Fission Product Iodine During Early Hanford-Site Operations: Its Production and Behavior During Fuel Processing, Off-Gas Treatment and Release to the Atmosphere

L. L. Burger

May 1991

Prepared for the Technical Steering Panel

DISCLAIMER

This report was prepared under the direction of the HANFORD ENVIRONMENTAL DOSE RECONSTRUCTION PROJECT Technical Steering Panel by Battelle Memorial Institute's Pacific Northwest Laboratories operating the Pacific Northwest Laboratory for the U.S. Department of Energy (DOE). While funding for the work was provided by DOE, the work is not under DOE direction or control. The views and opinions of the authors expressed in this document do not necessarily reflect those of the United States Government or any agency thereof. Reference herein to any specific commercial product, process or service by trade name, trademark, manufacturer or otherwise does not necessarily constitute or imply its endorsement, recommendation or favoring by the U.S. Government or any agency thereof, nor by Battelle Memorial Institute.

Printed in the United States of America

Available to DOE and DOE contractors from the
Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831;
prices available from (615) 576-8401. FTS 626-8401.

Available to the public from the National Technical Information Service,
U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161.

3 3679 00055 5724

FISSION PRODUCT IODINE DURING EARLY HANFORD-SITE
OPERATIONS: ITS PRODUCTION AND BEHAVIOR DURING
FUEL PROCESSING, OFF-GAS TREATMENT AND RELEASE
TO THE ATMOSPHERE

Hanford Environmental Dose
Reconstruction Project

L. L. Burger

May 1991

Prepared for
the Technical Steering Panel

Pacific Northwest Laboratory
Richland, Washington 99352

**FISSION PRODUCT IODINE DURING EARLY
HANFORD-SITE OPERATIONS: ITS
PRODUCTION AND BEHAVIOR DURING FUEL
PROCESSING, OFF-GAS TREATMENT AND
RELEASE TO THE ATMOSPHERE**

May 1991

This document has been reviewed
and approved by the Technical Steering Panel.

John E. Till, Chairman
Technical Steering Panel
Hanford Environmental
Dose Reconstruction Project

April 29, 1991
Date

FOREWORD

The appendix to this document is a record of TSP comments and Battelle's responses; the TSP has reviewed and approved Battelle's responses to its comments. The comment numbers appear in the left margin next to the paragraph in which the corresponding comment was addressed. Changed text is shown in italics. In addition to responding to TSP comments, some changes were made to correct errors or for further clarification.

SUMMARY

The Hanford Environmental Dose Reconstruction (HEDR) Project was established in 1987 to estimate radiation doses that people could have received from nuclear operations at the Hanford Site since 1944. Hanford Site operations began in 1944 to produce plutonium for nuclear weapons. This effort included fabricating fuel elements, irradiating the fuel in nuclear reactors, and separating the resulting plutonium from uranium and fission byproducts.

During the early years of Hanford Site plant operation, the quantity of radioactive iodine released to the atmosphere from the fuel processing plants, and its contribution to the total radiation dose to individuals, was greater than that of other radionuclides during this time period. It is important, therefore, to review the processes that resulted in the release of iodine, the methods developed to suppress its release, and the behavior of iodine in the atmosphere.

Three processes were developed for use at the Hanford Site for the separation of plutonium, and later uranium, from irradiated uranium metal fuel elements: 1) the bismuth phosphate process, using precipitation of insoluble plutonium compounds; 2) the REDOX process, using "hexone," an organic solvent, to extract plutonium and uranium; and 3) the PUREX process, using tributyl phosphate as a solvent. All three used nitric acid dissolution of the uranium fuel as the first step; the major release of iodine occurred during this stage.

4.20 *Because of the high yield of iodine from the fission process and a*
31 *knowledge of its volatility, iodine control was expected to be a problem.*
Unfortunately, little was known of iodine behavior in the solutions and at
the low concentrations involved. This information was based in part on the
known chemistry of iodine and in part on experiments done at the tracer level
at Oak Ridge (Site X) (Dreher 1945). Likewise, there was no experience in
removing iodine from large-volume gas streams. Therefore, the only initial
actions that could be taken were to 1) locate the processing plants in the
most favorable area with respect to dissipation and dilution by wind,
2) maximize the decay of iodine-131 by storage of the irradiated fuel before

processing, 3) dilute the off gas at the plant stack, and 4) carry out the dissolver operations during optimal atmospheric conditions. Attention was given to each of these items. A few months after start-up, dissolver operations were restricted to meteorological conditions that would provide a dilution of at least 500 before the stack plume could reach the ground.

The iodine species evolved to the gas phase was primarily molecular iodine. Iodine releases also consisted of considerable amounts of particulate matter and mists containing iodides and iodates, and an organic form that was primarily methyl iodide. The dissolver off gases and the ventilation off gases were at first released with no treatment. Deep-bed, high-efficiency sand filters (99.5%) were developed and installed in late 1948 to remove the radioactive aerosol from the plants' effluent gases. Deep-bed, high-efficiency fiber-glass filters (99.9%) were also developed and installed in the dissolver off-gas lines in late 1950 and early 1951; this type of filter was also used to treat the process vessel vent gases in the REDOX and PUREX plants.

21 At plant startup about 60% to 65% of the iodine was released to the off gases, roughly 50% from the metal dissolving operation, and another 15% from subsequent processing. After air sparging of the dissolver solution was started in 1951, the amount was closer to 85%. By this time, iodine trapping methods were being greatly improved, and it was much easier to trap the iodine from the relatively small volume of dissolver off gas than from the very large volume of gas from the processing facility. Of this 85%, sand filters introduced in 1948, fiber-glass filters in 1950, and the silver reactor filter early in 1951 were found to be capable of removing up to 99.99% of the iodine. However, the average removal or decontamination factor was considerably less than this because of less than optimum performance of the control processes.

The silver nitrate filter, or "silver reactor," became the workhorse for iodine trapping and was applied to all the separations plants. It was generally satisfactory, but suffered from occasional breakthroughs and deterioration with time, as well as from iodine release due to chlorine absorption. The fiber glass filter was the choice for particulate removal.

Once the gases were released from the plant, the iodine compounds were subject to oxidation and photochemical reactions. Direct deposition and washout by rainfall were the removal pathways. Present data suggest that the residence time in the atmosphere is only a few minutes for the iodine molecule and about 200 hours for methyl iodide. The final species, which may include iodine dioxide, iodides and iodates as particulates, and perhaps hypoiodous acid and hydroiodic acid in aqueous aerosols, are then deposited by the previously described mechanisms. *Stable iodine, iodine-127, is a normal component in the atmosphere, originating largely from sea water, and is therefore present in the atmosphere at all times. This iodine dilutes any radioactive iodine that is released. Accompanying the stable iodine is about one part in 1×10^{12} of iodine-129, which is produced by natural fission of uranium and by cosmic rays.*

CONTENTS

FOREWORD	iii
SUMMARY	v
1.0 INTRODUCTION	1
2.0 IODINE PRODUCTION	3
2.1 IODINE-129	3
2.2 IODINE-131	5
3.0 PLANT DESCRIPTION	7
3.1 THE BISMUTH PHOSPHATE PROCESS	7
3.2 REDOX PLANT	8
3.3 PUREX PLANT	8
4.0 OPERATION OF THE BISMUTH PHOSPHATE PLANTS	11
4.1 DISSOLVING OPERATIONS	11
4.2 BALANCE-OF-PLANT OPERATIONS	11
5.0 PROCESS CHEMISTRY	13
5.1 DISSOLUTION OF URANIUM	13
5.2 IODINE CHEMISTRY	13
5.3 IODINE EVOLUTION	16
5.4 IODINE BEHAVIOR IN THE REDOX PLANT	19
5.5 IODINE BEHAVIOR IN THE PUREX PLANT	20
6.0 FILTRATION OF GAS STREAMS	21
6.1 FILTER SYSTEMS	21
6.2 THE SILVER REACTOR	23
6.3 METHYL IODIDE TRAPPING	28
6.4 THE AMMONIA PROBLEM	29

6.5	NEWER METHODS OF IODINE TRAPPING	29
7.0	ATMOSPHERIC BEHAVIOR	31
7.1	IODINE FORMS	31
7.2	DISTRIBUTION	31
7.3	TRANSPORT OF IODINE.	36
7.4	CHEMICAL REACTIONS IN THE ATMOSPHERE	37
8.0	REFERENCES.	41
	<i>APPENDIX - SUMMARY OF TSP COMMENTS AND BATTELLE RESPONSES</i>	<i>A.1</i>

FIGURES

1	Fission Product Radioiodine	4
2	Process Used in B and T Plants	12
3	PUREX Dissolver Off-Gas Treatment	24
4	Distribution of Natural Iodine	33
5	Global Iodine Model	35

TABLES

1	Total Daily Iodine-131 Curie Emission for Several Cooling Times and Filter Efficiencies	25
2	Free Energies for Silver Iodide and Silver Iodate Formation from Nitrate	27
3	Distribution of Natural Iodine	34

1.0 INTRODUCTION

The Hanford Environmental Dose Reconstruction (HEDR) Project was established to estimate the radiological dose impact that Hanford Site operations may have made on the local and regional population. This impact is estimated by examining operations involving radioactive materials that were conducted at the Hanford Site from the startup of the first reactor in 1944 to the present. HEDR Project work is divided among several technical tasks. One of these tasks, Source Terms, is designed to develop quantitative estimates of all significant emissions of radionuclides by Hanford Site operations since 1944. Radiation doses can be estimated from these emissions by accounting for specific radionuclide transport conditions and population demography. This document provides technical information to assist in the evaluation of iodine releases.

The first full-level irradiated uranium was discharged from the Hanford Site reactors late in 1944 as the reactors were gradually brought up to the design power level. After a cooling period the discharged fuel elements, "slugs," were transported to the B and T Plant "canyons," the chemical processing facilities for the separation of plutonium. There the uranium fuel elements were dissolved, the plutonium precipitated, and the fission product waste, along with the excess uranium, was neutralized and sent to storage tanks. A portion of the volatile fission products, primarily iodine, krypton and xenon, was released from solution, and, after dilution with large volumes of air, was discharged to the atmosphere through high stacks. The first complete charge of irradiated uranium (from B Reactor) was dissolved December 26, 1944.

10,23 *Because of the high yield of iodine from the fission process and a*
33,34 *knowledge of its volatility, iodine control was expected to be a problem.*
Unfortunately, little was known of iodine behavior in the solutions and at
the low concentrations involved. This information was based in part on the
known chemistry of iodine and in part on experiments done at the tracer level
at Oak Ridge (Site X) (Dreher 1945). Likewise, there was no experience in
removing iodine from large-volume gas streams. Therefore, the only initial
actions that could be taken were to 1) locate the processing plants in the

most favorable area with respect to dissipation and dilution by wind, 2) maximize the decay of iodine-131 by storage of the irradiated fuel before processing, 3) dilute the off gas at the plant stack, and 4) carry out the dissolver operations during optimal atmospheric conditions. Attention was given to each of these items. A few months after start-up, dissolver operations were restricted to meteorological conditions that would provide a dilution of at least 500 before the stack plume could reach the ground.

The quantity of radioactive iodine released to the atmosphere from the fuel processing plants, and its contribution to the total radiation dose to individuals, was greater than that of other radionuclides during the early years of plant operation at the Hanford Site. This report gives a brief summary of the sources of radioactive iodine, the Hanford Site operations that released iodine to the environment, the chemistry involved in the processes, the methods used to trap the iodine at the source, and the behavior of iodine species in the atmosphere. Emphasis is on the first fifteen years of operation at the Hanford Site.

