For laboratory dissolvers, it was assumed that these were batch dissolvers that result in low acid concentrations as the UO<sub>2</sub> dissolution progresses. Continuous dissolvers can operate in several modes. A ferris-wheel-type continuous dissolver tends to have a more constant acid concentration, whereas a continuous stage-wise dissolver may have very different acid concentrations from stage to stage. Additional information on the relationship between dissolver conditions and iodine and other volatile emissions is needed.

Recycle acid in many cases appeared to be a contributing factor to the production of organic iodides in the head-end operations of actual facilities. Even the organics contained in the high purity acids (unlikely for plant operation) were found to have an impact in some studies. However, little or no information was presented on the actual constituents found in the recycle or incoming acids nor on the details of the recycle operations.

Throughout this review, a surprisingly small amount of information was found on the exact speciation of the organic iodides found either in the dissolver solutions, the DOG, or, more importantly, the VOG. A concerted effort at sampling and analysis of the organics would appear highly desirable to facilitate the understanding of the species formed and the quantities formed from specific points within the plant.

## 10. SUMMARY

In this effort, we attempted to review the available literature on the evolution of iodine into the various streams within a UNF reprocessing facility. From reviewing some 40 years' worth of literature, we can make the following key points:

- The head-end operations have always been the primary focus for iodine removal. But, in light of the high recovery factors required for iodine (>99.9%), the treatment of the dissolver off-gas is insufficient. Operating experience and tests with actual nuclear fuel show that iodine evolution from the dissolver into the DOG ranges between 95 and 99%. Iodine evolution from the dissolver can be improved to >95% through the additions of NO<sub>2</sub> sparging, KI, and iodate. Several studies have shown that much of the residual iodine in the dissolver solution is in the form of colloidal iodine (AgI and PdI<sub>2</sub>).
- The quantity of iodine found in the shear cell off gas is normally quite small. Typically this is less than 0.3% of the total iodine.
- The flow of the VOG stream may be on the order of 10 times greater than that of the DOG stream. This stream typically contains 40–50% of the iodine remaining in the dissolver solution. The iodine concentration in this stream may be lower by as much as a factor of 10<sup>5</sup>. A significant fraction of the iodine in this stream is present as organic iodides.
- The distribution of the iodine in the solvent extraction system indicates that 40 to 50% of the iodine that remains in the dissolver solution is transferred to the organic solvent. Caustic washing does not remove significant quantities of this iodine.
- A major source of particulates arises from the transfer of solutions. Aerosol loadings of up to 10 mg/m<sup>3</sup> of air have been estimated. The major sources of the aerosols are from air used to mix tanks and to transfer solutions and any sparging that is employed to change the chemical distribution of iodine and increase its release. The air used in such operations may be 5 to 10 times the volume of the normal DOG stream volume.
- A limited amount of information was found on the release of iodine during waste solidification operations. The quantities of release are process specific. The range of release is estimated to be between 0.1 and 1% of the iodine processed through the plant.

Figure 3 summarizes graphically the major iodine pathways and iodine distribution within an aqueous reprocessing facility. Based on this study, four major iodine release pathways have been identified as needing treatment to prevent the release of iodine to the stack:

- Dissolver off-gas, which includes the off-gas from the shear
- Vessel off-gas, which includes the vents from the process operations and tanks within the facility
- Off-gas from liquid waste solidification, which would also include the production of waste forms from the primary off-gas system traps
- Treatment activities on used solvent and on the solidification of discarded used solvent

The head-end cell gas may or may not need treatment for iodine removal, as it is not expected to contain more than about 0.2% of the iodine processed in the plant.

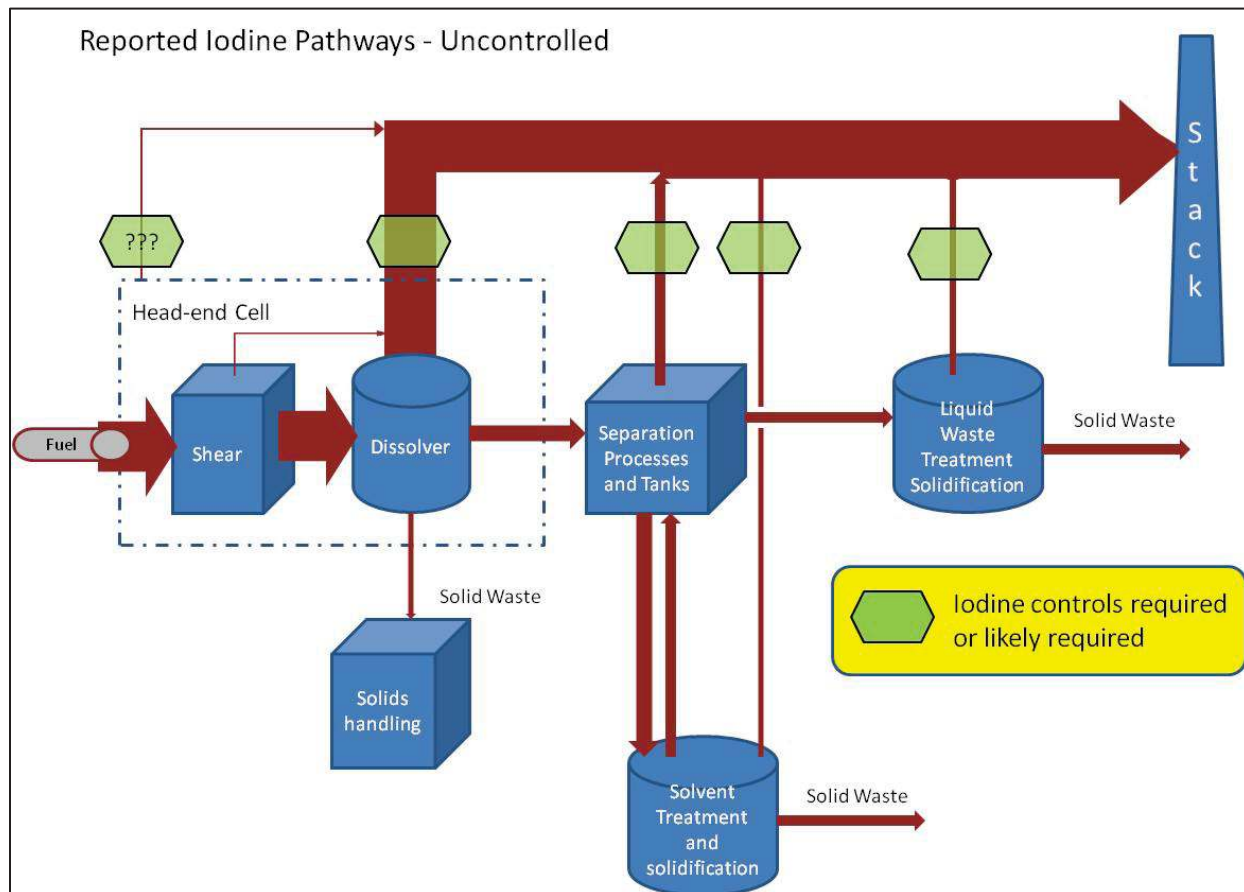


Figure 3. Summary iodine pathways and distribution throughout an aqueous reprocessing facility.

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