This report does not quantify the release of radioactive iodine from the Hanford Site operations. Quantities of radioactive materials released by Hanford Site operations will be addressed in separate reports.

The work described in this report was conducted in accordance with the requirements of ANSI/ASME NQA-1 1986 Edition, Quality Assurance Program Requirements for Nuclear Facilities, as interpreted by the PNL Quality Assurance (QA) program.

All procedures used to support this report were written and controlled in accordance with PNL QA program requirements. Records that support the data in this report were created and stored in accordance with applicable HEDR Project record control requirements.

Drafts of this document underwent internal independent technical review. Review comments were satisfactorily resolved, and there were no controversial resolutions to the comments.

2.0 IODINE PRODUCTION

Iodine has one stable isotope, of mass 127. It is widely distributed and occurs in all organisms, in rocks, and in large amounts in the oceans. There are 23 other isotopes, all radioactive. Of those produced from fission reactions, the more significant ones are shown in Figure 1 along with the decay half lives and the yields (Holland 1963). Iodine-127 is also produced, with a yield of about 25% that of iodine-129 (Soldat 1973).

2.1 IODINE-129

36,11 Iodine-129 is the most abundant iodine isotope in irradiated nuclear
37,38 fuel after a few weeks' decay time. It is of some concern in present day power reactor fuel as *possible emissions of iodine-129 during fuel reprocessing would be borderline with respect to acceptable levels*; in the early Hanford Site reactors, however, only about 1% as much iodine-129 was produced per ton of uranium as *is produced in power reactor fuel*. Because of the small amount produced and its long half life, iodine-129 was considered of minor importance. *As shown in Figure 1, the fission yield for iodine-129 is lower than for iodine-131. More importantly, the specific activity is lower by a factor of one billion. Actually, during the early years of the Hanford Site operation, the true value of the half life of iodine-129 was not known. Early estimates from the Metallurgical Laboratory were 10,000 to 16,000 days, and a later estimate based on samples taken at Hanford was "greater than 3.8 E+09 years" (Leader 1946). The correct value is 1.6 E+07 years.*

Iodine-129 also occurs in nature, being the result of natural fission of uranium as well as the product of high-energy particles in the upper atmosphere interacting with xenon. The natural ratio of iodine-129 to iodine-127 is in the range 1 E-15 to 1 E-12 (Soldat 1974). At the present time, with the contributions from nuclear testing, weapons production, and nuclear power, it may be in the range 1 E-12 to 3 E-11 (Burger 1980).

Atomic Number (element)							
Mass Number	49 (In)	50 (Sn)	51 (Sb)	52 (Te)	53 (I)	54 (Xe)	55 (Cs) 56 (Ba)
129	1.5 sec 11	6.2 min 34	4.2 hr 29 64% 36%	70 min 6 32 day	1.6 x 10 ⁷ yr 0	Stable 0	
131	1 sec 18	3 sec 97	23 min 131 95% 5%	25 min 46 22% 30 hr	8.05 day 1 78% 12% 12 day 0	Stable 0	
132	(?) 5	2.5 sec 88	2 min 206	78 hr 122	2.3 hr 17	Stable 0	
133		2 sec 66	4.5 min 266 28% 72%	2 min 261 63 min	20.8 hr 64 98% 2% 5.3 day 2.3 day 0	Stable 0	
134		(?) 11	10 sec 170	44 min 378	52.5 min 217	Stable 28	
135			6 sec 44	10 sec 225	6.7 hr 285 70% 30%	9 hr 93 3% 97% 2 x 10 ⁶ yr 3 x 10 ⁻¹⁰ sec	Stable 0

Note: The numbers shown below the half lives are the fission yields, in atoms per 10,000 fissions.

FIGURE 1. Fission Product Radioiodine

2.2 IODINE-131

12

From the environmental point of view, iodine-131 was the important iodine isotope resulting from Hanford processing activities. It decays to stable xenon, with a moderate energy β particle. The fission yield from uranium is about 2.9%, and from plutonium about 3.9% (Holland 1963; Walker et al. 1977). Because of its short half life of 8.05 days, it reaches a steady-state concentration in the reactor which is determined by the power level. This concentration, which is reached in about 40 days, is about 26 Ci (2.1 E-04 grams) per kW (Holland 1963), which would then be the level at discharge from the reactor. For the early Hanford Site reactors, the concentration at discharge was roughly 1 E+05 Ci per ton of uranium. At 70 days cooling (a typical value), the iodine had decayed to about 240 Ci per ton or about 0.002 g. Unlike iodine-131, the isotopes of mass 129 and 127 continue to build up in the reactor. Their corresponding concentrations in the typical fuel described here would be 1.6 and 0.4 g/ton, respectively. At this concentration, the activity of the iodine-129 would be 280 μ Ci/ton.

3.0 PLANT DESCRIPTION

Plants were built at the Hanford Site to separate plutonium, and later uranium, from irradiated fuel elements using three processes: the bismuth phosphate process, the REDOX process, and the PUREX process.

3.1 THE BISMUTH PHOSPHATE PROCESS

Three plants, the B, T, and U Plants, were built to use the bismuth phosphate process to separate plutonium from the irradiated fuel. Only the B and T Plants were used for the design purpose. Each building contained three dissolvers and two holding tanks for the dissolved metal solution. From these, the dissolver solution was jetted into the processing cells for subsequent treatment. A more detailed description of the facilities is given by Ballinger and Hall (1989).

24, 15 Of particular interest here is the ventilation system. All equipment
16 and buildings were under negative pressure relative to the atmosphere. Air
was pulled from the cells to the stack via a long ventilation tunnel. At
the time the plants were built, the process vessels vented directly to the
cells. Dissolvers and ventilation air systems exhausted separately to the
stack. (Zahn 1953a; 1953b). The dissolvers discharged their off gases,
diluted with *in-leakage* air, through separate 3-inch stainless steel lines.
Vacuum was maintained in the lines by steam jets. Air removal for the entire
plant was then provided by two electric fans rated at 32,500 cfm each; a
steam turbine fan rated at 30,000 cfm served as a standby. The fans were
designed to be operated together. After the first year of operation, *stack*
monitoring showed that *simultaneous operation of the two fans was unnecessary*
except when two dissolvers were *operating at the same time*. However, as an
added precaution, both fans were also used when canyon maintenance was being
done (Work 1946). Filters were installed in 1948 and will be described in
the next section.

Fuel elements were brought to the plants in "buckets" and dumped into the dissolvers. After the dissolution, the solution was transferred to another cell for feed adjustment, and from there through the remainder of the

process. Solutions were normally moved from one step to another by steam jetting, which is a common engineering practice for transporting liquids.

25 The separation plant locations were identified after extensive meteorological studies were made of the area. A meteorology station was then constructed to provide wind data and other information to the plant operators. This was transmitted on a regular round-the-clock basis. The station also received data, including 24- and 48-hour forecasts, from Seattle and from the Pasco Naval Air Station.

3.2 REDOX PLANT

The REDOX plant was the first processing plant to use solvent extraction for separations. It also differed from the bismuth phosphate plants in that uranium as well as plutonium, was separated and purified. The solvent used was hexone (methyl isobutyl ketone). Countercurrent extraction, scrubbing, and stripping (back extraction) of the plutonium and uranium were carried out in long packed columns. The separation steps through the dissolving operation were the same as in the bismuth phosphate plants.

The feed makeup for the extraction steps was different in that the plutonium was oxidized to the +6 state with dichromate rather than being reduced. Both plutonium and uranium were extracted into hexone from an aluminum nitrate solution.

The REDOX plant went on line in January 1952 and continued operation through December 1966.

3.3 PUREX PLANT

5,39 The PUREX (plutonium-uranium extraction) Plant was similar in principle to REDOX but employed relatively nonflammable tributyl phosphate in a hydrocarbon diluent as the solvent. Here, plutonium was kept in the +4 state for the extraction process. Nitric acid served as the salting agent in this process in place of the aluminum nitrate used in REDOX. Another change was the use of pulsed extraction columns, which were more efficient than packed columns. The plant was made operational in January 1956. It was shut down

in 1972 for several reasons, all of which reflected the decision that no more weapons-grade plutonium was needed. The plant started again early in 1984.

The PUREX Plant was designed for a higher throughput, and the capacity was further expanded as operating experience developed. A significant difference was the design of the dissolver, which used a downdraft condenser in place of the conventional condensing system.

Both the REDOX and PUREX plants are further described by Ballinger and Hall (1989). Both plants were designed with off-gas filtration systems. All fuel reprocessing plants at the Hanford Site were designed to have separate off-gas systems for the fuel dissolvers. *The REDOX and PUREX plants also had separate process vessel vent systems.*

Two other plants, the Uranium Recovery Plant, sometimes referred to as the Tributyl Phosphate (TBP) Process Plant, which recovered uranium from the bismuth phosphate plant wastes, and the Hot Semiworks Plant used for process testing, were important in historical context but did not involve iodine releases and are not discussed here.

4.0 OPERATION OF THE BISMUTH PHOSPHATE PLANTS

Bismuth phosphate plant operations relevant to iodine release are divided into dissolving operations and balance-of-plant operations.

4.1 DISSOLVING OPERATIONS

Dissolving was done batchwise with several tons of fuel elements charged at a time. The aluminum cladding was first dissolved in sodium hydroxide to which sodium nitrate was added to control hydrogen evolution. This solution was discharged to waste along with a water rinse. Concentrated nitric acid was then used to dissolve the uranium. The solution was kept at the boiling point and the volatilized acid refluxed in the attached condenser. When the desired specific gravity was attained, signifying the correct uranium concentration, the solution was removed to a storage cell and fresh acid was added to the dissolver. A heel of one to two tons of metal was kept in the dissolver. Normally three "dissolver runs" were made, each of which dissolved about one ton of metal and produced a solution containing about 20% uranyl nitrate hexahydrate (UNH). *Starting in early 1945, the dissolution operation was restricted to meteorological conditions that would ensure a dilution ≥ 500 before the plume could touch the ground. Often the required conditions occurred at night.*

4.2 BALANCE-OF-PLANT OPERATIONS

40 In the first process cell, sulfuric acid was added to the dissolver solution to complex the uranium, and sodium nitrite was added to reduce the plutonium to the +4 state. Following this, the precipitation steps were carried out. Most of the iodine that escaped the plant appeared at the dissolving step. A further fraction was volatilized during the subsequent valence adjustment step. The balance-of-the plant operations will not be discussed here. However, the complete flowsheet is shown in Figure 2, which includes the vent gas flow path. *Detailed process description is given in the Hanford Technical Manual Section C (1944), and is reviewed by Ballinger and Hall (1989).*

5.0 PROCESS CHEMISTRY

Complex chemical reactions in the separations process affect iodine production, evolution and behavior. Various approaches to preventing iodine evolution have been studied since 1945.

5.1 DISSOLUTION OF URANIUM

The dissolver reaction is represented schematically (not balanced) by

The NO-NO₂ ratio depends primarily on the acid concentration and varies over time. Commonly the mix is referred to as NO_x. Much of the NO is oxidized to NO₂ by the air present before the gases reach the stack. The noble gas escape is essentially complete at the end of the dissolution. Some ruthenium may also volatilize as the tetroxide. Very little iodine was normally released on dissolution of the cladding by the caustic solution. However, at least one measurement made at T Plant indicated some iodine evolved during this step. [In the late 1960s when zirconium clad fuels were dissolved further consideration was given to this step (Jeppson 1976; Bray 1980).]

5.2 IODINE CHEMISTRY

The iodine chemistry is complex, but probably the most important initial reaction is the oxidation of iodides by the nitric acid solution as shown by

where MI represents a metal iodide present in the irradiated uranium. The ratios of species formed may vary widely, but the controlling mechanism is largely the nitric/nitrous acid system, which tends to oxidize iodide ions and reduce iodate ions to elemental iodine. Nitric acid does oxidize iodine

to iodate, but the latter is unstable in the presence of NO_x and its aqueous product NO_2^- . They convert back to molecular iodine as indicated by Equation (3):

The exception is the behavior in concentrated acid, greater than about 10 M, where iodate becomes the stable species. It is significant that elemental iodine is the stable species in the dissolver solution. Thus, all iodine should evolve as I_2 . However, some species have an appreciable lifetime before conversion and only a portion of the total iodine is immediately released with the dissolver off gas. For example, any insoluble metal iodides that might have formed in the fuel would be slow to dissolve; iodates may not be reduced immediately and/or may be reformed by the oxidation of iodine with nitric acid. It may be noted that palladium is present as a fission product in quantities greater than iodine, and silver quantities are nearly as great. In support of this argument Sakurai and coworkers (1989) have recently performed experiments demonstrating that colloidal iodine is formed in simulated dissolver solution containing palladium and silver and that this iodine fraction was difficult to expel from solution.

Radioactive iodine released to the vapor phase may continue to react forming other species (Atkins and Eggleton 1963). The chemical reactions in the atmosphere are discussed in Section 7.0.

The above description is oversimplified if chlorides are present. The equilibrium constant for the reaction

is calculated to be 446 at room temperature and about 550 at the boiling point of HNO_3 .^(a) Since many industrial chemicals have chlorine impurities in greater concentration than the iodine present in the dissolver solution, about 10^{-6} to 10^{-5} M, ICl can become the dominant iodine species. The

(a) Calculated from data in Barin and Knacke (1973).

formation of NOCl is a competitive reaction. In any case the chlorine species is reactive, and it will be seen that the presence of chlorides has serious consequences for some of the methods used for trapping iodine (Section 7.0). In others it is of little consequence. In the processes discussed in the remainder of the report I_2 may also imply the presence of ICl.

A second group of compounds that are very important are the organic iodides, primarily methyl iodide. The major source of methyl iodide is not certain. However, most methyl iodide that appears in the process off gases is probably formed external to the dissolver by reactions of iodine with oils, solvents, etc. The radiation field assists by providing free radicals. It is notable, however, that traces of organic iodides have been detected from heated irradiated fuel (Eggleton and Atkins 1964). Thus, carbon impurity in uranium is a potential source. In any case, it seems to be true that wherever radioactive iodine exists, some (perhaps as much as several percent) methyl iodide will also be present. Although methyl iodide is unstable in the nitric acid environment, it may last for an appreciable period of time. Mishima (1966) and Parsly (1971) have prepared comprehensive reviews of methyl iodide behavior.

Iodine is moderately soluble in water. At 20°C, where its vapor pressure is 0.2 torr, the solubility is 0.30 g/L, or a mol fraction of I_2 of 2.1×10^{-5} . This gives a partition ratio, $P = \text{aqueous/vapor}$, of 108. Eggleton (1967) has surveyed the solubility data and reported the partition as a function of pH and iodine concentration. His values of P at a concentration of 0.1 g/L (slightly below saturation) are 80 at pH = 1, 100 at pH = 7, and 360 at pH = 9. At pH values above 5, P increases rapidly with dilution. The solubility of methyl iodide at 15°C is 1.8 g/100g water (Dean 1985). The vapor pressure of methyl iodide at this temperature is 300 torr and the partition ratio is calculated to be 7.5. Extrapolation to low concentrations assumes Henry's law, reasonable perhaps for methyl iodide but not for I_2 , as is confirmed by Eggleton's data. Hasty (1967) measured the partition of methyl iodide at low concentrations and found $P = 2.8$ at 30°C. It would appear that, theoretically, a water scrub is not very efficient for methyl iodide removal and only fair for iodine.

At high pH values other species are important. Among these is hypoiodic acid, HOI. Although less stable than its chlorine counterpart, it is a primary product in the reaction of iodine with water. It exists in solution but there is no unambiguous evidence for its existence in the gas phase (Paquette and Ford 1985). The chemistry of aqueous iodine pertinent to fuel processing is discussed in detail in many references (Eggleton 1967; Morgan 1954; Lin 1981; Paquette et al. 1983; Paquette, Wren and Ford 1985, to cite just a few). The equilibria involved have been evaluated and the volatility from aqueous solutions calculated (Eggleton 1967), as have the kinetics of release (Wren and Paquette 1985). In summary, the species of importance in the Hanford Site processes discussed here are iodine, iodine chloride, iodide ion, iodate ion, organic iodides (primarily methyl iodide), and particulate matter containing adsorbed iodine or solid iodine compounds.

6 When processing began it was found that a burst of iodine was released on first contact of the metal with acid. Maximum release was reached as the boiling point was reached. This decreased as acid reflux began in the condenser, then reached another peak after a steady state was reached in the condenser. *Iodine release was followed by taking samples of the stack gas* (Dreher 1945; Browne 1955). This was normally a 4- to 8-hour cycle, occasionally longer, but traces of iodine continued to be emitted many hours after dissolving. The time dependence of iodine release is consistent with the aqueous chemistry of iodine, but also suggests its holdup in portions of the plant.

5.3 IODINE EVOLUTION

41,2 Before plant startup, tests were made of iodine evolution by dissolving uranium metal with tracer iodine added. It was soon discovered that the fraction released increased with the iodine concentration; higher releases than expected were observed in plant operation (Dreher 1945). Early tests indicated that about 50% of the iodine was released in the dissolving step and about 10% more in the following reduction step (Lyon 1949; Dreher 1945). Various measurements and estimates of the fraction released were made during the first few years of operation. These were based on the following data: 1) the fuel exposure (burnup of uranium-235) and the power level of the

reactor, 2) cooling time before processing, 3) analysis of the process solutions for iodine, and 4) monitoring of gases released. Each was difficult, *especially* considering the *limited* information and the *relatively crude* instrumentation *available* at the time. Parker (1945) obtained some reliable stack analyses and calculated a total release of 72%. He noted that emissions continued over a 15-h period, suggesting holdup in portions of the plant.

- 7 Provisions for gas monitoring included a sample line at the 50-ft level of the stack. The gas was pulled through a filter then scrubbed with caustic to trap the iodine for counting. Problems associated with the gas sampling included condensation in the sample lines and contamination of the counting equipment (Browne 1955). Even today, monitoring gas streams for low concentrations of radioactive iodine is considered a formidable task with rather unreliable results. A major difficulty is "plating out" (deposition) of iodine on surfaces, for example, the sample lines, before the gas reaches the instrumentation.

Plant information continued to suggest a 50% release at the dissolver (Szulinski 1950). About 5% was found in condensate drained from the stack (Work 1946). A similar result was reported for the Savannah River Plant (Marter 1963; Smith 1968), thereby supporting the Hanford Site information since similar separations plants exist at both sites.

The first laboratory study of the evolution problem was carried out by Dreher (1945) shortly after plant startup. Using tracer iodine as iodide and iodate he examined the kinetics under typical plant conditions for dissolving uranium. He found little effect of either uranium or acid concentration on rate of evolution. The added iodine was evolved rapidly, the rate proportional to the second power of the iodine concentration, but 70% to 80% was retained by the reflux condenser. Conversion of added iodate was somewhat slower than of the iodide but rapid enough in both cases to suggest that a more stable complex exists in the original dissolver solution.

By the end of 1949 it was apparent that instead of trying to trap the 10% to 15% of the iodine residing in the process solutions from the large volume of ventilation air, it would be more reasonable to volatilize all the

iodine out of the dissolver and trap it in the smaller volume dissolver off gas. Preliminary tests at the Oak Ridge Plant suggested that this was achievable and plans were made to do further studies at the Hanford Site (Blasewitz 1949a; and Kane and Burns 1952).

43 Holm (1951b) carried out extensive tests on iodine release during metal dissolution. He added iodine in elemental form, as iodide, or as iodate to simulated dissolver solutions and studied the evolution of iodine as a function of temperature, presence or absence of metallic uranium, acid concentration, uranyl nitrate concentration, sparging gas composition and gas flow rate. Temperature was found to be the most important variable; the release rate increased *by a factor of about 2 to 5, depending on the species present in solution, as the temperature was raised from 50 to 100-105°C.* Nitric acid concentration had a significant and variable effect, and the rate was insensitive to the presence of uranyl nitrate. Metallic uranium hindered the oxidation of iodide but favored the release if the iodine or iodate form was used. Nitrogen was more effective than air or oxygen for iodine and iodate but less effective for iodide. The results are consistent with the known iodine chemistry and probably inspired the recent consideration of oxides of nitrogen as sparge gases. It may be noted, however, that there is evidence for the direct oxidation of the iodide ion by dissolved oxygen in acid solutions (Sigalla and Herbo 1957).

8,26
42 *The study by Holm provided new information.* An important conclusion of the work was that sparging the dissolver solution in the later stages of dissolution would increase greatly the fraction of iodine released and thus reduce the amount that might be released to the canyon ventilation air in later process steps. This was recommended by Holm and made part of the operation in *the separations plants in January 1951.* The fraction released from the dissolver was approximately 85% after this change (Blasewitz 1951).

Recently Bray (1980) carried out dissolving tests with N Reactor fuel in a sealed dissolver with downdraft condenser to which he added tracer iodine-131. He found 89% evolved in 6 hours and another 5% with 2 hours of air sparging. Clearly, there were slow chemical steps inhibiting the release of the last fraction of iodine from the dissolver solution.

It is of course possible to take the opposite approach: to prevent iodine evolution from the dissolver by keeping the iodine in reduced form (i.e., as I^-) and either complexing it with a metal such as mercury (Holm 1951a; Smith 1968; Schmidt 1957) or precipitating it, for example, with palladium, which is present as a fission product. This concept has been examined (Thompson and Kelley 1975). An alternative concept studied by Burns and McMullen (1950) used carrier precipitation with CuI . Precipitation requires maintaining reducing conditions in the solution. These methods were not completely compatible with Hanford Site processing steps.

The mercuric iodide complex is also slowly reoxidized by nitric acid; however, it is sufficiently stable that a recommendation was made to use mercuric nitrate in the plutonium precipitation step (Holm 1951a). A 45-day plant test was carried out in 1952 in T Plant. Mercuric nitrate was added along with the dilution water to 10^{-3} to 10^{-4} M. With the higher concentration the release from the canyon was cut from 5.7 to 0.2 Ci for a 24-h period. Mercury addition before feed makeup became part of the plant process.

- 13 Later, mercuric nitrate was added to the REDOX dissolver prior to each acid cut. Sporadic bursts of iodine occurred and *Hanford plant management* concluded that *the use of mercuric nitrate* was undesirable (Hill et al. 1955).

The methyl iodide that accompanies the evolved I_2 is reasonably stable and is not easily destroyed. It is subject to oxidation and is removed from gas streams by some, but not all, of the iodine trapping systems that are discussed later. Methyl iodide is a colorless dense liquid with a very low boiling point, $42.4^\circ C$. The oxidation and photochemical reactions will be discussed in Section 7.0.

5.4 IODINE BEHAVIOR IN THE REDOX PLANT

In the REDOX and PUREX plants an added complication resulted from the reaction of iodine with the organic solvent. Kane and Burns (1952) performed an investigation to determine the iodine path through the REDOX plant. Laboratory studies showed that less than one percent of the remaining iodine in

the dissolver solution was evolved during the feed preparation treatment, which included a permanganate addition and sparging with air to remove ruthenium. Most of the iodide was carried on the MnO_2 precipitate, which had to be dealt with later. Of that remaining in solution, about one percent was extracted into the hexone solvent and remained there. Control of iodine at the REDOX plant rested with the iodine trapping system discussed in Section 6.0. The vessel vent gases, the condenser vent gases, and the dissolver off gas were handled separately.

5.5 IODINE BEHAVIOR IN THE PUREX PLANT

Iodine that remained in the dissolver solution showed a strong tendency to extract into the TBP-hydrocarbon solvent. In addition to presenting a solvent purification problem, it provided an additional mode of formation and release of organic iodides during evaporation of solutions and other process steps. Some of the iodine that is extracted into the solvent becomes further partitioned into aqueous streams. However, the iodine that enters the organic phase is very difficult to wash out (Hill 1953). Using a pure paraffin hydrocarbon diluent in place of a kerosene type material alleviated the problem considerably, but the TBP still extracted the iodine.

In plants utilizing solvent extraction it became very desirable to maximize the iodine evolution at the dissolving step, thus eliminating problems later in the process. An operational perturbation of iodine release came from the use of recycled nitric acid (recovered from plant stream evaporators). The organic content of these solutions provided yet another source of methyl iodide. Note that some iodine is also recycled. The carbon content of recycled acid may be orders of magnitude greater than the iodine concentration. It is not surprising, then, that monitoring of the PUREX Plant environs revealed several organic iodine compounds (Haller and Perkins 1966).

In the PUREX Plant operation with aluminum clad fuels, about 95% of the iodine was evolved during the air sparging and recycling of the dissolver condensate via the downdraft condenser (Schmidt 1957).

6.0 FILTRATION OF GAS STREAMS

45 In 1946, iodine emissions were becoming a matter of increasing concern and efforts to reduce these emissions increased. Electrostatic precipitation was the first filtration process investigated (Work 1947). The device was not successful, but the detection of particulate radioactive material around the B and T Plant stacks in the fall of 1947 (Parker 1948a) intensified the study. The particulates were identified as coming from the ductwork, and a separate problem was identified as mists produced from boiling solutions and from the transfer of liquids by steam jetting. *The activity was identified as cerium-144, yttrium-90, and strontium-90, with some alpha activity due to plutonium.* An intensive study of gas stream filtration was carried out in the winter and spring of 1948 (Gross 1948; MacCready 1948; Lapple 1949; Zahn 1953b). Two problems received concentrated effort: 1) filtering of the particulates, including liquid aerosols, and 2) iodine trapping. This effort, especially for iodine trapping, intensified over the next 15 years; it was revived in the early 1970s and again in the 1980s.

6.1 FILTER SYSTEMS

As early as 1946, surveys of possible methods of trapping iodine had been made (Work 1946). The actual testing included a further investigation of electrostatic precipitation, testing of "chemical warfare service" (CWS) filters, laboratory tests of silver as an iodine trapping material by the Air Reduction Sales Co., a water dissolver off-gas scrubber in B Plant, tests on reduced air flow to control aerosol formation, and tests of sand bed filtration (Work 1948; MacCready 1948). The conclusion had been reached that all gas streams should be filtered or scrubbed. In May 1948 new stainless steel fans and ductwork (Parker 1948b) remedied the early particulate emissions. Water scrubbers were installed in 1948 and removed an estimated 85% of the iodine (Roberts 1958). By midsummer 1948, the water scrubber design for vessel vent gas treatment was scrapped and excavation was started for gas filtration buildings for both B and T Plants. Large, 110-ft by 48-ft sand filters were to be installed. The effluents were diverted through the sand filters before release to the atmosphere. The filter beds became operational

in October 1948 in T Plant and in December at B Plant (Zahn 1953b). They proved to be greater than 99.5% efficient for total radioactivity retention, but some operating troubles were experienced involving re-emission of adsorbed iodine. The fact that sand filters did anything at all for iodine removal confirmed the presence of particulate iodine as well as the adsorption phenomena.

28 The general concern for the iodine emission problem was exemplified by the recommendation by H. M. Parker that a maximum cooling time be applied before fuel dissolution (1948c); i.e., no fuel processed until radioactive decay had eliminated most of the iodine-131. *Nominally, this resulted in decay of from 98.8% to more than 99.9% of the iodine-131.*

By January 1949 the newly developed fiber glass filter was also tested (Parker 1949) and found to be equal to or better than the sand bed filter and much less expensive (Zahn 1953a). These filters were subsequently installed and became operational in B Plant October 1950 and in T Plant in December (Roberts 1958). The REDOX plant was equipped with fiber glass filter systems on each gas stream, and the PUREX Plant design included the improved fiber glass filters.

By this time information on the use of silver as an iodine trap was favorable enough (Lyon 1949) that designs were being considered to employ silver nitrate as an iodine filter medium for emission control of the dissolver off-gas system. Both laboratory-scale experiments and plant tests of filters were carried out during the remainder of 1949 and in 1950, and knowledge of gas treatment methods greatly expanded. The development history of these filter systems was briefly reviewed by Blasewitz (Blasewitz 1949b; Blasewitz et al. 1951) and by Roberts (1958). The first silver nitrate-fiber glass assembly was placed in operation in the 4-5L dissolver cell of B Plant in October 1950 (Work 1951). Four silver nitrate filters, "silver reactors," were installed in the B and T Plants by February 1951 (Soule and Taylor 1953; Blasewitz et al. 1951; Blasewitz and Judson 1951). The silver reactor was accepted as the ultimate iodine removal device and the fiber glass filter as the choice for particulate removal.

The PUREX Plant dissolver off-gas system is shown in Figure 3. Each of the three dissolvers had a silver reactor filter system. A fourth was used for the vessel vent gases. In 1957 a backup system was added. Originally, it consisted of a 12-tray nitric acid absorber and a caustic scrubber with valving such that different components could be bypassed (Warren 1961). Since the caustic scrubber appeared to be unneeded for additional iodine removal, it was converted to an acid scrubber in 1958. The acid scrubbers removed most of the oxides of nitrogen and some of the remaining iodine. An excellent description of the PUREX Plant gas treatment system is given by Raab and Van der Cook (1970).

The original REDOX system consisted of a sand filter for the vessel vent gas, and separate high efficiency fiber glass filters for each dissolver and condenser and also for the vessel vent system (Zahn 1953b).

It must be noted that during these years and in the subsequent decade both the reactor power level and processing rate were being continuously increased, resulting in much more radioactive iodine entering the processing facilities. By the late 1950s power levels and burnup had doubled and processing rate had increased by an order of magnitude. These effects are illustrated by Table 1 (Smith 1955b) in which the efficiencies of iodine removal are shown as a function of the fuel cooling time.

26,42

Tests were also continuing on the extent of iodine evolution during dissolution. A maximum of 85% release was cited in Parker's report (1948c) but the bulk of the measurements continued to show about 50% during dissolution and 10% during later chemical steps. When air sparging of the dissolvers was introduced *in the separations plants* in January 1951 the fractional iodine evolution approached the 85% value (Work 1950; Blazewitz 1951b).

6.2 THE SILVER REACTOR

The silver nitrate iodine absorber, or silver reactor, consisted of a packed bed of ceramic material over which a concentrated solution of silver

FIGURE 3. PUREX Dissolver Off-Gas Treatment

TABLE 1. Total Daily Iodine-131 Curie Emission for Several Cooling Times and Filter Efficiencies

Cooling time, Days	Daily Iodine-131 Emission at Various Filter Efficiencies, Ci		
	99.5%	99.95%	99.995 %
75	90-100	10	1.0
90	25-30	3	0.3
105	7-8	0.6	0.06

nitrate had been poured. Berl saddles, saddle-shaped ceramic pieces, were usually used as the packing material. After air drying, the bed was heated to about 190°C for operation. This design was the culmination of studies of various silver containing materials that began in 1947. This was a truly chemical process for removing iodine as opposed to physical processes previously employed. It remained as the principal iodine control process in all the Hanford Site reprocessing facilities and warrants a brief description.

The *silver iodine absorber* ("*silver reactor*"), about 4.5 ft in diameter and 5 ft deep, contained unglazed, *silver nitrate coated* Berl saddles supported on a wire screen. A later PUREX Plant version was modified somewhat (PUREX Technical Manual 1955) as seen in Figure 3. The gas was heated before entering the filter and the temperature was monitored. The performance was carefully observed (Blasewitz et al. 1951; Blasewitz 1951; Browne 1955). Temperatures greater than about 210°C were suspected to damage the bed, presumably by melting the silver nitrate coating and allowing it to drain from the packing. (This explanation is probably not adequate since it is almost certain that the mixture of silver compounds present will have a much lower melting point than silver nitrate, 213°C.) However, temperature control was important, and in at least one case the silver nitrate had drained off the Berl saddles to the bottom of the bed (Soule and Taylor 1953).

During the same time period, methods were developed to regenerate the bed by adding fresh silver nitrate (Ames 1955; Blasewitz 1951).

The efficacy of the silver reactor is due to the chemical stability of silver iodide and silver iodate formed in the reactions

The reaction has been studied in considerable detail (Burger 1955; Barton and McClanahan 1956; Lacksonen et al. 1963; du Plessis 1970; Patil et al. 1967). The detailed reaction mechanisms are not known. It is possible, for instance, that INO_3 is a reaction intermediate as suggested by Lacksonen. If this is the case, and if the INO_3 is not otherwise destroyed, then two molecules of iodide are produced for one of iodate. The same conclusion is reached if reactions (5) and (6) are adjusted to balance the oxidation-reduction processes. Experiments have shown that both compounds are formed (Barton and McClanahan 1956; Patil et al. 1967), but the questions of kinetics and of mechanism are still open.

It is useful to examine the equilibrium thermodynamics. The free energies for (5) and (6) are given in Table 2.

The iodide is more stable at high temperatures and the iodate at low temperatures with a crossover point at about 135°C. The reactions are reversible. The latter fact implies that the iodide should be the stable form at the operating temperature of 190°C. It may also be seen that the equilibrium iodine pressure is proportional to the square of the NO_2 concentration, a fact of considerable importance in treating the off gas. At 10% NO_2 the calculated iodine pressure at 200°C is about 1 E-09 atm, or a concentration of 4 E-05 $\mu\text{mol/L}$. The calculations are based on the pure solids being present. The solid compounds may be mutually soluble, thus introducing an error due to unknown activity coefficients.

In general, it can be said that the silver reactors worked reasonably well and satisfied the needs at the time. Operational upsets occurred occasionally; release of iodine by replacement with chlorine was a problem resulting from impurities in process chemicals. Regeneration of the bed by adding fresh silver nitrate solution became necessary as the filters became less efficient. Initially the iodine removal efficiency was better than 99.9%. An average value was probably more like 99.7%, although there were

TABLE 2. Free Energies for Silver Iodide and Silver Iodate Formation from Nitrate

Temp, °C	Free Energy, kcal	
	$\Delta G, \text{AgI}^{(a)}$	$\Delta G, \text{AgIO}_3^{(b)}$
100	-2.2	-4.2
150	-4.5	-3.1
200	-6.7	-1.8
250	-8.8	-0.2

(a) Calculated from data in Barin and Knacke (1973) and Barin et al. (1977).

(b) Estimated from NBS 298K data and entropy values.

47 operating periods when the efficiency reached 99.99% (Blasewitz and Judson 1951). After regeneration the removal efficiency dropped to around 99.5% (Smith 1955a). *No firm figure can be given for the removal efficiency averaged over time. The value 99.5% is often quoted as easily attainable (Michels and Zahn 1955), though 99.9% was often reached (Blasewitz et al. 1951). An average value of 99.5% is a reasonable estimate.*

The goal in the mid 1950s was to limit the total iodine release from all Hanford Site plants to 10 Ci per week, and a 1 Ci per day goal seemed reachable (Parker 1955). Consideration was given to using back-up silver reactors, i.e., two in series, in place of or in addition to the acid scrubbers. Studies were also made of the feasibility of using a caustic scrub (Seyfrit 1957; Smith 1955b). Acid absorbers were later installed as back-up devices in the REDOX and PUREX plants (Warren 1961). The silver reactor used in the vessel vent system proved to be less efficient than those in the dissolver off-gas system. Whether this was due to the much lower iodine concentration in the gas, the normally lower operating temperature, or the greater presence of chlorine (HCl) in the gases was not determined.

In retrospect it is likely that one of the more important contributions of the silver reactor was that the iodine residence time in the bed was long enough to permit the iodine-131 to decay. For present day iodine control (based on conceptual reprocessing plants for commercial reactor fuels) with two orders of magnitude higher fuel burnup and the need to control iodine-129

as well, the system is at best, marginal, and probably would not be used. The magnitude of the chloride problem became apparent in the 1960s (duPlessis 1970), and was confirmed by analysis of used silver reactor beds which showed the presence of predominantly silver chloride (duPlessis and Sutter 1969; Strachan 1978).

6.3 METHYL IODIDE TRAPPING

Most of the filters discussed here would not have removed methyl iodide, because of its low water solubility, high vapor pressure, and inertness. The sand filter or the water scrubber would have trapped only a small portion of the organic iodides. The silver reactor operating at 190°C should have converted the compound to silver iodide and iodate, and probably removed much of it. However, at the time the silver reactors were first installed the methyl iodide problem was unknown and thus not investigated. The observations of duPlessis (duPlessis and Sutter 1969; duPlessis 1970) showed that gases exiting from the PUREX Plant vessel vent system silver reactor contained both methyl iodide and carbon tetrachloride. The concentration of CH_3I ranged from 1 E-06 to 1 E-04 $\mu\text{g/L}$, and the CCl_4 from 1 E-04 to 4 E-03 $\mu\text{g/L}$. Not only was the silver reactor not doing its job, but if it did, it would be depleted by the chloride reaction quite rapidly. Sample Berl saddles taken from a reactor indicated that the silver nitrate was largely converted to silver chloride and silver metal (DuPlessis and Sutter 1969). This problem was probably more acute in the PUREX Plant facility where chemical thruputs were 10 to 20 times those of the old B and T Plants. In a separate study duPlessis demonstrated that ethyl iodide reacted with silver nitrate at temperatures well below the 160°C operating temperature (duPlessis 1969). He found that ethyl nitrate was the initial organic reaction product. Presumably, methyl iodide reacts the same way.

Recent work has demonstrated that solids containing silver either as the nitrate or the metal on zeolites (Scheele, Burger, and Matsuzaki 1983) or silver nitrate-loaded silica gel (Wilhelm and Furrer 1978) do trap methyl iodide very efficiently at a temperature of 150 to 200°C.

6.4 THE AMMONIA PROBLEM

The dissolution of aluminum cladding by sodium hydroxide used sodium nitrate addition to eliminate or greatly reduce hydrogen production. A portion of the nitrate ion was reduced all the way to the -3 state, and ammonia was evolved. This was noted early in the processing program but tests showed that this emission was not a problem (Lyon 1949). With higher processing rates and the installation of high-efficiency particulate filters a problem did appear. Alternate flows of ammonia and NO_x resulted in the formation of ammonium nitrate, which occasionally plugged the filters. In addition to operating difficulties, there was concern about possible explosive reactions. Also there was the possibility that ammonia could cause release of iodine from the silver reactor (Smith 1955a).

Experiments by Barton and McClanahan (1956) did indeed show that at a high temperature, 360°C , gross quantities of iodine were released in an ammonia atmosphere and that particulate matter including absorbed iodine can be released by 5% ammonia in air. It was postulated that one of the reactions was reduction of silver nitrate to the metal.

The solution to the problem was to either 1) bypass the silver reactor while decladding, or 2) provide a separate exhaust. A later PUREX Plant modification used a water scrubber ahead of the silver reactor (Figure 3) to remove any ammonia or ammonium compounds.

6.5 NEWER METHODS OF IODINE TRAPPING

In recent years the knowledge of iodine process chemistry in aqueous systems has greatly improved (Swanson 1978; Bray 1980) and new information on alternative trapping materials has been accumulated (Burger and Scheele 1983; Holladay 1979; Jubin 1979).

Recent methods of iodine removal from gas streams have included a re-examination of caustic scrubbing, an established technology. This is very effective but not practical where excess acid vapors are present; nor does it remove methyl iodide. Other methods include the Mercurex process and the Iodox process. In the Mercurex process the gas is scrubbed with an acid mercuric nitrate solution to complex the iodine. If the solution contains a

high concentration of nitric acid, organic iodides are trapped as well as iodine. The Iodex process consists of scrubbing with hyperazeotropic nitric acid to convert all iodine species to iodate ion, which can be precipitated. Neither the Mercurex process nor the Iodex process is as attractive as the use of solid sorbents containing silver. Activated carbon sorbers, used for years in reactor ventilation filtration, are not feasible for use in a fuel reprocessing plant because of the potential of a hazardous NO_x -carbon reaction. The general topic of iodine control in reprocessing has been reviewed by Burger and Scheele (1983) and by Scheele, Burger, and Soldat (1984). The optimal method may involve a silver sorbent with its effectiveness enhanced by placing it in a zeolite matrix.

Finally, it must be noted again that determining accurate release data for iodine through analysis of stack gas is subject to considerable uncertainty because of holdup in sampling lines and contamination of the counters themselves. This was recognized early (Browne 1955) and remains a problem today.

7.0 ATMOSPHERIC BEHAVIOR

The behavior of effluent iodine from separations plants is affected by the form of the iodine, atmospheric physics, deposition mechanisms, and chemical reactions in the atmosphere.

7.1 IODINE FORMS

Three forms of iodine survive long enough to be considered as atmospheric emissions: particulates, elemental iodine (or I_2), and organic iodides. Particulates carry iodine primarily as the iodide and iodate ions and may exist either as solid compounds of iodine or as iodine adsorbed or dissolved in the particulate. The composition of the organic form varies with the source. While methyl iodide is the predominant species emitted from the PUREX Plant, higher alkyl iodides, resulting from the large inventory of hydrocarbon solvent, were also detected (Perkins 1964). Later, Haller and Perkins (1966) analyzed PUREX Plant stack gas by gas chromatography and γ -ray spectroscopy and identified alkyl iodides with chain lengths up to C_8 . The C_4 component was large, perhaps arising from the tributyl phosphate. As mentioned earlier, HOI has been postulated and data are sometimes given for its concentration in gas streams, but it is usually defined only as an unidentified inorganic iodine compound. It is possible that its gaseous existence is an artifact of the detection system.

7.2 DISTRIBUTION

Before considering the atmospheric chemistry it is instructive to examine the distribution of natural iodine. Iodine enters the atmosphere from the ocean surface where it exists at a concentration of about 0.06 g/m^3 . The mechanism is probably a photochemically induced oxidation of iodide ion (Miyake and Tsunogai 1963). Korzh (1984) showed that iodine was transferred via aerosols from seawater to the atmosphere in quantities 110 times as great as is sodium. He speculated that organically bound iodine was the source. Moyers and Duce had previously noted a similar discrepancy in the I/Cl ratio

(1972). The resulting atmospheric concentration, discussed later, varies from about 10 to several hundred ng/m^3 . The distribution of natural iodine is shown in Figure 4 and in Table 3.

Radioactive iodine occurs naturally from spontaneous fission of uranium and by cosmic ray production from xenon. Only the mass 129 isotope is present in significant quantity, and this quantity is greatly perturbed by residues from weapons testing. The present 129/127 ratio is probably in the range 1 E-12 to 3 E-11 .

The iodine cycle can be thought of as starting with the weathering of rocks and ending with ocean deposits. A global model has been presented by Kocher (1979) and is shown in Figure 5. The amount of the iodine in the top 100 m of ocean is about 2.2 E+15 g , and in the atmosphere about 1.2 E+11 g at a concentration of about $1\text{-}4 \text{ E-08 g/m}^3$ (Brauer, Rieck, and Hooper 1973; Burger 1980). Moyers and Duce (1972) reported 0.5 to 2.0 E-08 g/m^3 on the windward side of Oahu, Hawaii. They also noted, in addition to the high I/Cl ratio, that gaseous iodine was proportional to particulate iodine and that the gaseous to particulate ratio was about 2. No correlation was seen between gaseous iodine and particulate chloride, total sea salt, gaseous bromine or wind speed. Much higher atmospheric concentrations have also been reported: as great as 2 E-06 g/m^3 over central Europe, and up to 10 times that amount in coastal regions (Soldat et al. 1973). Recent measurements by Rasmussen et al. (1982) gave the organic iodine content as 0.05 to 1.8 E-08 g/m^3 as background, and 5 to 10 E-08 g/m^3 over ocean areas of high biomass activity.

In the atmosphere, iodine is largely in the form of I_2 and aerosols, the latter in widely varying amounts. Organic iodine also contributes a large amount. Other forms of atmospheric iodine include minor and generally unknown amounts as HI, IO_2 , and perhaps ephemeral amounts of HOI. The estimated concentrations and residence times of natural iodine are included in Table 3 (Burger 1980). Brauer et al. (1973) and Voilleque (1979) present data on the fraction existing in the particulate, inorganic gaseous, and organic gaseous forms. The ratios vary from 1/20/15 to 1/3/6, to 1/6/2. The residence time in the atmosphere is of the order of 15 to 25 days for

S9103080.2

FIGURE 4. Distribution of Natural Iodine

particulate and inorganic forms and ten times as long for organic iodine. Residence time (τ) is defined as the reciprocal of the first order reaction rate constant and is related to half life by $t_{1/2} = \tau \ln 2$. The naturally occurring organic gaseous iodine is largely methyl iodide. For the other halogens, Rahn, Borys, and Duce (1976) gave, on the basis of four diverse and remote locations, the bromine/iodine ratio as about one; the chlorine content was 50 times as great. The inorganic component of each was somewhat less than the organic, and the gas-to-particulate ratio ranged from about 5 to 50 for all the halogens.

TABLE 3. Distribution of Natural Iodine^(a)

Compartment	Volume, m ³	Concentration, g/m ³	Total I, g	Residence Time, yr	Notes
Atmosphere	3.8E18 (STP)	~4E-8	1.2E11	~0.06	(b)
Ocean, 100 m mixed layer	3.8E16	6E-2	2.2E15	20	(c)
Biosphere	1E12	0.1	1E11	20	(d)
Fresh water, lakes	5E14	3E-3	1.5E12	?, variable	(e)
Rivers	5E12	2E-3	1E10	<0.1, highly variable	
Deep ocean	1.3E18	6E-2	8E16	1E3-5E5	(f)
Soil, 1 m depth	1.5E14	10	1.5E15	1E4	(g)
Subsurface, 1 km depth	1.5E17	0.8	1.2E17	1E5-1E7	(h)

(a) Physical data (Krauskop 1979).

(b) Concentrations highly variable over land, much higher over oceans.

(c) Mixing time of the order of 10 yr (Michel 1975).

(d) Assumes density, $\rho = 1$ at 0.1 ppm (Kocher 1979).

(e) About 1% in rivers, 99% in lakes, river flow is 3E19 g/hr, rainfall over land ~1E20 g/hr.

(f) Lower value is for transfer to ocean mixed layer. Higher one is for deposition in ocean sediments, not accurately known. Other models give longer times. Mixing time of the order of 1E3 yr. (Arnold 1959).

(g) Assumes $\rho = 2$ at 5 ppm (Kocher 1979). Bruner's value for total iodine is a factor of 4 higher (Bruner 1963).

(h) Assumes $\rho = 2.5$ at 3 ppm.

S9103080.1

FIGURE 5. Global Iodine Model

Particulate forms include dust particles, aqueous mists, smoke, fume condensates, natural organic matter, etc. Particles in the size range 0.01 to $0.1 \mu\text{m}$ are known as Aitken particles and may number about $1 \text{ E}+09$ per m^3 in rural air and much higher in urban atmospheres (Chamberlain and Chadwick 1953; Chamberlain et al. 1960).

Iodine is removed from the atmosphere by direct deposition and by rain-fall washout. Chamberlain and coworkers have done classic studies on the physical chemistry of iodine in gas streams and the deposition of iodine (Chamberlain and Chadwick 1953; Chamberlain 1960; Chamberlain et al. 1963). They point out that several processes are involved: diffusion to a surface, electrostatic precipitation, coagulation and gravity fallout, and washout by rain. Molecular iodine has a very strong tendency to adsorb on organic or

metal surfaces, a fact that makes study of iodine behavior at very low concentrations extremely difficult. (The same fact, as noted above, has made much of the monitoring of process exhaust gases using long sample lines of dubious validity.)

The residence times given above result from a combination of chemical reactions discussed in Section 7.4 and the above mechanisms.

Description of iodine forms or species depends largely on experimental analysis, and the results are open to different interpretations. A typical air analysis involves a particulate filter of known pore size, and activated carbon to absorb gaseous iodine. Many modifications have been employed, including a cadmium iodide bed to absorb elemental iodine; iodophenol to adsorb an unknown inorganic component, ostensibly HOI; and finally activated charcoal or silver zeolite to absorb organic iodides. The uncertainties result from the following observations: 1) many of the particle filters used were cellulose or other similar material notable for sorbing gaseous iodine at low concentrations, 2) some particulate matter passes the filter, 3) methyl iodide trapping by charcoal is not very efficient, 4) molecular iodine tends to partition between all portions of the trapping assembly, and it rapidly adsorbs many monolayers thick on most metal surfaces, and 5) the problems become worse as the concentration goes down. It is not an easy task; consider for example, that there may be one aerosol particle for every 10 to 1000 iodine molecules. Thus, although much careful and excellent work has been done on analysis of air samples, the results are often uncertain.

7.3 TRANSPORT OF IODINE

To the above described natural concentration of iodine, about 1 to $10 \text{ E-}10 \text{ mol/m}^3$, we can input typical stack effluent iodine from an early bismuth phosphate separation plant (Section 2.2). If we assume two grams iodine per ton of metal dissolved, 100% evolution of the iodine in 1 hour, dilution with a stack discharge volume of $35000 \text{ cfm} \times 60 \text{ minutes per hour}$, and a mixing dilution at the stack exit of 500, we have a concentration of $5.3 \text{ E-}09 \text{ moles of iodine (} 6.8 \text{ E-}07 \text{ g)}$ per cubic meter in the immediate plant

atmosphere. This is a factor of 100 above the normal atmospheric iodine concentration. At this point the iodine 131/127 ratio would remain, as in the separation plant off gas, about 0.005. A further large dilution occurs as the stack plume disperses in the atmosphere. Atmospheric physics, which control the plume travel and subsequent dilution, will not be considered in this report.

Deposition that is controlled by the mechanisms previously discussed is normally measured as Ω/X where Ω is the total deposition per unit area and X is the time-integrated concentration. The dimensions are rates, given as cm/second. Chamberlain et al. (1960) found deposition velocities of the order of 1 cm/sec for dry deposition of gaseous iodine in the laboratory and in the field, and 1 E-02 to 1 E-01 cm/sec for rates of deposition of condensation nuclei.

- 14 The fate of deposited iodine is fixation by the soil, dissolution, absorption by living matter, or resuspension. This is not a topic for this report. It is notable, however, that Brauer found most of the deposited iodine-129 in the Hanford Site environs to be located in the *top 2.5 cm* of soil (Brauer 1974; Soldat et al. 1973).

7.4 CHEMICAL REACTIONS IN THE ATMOSPHERE

The reactions of gaseous iodine in the atmosphere would be expected to be those of the iodine atom since photochemical decomposition of the iodine molecule requires only moderate energy photons. Zafiriou (1974) estimated the minimum half life of I_2 in bright sunlight as less than 10 sec. More recently he has apparently suggested an average daylight half life of 15 to 300 seconds (Voilleque 1979). Voilleque gives an average atmospheric residence time of about 5 min for I_2 and 200 hours for CH_3I . The fate of the iodine atoms is uncertain. The most probable reaction would seem to be with oxygen to form IO_2 , or IO , or with water to form HOI . However, photochemistry of trace elements in the atmosphere is exceedingly complex. One only has to note that there are dozens of molecular species in the troposphere in orders of magnitude greater concentration than iodine, e.g., organic materials such as CH_2O , and

CH₄, inorganics such as H₂, NO_x, CO, O₃, Cl₂, and HNO₃, and a variety of pollutants, all of which undergo photochemical reactions. Even the HO₂ radical is at a concentration of 1.2 E+09 to 1.2 E+12 molecules per liter, or 6.6 E-11 to 6.6 E-08 g/m³. The very reactive oxidant, HO, has a concentration ranging from 1.8 E-11 to 4.8 E-10 g/m³ (McEwan and Phillips 1975). The higher values occur during the daylight hours.

Zafiriou suggests the reactions

The ozone-iodine reaction has recently been considered as a candidate for ozone depletion (Chameides and Davis 1980; Jenkin, Cox, and Candeland 1985). The reactions are

Many of the trace components listed above could also react with iodine. Urban air adds a variety of organic species that could react rapidly. It seems likely that in clean air the stable product might favor I₂O₅, and in polluted air, organic iodides and particulates. In the latter the iodine might exist primarily as either iodide or iodate. In solution (e.g., aqueous aerosols), thermodynamic equilibrium in the following reaction strongly favors the iodate ion.

Thus, clouds may be a trap for gaseous iodine. It may also be noted that the reaction

also occurs.

A somewhat enhanced deposition rate should result with large particulates, e.g., $>1 \mu\text{m}$, regardless of the chemical form of the iodine. Very small particles do not settle, nor are they easily washed from the air.

Methyl iodide is more stable than iodine toward atmospheric reactions. The photo-oxidation has been studied extensively (Christie 1958; McKellar and Norrish 1961; Heicklen and Johnston 1962; Barber, Farren, and Linnett 1963). The products are the iodine atom and the methyl radical.

These workers were interested as much in the methyl iodide as a source of methyl radicals for subsequent study as they were in the compound itself.

The CH_3 radical follows the same oxidation steps as ordinary methane. Methane reacts primarily with the OH radical as a first step. The same mechanism would apply to CH_3I but the much shorter atmospheric residence time of the latter compared to methane suggests that the photodecomposition first step, reaction (13), predominates. Tang and Castleman (1968; 1970) used cobalt-60 radiation to induce decomposition and arrived at similar mechanisms.

The oxidation of methane in the atmosphere has been investigated in great detail. Kitada and Peters (1980) reviewed the steps that convert the CH_3 radical to water and CO_2 .

There have been fewer studies of the atmospheric chemistry of methyl iodide. Recently, Chameides and Davis (1980) suggested that the compound can remove ozone and influence the NO_2/NO and OH/HO_2 ratios. Rasmussen and coworkers (1982) made extensive measurements of CH_3I background concentrations worldwide and concluded that 1) most of the natural CH_3I comes from

seawater areas of high biomass activity, and 2) the effect on ozone and NO_x may be small. As with much of atmospheric chemistry, many uncertainties still exist.

8.0 REFERENCES

- Amos, L. C. 1955. Regeneration of Silver Reactors. HW-41053, Hanford Atomic Products Operation, Richland, Washington.
- Arnold, J. R., and E. A. Martell. 1959. "The Circulation of Radioactive Iosotpes." Sci. Am. 201(3):84-93.
- Atkins, D. H. F., and A. E. J. Eggleton. 1963. Iodine Compounds Formed on Release of Carrier-Free Iodine-131. AERE-M-1211, Atomic Energy Research Establishment, Harwell, Berkshire, UK.
- Ballinger, M. Y., and R. B. Hall. 1989. A History of Major Hanford Operations Involving Radioactive Material. PNL-6964 HEDR, Pacific Northwest Laboratory, Richland, Washington.
- Barber, M., J. Farren, and J. W. Linnett. 1963. "The Mass Spectrometric Study of the Reaction of Methyl Radicals with Oxygen." Proc. Royal Soc. of London, Ser. A 274(1358):306-18.
- Barin, I., and O. Knacke. 1973. Thermochemical Properties of Inorganic Substances. Springer-Verlag. Berlin, New York.
- Barin, I., O. Knacke, and O. Kubaschewski. 1977. Thermochemical Properties of Inorganic Substances: Supplement. Springer-Verlag. Berlin, New York.
- Barton, G. B., and E. D. McClanahan. 1956. Chemistry of the Silver Reactor. HW-42408, Hanford Atomic Products Operation, Richland, Washington.
- Blasewitz, A. G. 1949a. Iodine Evolution During Metal Dissolution. HW-15367, Hanford Atomic Products Operation, Richland, Washington.
- Blasewitz, A. G. 1949b. Information for the Fourth Meeting of the Stack Gas Decontamination Working Group. HW-13610, Hanford Atomic Products Operation, Richland, Washington.
- Blasewitz, A. G. 1951. Performance of Replacement and Regenerated Silver Reactors-Operated at 375°F. HW-21957, Hanford Atomic Products Operation, Richland, Washington.
- Blasewitz, A. G., et al. 1951. Decontamination of Dissolver Vent Gases at Hanford. HW-20332, Hanford Atomic Products Operation, Richland, Washington.
- Blasewitz, A. G., and B. F. Judson. 1951. Variation in Silver Reactor Performance. HW-21826, Hanford Atomic Products Operation, Richland, Washington.

Brauer, F. P., H. G. Rieck, Jr., and R. L. Hooper. 1973. Particulate and Gaseous Atmospheric Iodine Concentrations. BNWL-SA-4723, Pacific Northwest Laboratory, Richland, Washington.

Brauer, F. P. 1974. Environmental I-129 Measurements. BNWL-SA-4983, Pacific Northwest Laboratory, Richland, Washington.

Bray, L. A. 1980. Laboratory Studies on the Evolution of Iodine-129 During Purex-Uranium Metal Dissolution. PNL-3359, Pacific Northwest Laboratory, Richland, Washington.

Browne, W. G. 1955. I-131 Emission Problem-Bismuth Phosphate Plant. HW-36112, Hanford Atomic Products Operation, Richland, Washington.

Bruner, H. D. 1963. "Symposium on the Biology of Radioiodine. Statement of the Problem." Health Physics 9(12):1083-1089.

Burger, L. L. 1955. Thermodynamics of Iodine Removal with the Silver Reactor. HW-38311-Rev, Hanford Atomic Products Operation, Richland, Washington.

Burger, L. L. 1980. Determining Criteria for the Disposal of Iodine-129. PNL-3496, Pacific Northwest Laboratory, Richland, Washington.

Burger, L. L., and R. D. Scheele. 1983. The Status of Radioiodine Control for Nuclear Fuel Reprocessing Plants. PNL-4689, Pacific Northwest Laboratory, Richland, Washington.

Burns, R. E., and C. R. McMullen. 1950. Removal of Iodine from Dissolver Solution by Carrier Precipitation. HW-19573, Hanford Atomic Products Operation, Richland, Washington.

Chamberlain, A. C., and R. C. Chadwick. 1953. "Deposition of Airborne Radioiodine Vapor." Nucleonics 11(8):22-25.

Chamberlain, A. C. 1960. "Aspects of the Deposition of Radioactive and Other Gases and Particles." International J. Air Pollution 3(1-3):63-88.

Chamberlain, A. C., et al. 1960. "Behavior of Iodine Vapor in Air." Disc. Faraday Soc. (30):162-169.

Chamberlain, A. C., et al. 1963. "Physical Chemistry of Iodine and Removal of Iodine from Gas Streams." Reactor Science and Technology (Journal of Nuclear Energy Parts A/B), 17(11/12):519-550.

Chameides, W. L., and D. D. Davis. 1980. "Iodine: Its Possible Role in Tropospheric Chemistry." J. Geophys. Res. 85(C12)7383-98.

Christie, M. I. 1958. "Elementary Reactions in the Photochemical Oxidation of Methyl Iodide." Proc. Royal Soc. of London Ser. A 244(1238):411-423.

- Dean, J. A. (ed.) 1985. Lange's Handbook of Chemistry, 13th Edition, McGraw-Hill, New York.
- Dreher, J. L. 1945. The Evolution of Iodine During Metal Dissolution. HW-3-3003del, Hanford Works, Richland, Washington.
- duPlessis, L. A. 1969. The Reaction of Gaseous Iodoethane with Silver Nitrate. BNWL-CC-2048, Pacific Northwest Laboratory, Richland, Washington.
- duPlessis, L. A., and S. L. Sutter. 1969. Analysis of Samples from the PUREX Vessel Vent Silver Reactor. BNWL-CC-2188, Pacific Northwest Laboratory, Richland, Washington.
- duPlessis, L. A. 1970. Some Observations Concerning the Chemistry of the PUREX Vessel Vent System. BNWL-CC-2378, Pacific Northwest Laboratory, Richland, Washington.
- Eggleton, A. E. J., and D. H. F. Atkins. 1964. "The Identification of Trace Quantities of Radioactive Iodine Compounds by Gas Chromatographic and Effusion Methods." Radiochim. Acta 3(3):151-158.
- Eggleton, A. E. J. 1967. A Theoretical Examination of Iodine-Water Partition Coefficients. AERE-R-4887, Atomic Energy Research Establishment, Harwell, Berkshire, UK.
- Gross, C. N. 1948. Stack Gas Decontamination, Separation Plants Development of Decontamination Systems. HW-9175, Hanford Atomic Products Operation, Richland, Washington.
- Haller, W. H., and R. W. Perkins. 1966. "Organic Iodine-131 Compounds Released from a Nuclear Fuel Chemical Process Plant." Health Physics 13(7):733-738.
- Hasty, R. A. 1967. The Partition Coefficient of Methyl Iodine Between Vapor and Water. BNWL-SA-1293, Pacific Northwest Laboratory, Richland, Washington.
- Heicklen, J., and H. S. Johnston. 1962. "Photochemical Oxidations, II. Methyl Iodide." J. Am. Chem. Soc. 84(4):4030-4039.
- Hill, O. F. 1953. Quarterly Report October through December 1952, Chemical Research. HW-26937, Hanford Atomic Products Operation, Richland, Washington.
- Hill, O. F., et al. 1955. Symposium on Iodine Problem. HW-39073, Hanford Atomic Products Operation, Richland, Washington.
- Holladay, D. W. 1979. A Literature Survey: Methods for the Removal of Iodine Species from the Off-Gases and Liquid Waste Streams of Nuclear Power and Nuclear Fuel Reprocessing Plants with Emphasis on Solid Sorbents. ORNL/TM-6350, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Holland, J. Z. 1963. "Physical Origin and Dispersion of Radioiodine." Health Physics 9(12):1095-1103.

Holm, C. H. 1951a. Retention of Iodine in Process Solutions by Mercuric Salts. HW-21103, Hanford Atomic Products Operation, Richland, Washington.

Holm, C. H. 1951b. Removal of Iodine from Aqueous Solutions by Sparging. HW-20803, Hanford Atomic Products Operation, Richland, Washington.

Jenkin, M. E., R. A. Cox, and D. E. Candeland. 1985. "Photochemical Aspects of Tropospheric Iodine Behavior." J. Atm. Chem. 2(4):359-76.

Jeppson, D. W. 1976. Program for Control of Iodine 129 During Zirconium Clad Fuel Reprocessing at PUREX. ARH-CD-583, Atlantic Richfield Hanford Company, Richland, Washington.

Jubin, R. T. 1979. A Literature Survey of Methods to Remove Iodine from Off-Gas Streams Using Solid Sorbents. ORNL/TM-6607, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Kane, J. S., and R. E. Burns. 1952. Behavior of Iodine in the Redox Process. HW-23312, Hanford Atomic Products Operation, Richland, Washington.

Kitada, T. and L. K. Peters. 1980. "A Model of Carbon Monoxide-Methane Global Transport Chemistry I. Chemistry." Taiki Osen Gakkaish: 15(3):91-108.

Kocher, D. C. 1979. A Dynamic Model of the Global Iodine Cycle for Estimation of Dose to the World Population from Releases of Iodine-129 to the Environment. NUREG/CR-0717, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Korzh, V. D. 1984. "Ocean as a Source of Atmospheric Iodine." Atm. Environment 18:(12):2707-10.

Krauskopf, K. B. 1979. Introduction to Geochemistry. 2nd Edition, McGraw-Hill, New York.

Laksonen, J. W., W. H. Kirby, and C. E. Dryden. 1962. "Iodine Vapor-Silver Nitrate Reaction Mechanisms and Phase Equilibria." TID-16914.

Lapple, C. E. 1949. 200 Area-Dissolver Off-Gases. HDC-969, Hanford Atomic Products Operation, Richland, Washington.

36,37 Leader, G. L. 1946. Fission Product Studies with Plant Dissolver
38 Solutions. HW-3-3365, Hanford Atomic Products Operation, Richland, Washington.

Lin, Chien-Chang. 1981. "Volatility of Iodine in Dilute Aqueous Solutions." J. Inorg. Nuc]. Chem. 43(12):3229-3238.

Lyon, A. M. 1949. Results of I-131 Tests of Laboratory Scale Silver Nitrate Absorber. GEH-15058, Air Reduction Sales Company, Murray Hill, New Jersey.

MacCready, W. K. 1948. Stack Gas Decontamination. HW-9180, Hanford Atomic Products Operation, Richland, Washington.

Marter, W. L. 1963. "Radioiodine Release Incident at the Savannah River Plant." Health Physics 9(12):1105-1109.

McEwan, M. J., and L. F. Phillips. 1975. Chemistry of the Atmosphere. Wiley, New York.

McKellar, J. F., and R. G. W. Norrish. 1961. "The Combustion of Gaseous Methyl Iodide Studied by Flash Photolysis and Kinetic Spectroscopy." Proc. Royal Soc. of London Ser. A 263(1312):51-57.

Michel, R. L., and H. E. Suess. 1975. "Bomb Tritium in the Pacific Ocean." J. Geophys. Res. 80(30):4139-4152.

47 Michels, L. R., and L. L. Zahn. 1955. Nitric Acid Recovery and Iodine Removal from Purex Dissolver Off-Gas. HW-40238, General Electric Company, Richland, Washington.

Mishima, J. 1966. Review of Methyl Iodide Behavior in Systems Containing Airborne Radioiodine. BNWL-319, Pacific Northwest Laboratory, Richland, Washington.

Miyake, Y., and S. Tsunogai. 1963. "Evaporation of Iodine from the Ocean." J. Geophys. Res. 68(13):3989-93.

Morgan, K. J. 1954. "Some Reactions of Inorganic Iodine Compounds." Quarterly Reviews 8(2):123-146.

Moyers, J. L., and R. A. Duce. 1972. "Gaseous and Particulate Iodine in the Marine Atmosphere." J. Geophys. Res. 77(27):5229-5238.

Paquette, J., et al. 1983. "The Chemistry of Iodine and Cesium under Reactor Accident Conditions." In Water Chemistry of Nuclear Reactor Systems 3, pp. 71-79. British Nuclear Energy Society, London.

Paquette, J., D. J. Wren, and B. L. Ford. 1985. "Iodine Chemistry." ACS Symposium Series, #293, The TMI Accident: Diagnosis and Prognosis, pp. 193-210. American Chemical Society, Washington, D.C.

Paquette, J., and B. L. Ford. 1985. "Iodine Chemistry in the +1 Oxidation State. I. The Electronic Spectra of OI^- , HOI , and H_2OI^+ ." Can. J. Chem. 63(9):2444-2448.

Parker, H. M. 1945. Xenon and Iodine Concentrations in the Environs of the T and B Plant. HW-7-3005del, Hanford Works, Richland, Washington.

- Parker, H. M. 1948a. Review of the Stack Discharge Active Particle Contamination Problem. HW-9259, Hanford Atomic Products Operation, Richland, Washington.
- Parker, H. M. 1948b. Health Instrument Division Report For The Month of April 1948. HW-9922-K, Hanford Atomic Products Operation, Richland, Washington.
- Parker, H. M. 1948c. Effect of Dissolver Off-Gas Scrubbers on Required Cooling Time. HW-10568, Hanford Atomic Products Operation, Richland, Washington.
- Parker, H. M. 1949. Health Instruments Division Report for the Month of January 1949. HW-12391-E, Hanford Atomic Products Operation, Richland, Washington.
- Parker, H. M. 1955. Letter to J.E.Maider, "Current Views on the I-131 Emission Limits". April 4. HW-36207, Hanford Atomic Products Operation, Richland, Washington.
- Parsly, L. F. 1971. Chemical and Physical Properties of Methyl Iodide and Its Occurrence Under Reactor Accident Conditions. ORNL-NSIC-82, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- Patil, K. C., et al. 1967. "The Silver Nitrate-Iodine Reaction: Iodine Nitrate as a Reaction Intermediate." J. Inorg. Nucl. Chem. 29(2):407-412.
- Perkins, R. W. 1964. "Physical and Chemical Forms of I-131 from Fallout and Chemical Processing Plants." In Hanford Radiological Sciences Research and Development Annual Report for 1963, pp. 3.55-3.58. HW-81746, Hanford Atomic Products Operation, Richland, Washington.
- PUREX Technical Manual. 1955. HW-31000-De1, Hanford Atomic Products Operation, Richland, Washington.
- Raab, G. J., and R. E. Van derCook. 1970. Operating Experience Using Silver Reactors for Radioiodine Removal in the Hanford PUREX Plant. ARH-SA-67, Atlantic Richfield Hanford Company, Richland, Washington.
- Rahn, K. A., R. D. Borys, and R. A. Duce. 1976. "Tropospheric Halogen Gases: Inorganic and Organic Components." Science 192(4239):549-550.
- Rasmussen, R. A., et al. 1982. "Atmospheric Methyl Iodide (CH₃I)." J. Geophys. Res. 87(C.4):3086-90.
- Roberts, R. E. 1958. History of Airborne Contamination and Control--200 Areas. HW-55569 RD, Hanford Atomic Products Operation, Richland, Washington.
- Sakurai, T., et al. 1989. "The Behavior of Iodine in a Simulated Spent-Fuel Solution." Nuclear Technology 85(2):206-212.

Scheele, R. D., L. L. Burger, and C. L. Matsuzaki. 1983. Methyl Iodide Sorption by Reduced Silver Mordenite. PNL-4489, Pacific Northwest Laboratory, Richland, Washington.

Scheele, R. D., L. L. Burger, and J. K. Soldat. 1984. The Adequacy of Radioiodine Control and Monitoring at Nuclear Fuels Reprocessing Plants. PNL-5108, Pacific Northwest Laboratory, Richland, Washington.

Schmidt, W. C. 1957. Treatment of Gaseous Effluents. HW-49549, Hanford Atomic Products Operation, Richland, Washington.

Seyfrit, K. V. 1957. The Removal of Iodine from Dissolver Off-Gas by Caustic Scrubbing. HW-50259, Hanford Atomic Products Operation, Richland, Washington.

Sigalla, J., and C. Herbo. 1957. "Cin tique et Mechanisme de l'Oxydation de l'Iodure par l'Oxygene Dissous." J. Chim. Phys. 54(10):733-38.

Smith, R. E. 1955a. Iodine Emission from Separations Processes and Flowsheets for Improved Emission Control. HW-36819, Hanford Atomic Products Operation, Richland, Washington.

Smith, R. E. 1955b. Flowsheets for Iodine 131 Emission Control at 1961 Power and Enrichment Levels. HW-39261, Hanford Atomic Products Operation, Richland, Washington.

Smith, S. R. 1968. "Suppression of Radioiodine Releases from a Radiochemical Separations Plant." Nuclear Applications 5(1):20-23.

Soldat, J. K., et al. 1973. The Radioecology of Iodine-129: An Interim Report. BNWL-1783, Pacific Northwest Laboratory, Richland, Washington.

Soldat, J. K. 1976. "Radiation Doses from Iodine-129 in the Environment." Health Physics 30(1):61-70.

Soule, H. F., and R. E. Taylor. 1953. Review of Silver Reactor Performance in the Separation Facilities. HW-27580, Hanford Atomic Products Operation, Richland, Washington.

Strachen, D. M. 1978. Analysis of the Dissolver Silver Reactors from Hanford's PUREX Plant. RHO-ST-2, Rockwell Hanford Operations, Richland, Washington.

Swanson, J. L. 1978. Control of Radioiodine in the Excess Water Stream of a Nuclear Fuels Reprocessing Plant. PNL-2080-9, Pacific Northwest Laboratory, Richland, Washington.

Szulinski, M. J. 1950. Elimination of Iodine from Canyon Building Exhaust Air. HW-19609, Hanford Atomic Products Operation, Richland, Washington.

Tang, I. N., and A. W. Castleman, Jr. 1968. Radiation Induced Decomposition of Methyl Iodide in Air. BNL-12219, Brookhaven National Laboratory, Upton, New York.

Tang, I. N., and A. W. Castleman, Jr. 1970. "Kinetics of τ -induced Decomposition of Methyl Iodide in Air." J. Phys. Chem. 74(22):3933-39.

Thompson, G. H., and J. A. Kelley. 1975. Evaluation of Methods for Retention of Radioiodine During Processing of Irradiated Np-237. DP-1373, E.I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, South Carolina.

Voilleque, P. G. 1979. Iodine Species in Reactor Effluents and in the Environment. EPRI-NP-1269, Electric Power Research Institute, Palo Alto, California.

12 Walker, F. W., G. J. Kirovac, and F. M. Rourke. 1977. Chart of the Nuclides. General Electric Company, Schenectady, New York.

Warren, J. H. 1961. Control of I-131 Releases to Atmosphere. HW-68392, Hanford Atomic Products Operation, Richland, Washington.

Wilhelm, J. G., and J. Furrer. 1978. Iodine Separation in Reprocessing Plants. BNWL-TR-312.

Work, J. B. 1946. Disposal of Separation Plant Off-Gases. HW-7-5520-Del, Hanford Atomic Products Operation, Richland, Washington.

Work, J. B. 1947. "Radioiodine Deposition From Stack Gases." Letter to L. R. Koller (Schenectady, NY). HW-7-6280, Hanford Atomic Products Operation, Richland, Washington.

Work, J. B. 1948. "Stack Gas Problem." Letter to L.I. Gilbertson. HW-9167, Hanford Atomic Products Operation, Richland, Washington.

Work, J. B. 1951. Efficiency Evaluation of the Dissolver Cell Silver Reactor and Fiber Glass Filter. HW-19898, Hanford Atomic Products Operation, Richland, Washington.

Wren, D. J., and J. Paquette. 1985. The Kinetics of Iodine Release from Aqueous Solution. AERE-R-11974. OECD Workshop on the Chemistry of Iodine in Reactor Safety, Harwell, Berkshire, UK, pp. 63-89.

Zafirou, O. C. 1974. "Photochemistry of Halogens in the Marine Atmosphere." J. Geophys. Res. 79(18):2730-32.

Zahn, L. L. 1953a. Comparative Study of Alternative Fibrous Glass and Sand Exhaust Ventilation Air Filter Installations for PUREX. HW-30142, Hanford Atomic Products Operation, Richland, Washington.

Zahn, L. L. 1953b. Review of Exhaust Ventilation Air Filtration Requirements for PUREX. HW-30337, Hanford Atomic Products Operation, Richland, Washington.

APPENDIX

SUMMARY OF TSP COMMENTS AND BATTELLE RESPONSES

APPENDIX

Page 1 of 8

SUMMARY OF TSP COMMENTS AND BATTELLE RESPONSES

Document Number PNL-7210 HEDRDocument Title Fission-Product Iodine During Early Hanford-Site Operations:
Its Production and Behavior During Fuel Processing, Off-Gas
Treatment, and Release to the Atmosphere

Comment Number	Commenter	Page, Paragraph	Comment Summary	Resolution
1.	D. Barth		Add section summarizing specific assumptions made for Phase I, including possible uncertainties inherent in acceptance of assumptions.	NA - There are no assumptions used in this report.
2.	K. Garlid		Eliminate all comments that defend the "establishment."	Done (see page 17).
3.	G.S. Roessler	Page v, para. 2, line 1	Identify contribution of fission-product iodine to the total release, to support statement that quantity released is not subject of report.	NA - This would not add enough to the report to justify the required effort. Each process, at a multitude of times, would have to be considered. It would be a lengthy undertaking.
4.	GSR	Page v, para. 4, line 1	Is there a reference for this statement?	Replaced paragraph with additional information and included reference.
5.	GSR	Page 8, para. 6, last sentence	Why was it shut down in 1972?	Addressed in text.
6.	GSR	Page 16 para. 2, line 1	How was the burst of iodine measured?	Addressed in text.
NA = No action.				

A.1

SUMMARY OF TSP COMMENTS AND BATTELLE RESPONSES

Document Number PNL-7210 HEDRDocument Title Fission-Product Iodine During Early Hanford-Site Operations:
Its Production and Behavior During Fuel Processing, Off-Gas
Treatment, and Release to the Atmosphere

Comment Number	Commenter	Page, Paragraph	Comment Summary	Resolution
7.	GSR	Page 17, para. 2, line 5	Eliminate "It may be mentioned at this point that..."	Phrase was deleted.
8.	GSR	Page 18, para. 3, line 1	"Holm's study was thorough and a significant contribution" doesn't sound like an objective comment.	Sentence was revised.
9.	GSR	Page 30, last para., line 1	Valid comment, but these uncertainties will cast doubt on final numbers unless monitoring data support calculations.	NA - Future work.
10.	G. G. Caldwell	Page 1, para. 3, line 2-5	What is the documentation for the statement, "designers were concerned about controlling iodine..."? Their actions did not show it.	Paragraph was rewritten.
11.	GGC	Page 3, para. 2, line 5-6	1% of what -- iodine-131?	Sentence was clarified.
12.	GGC	Page 5, para. 1, lines 3-4	2.9% of what -- xenon, iodine-131?	Sentence was rewritten.
13.	GGC	Page 19, para. 3, line 2	What do "it" and "its" refer to -- Hanford Plant management and mercuric nitrate?	Sentence was revised.
NA = No action.				

SUMMARY OF TSP COMMENTS AND BATTELLE RESPONSES

Document Number PNL-7210 HEDRDocument Title Fission-Product Iodine During Early Hanford-Site Operations:
Its Production and Behavior During Fuel Processing, Off-Gas
Treatment, and Release to the Atmosphere

Comment Number	Commenter	Page, Paragraph	Comment Summary	Resolution
14.	GGC	Page 37, para. 3, line 4	Change "few" to a specific number or range.	Replaced "few centimeters" (the term used by Brauer) with "2.5 cm" (used by Soldat et al.); added reference.
15.	Mary Lou Blazek	Section 3.1	What is "adequate" in the sentence "After the first year of operation, however, tests showed that it was adequate to operate them [fans] singly except when two dissolvers were being used simultaneously ..."?	Sentence was rewritten.
16.	MLB	Section 3.1	What tests were done to show adequacy [of operating fans singly]?	See comment number 15.
17.	MLB	Section 3.1	Are records available to show patterns of fan use? Do records show that both fans were indeed used when two dissolvers were used simultaneously?	See comment number 15. General policy is stated in report; there may be no detailed records.
18.	MLB		Will Battelle use an estimate of, or change in, source term to account for changes in, or inadequate use of, ventilation systems?	NA - Not a subject for this report. Future work?
19.	M. Robkin	Page 38	If molecular iodine is rapidly converted to other forms in times short compared to atmospheric transport items, is this taken into account in the HEDR calculations in setting a value for the	NA - Future work.
NA = No action.				

APPENDIX

Page 4 of 8

SUMMARY OF TSP COMMENTS AND BATTELLE RESPONSES

Document Number PNL-7210 HEDRDocument Title Fission-Product Iodine During Early Hanford-Site Operations:
Its Production and Behavior During Fuel Processing, Off-Gas
Treatment, and Release to the Atmosphere

Comment Number	Commenter	Page, Paragraph	Comment Summary	Resolution
20.	B. Shleien	Page v, para. 4	deposition velocity, retention on plants, weathering, transfer from ingestion by the cow into milk, etc.? Statement "It was known before Hanford Site operations iodine control would be important" is true, but designed to arouse opposition and ire.	See comment number 4.
21.	BS	Page vi, para. 3	Provide dates with values for iodine release fraction and for introduction of sand filter and silver reactors. Provide reasons for air sparging, because it increased airborne releases.	Done; paragraph was rewritten.
22.	BS	Page vii	Why is presence of stable iodine mentioned -- because of release of stable iodine in press?	Done; new text was added.
23.	BS	Page 1, para 3, last line	It is controversial whether or not the early processing of fuel was "designed and operated" to reduce iodine releases, even though dilution was maximized.	See comment number 10.
24.	BS	Page 7, Section 3.1, para. 2	Typo: "inleakage"	Corrected.
25.	BS	Page B, para 2, line 1	Typo: "identified"	Corrected.
NA - No action.				

A.4

SUMMARY OF TSP COMMENTS AND BATTELLE RESPONSES

Document Number PNL-7210 HEDRDocument Title Fission-Product Iodine During Early Hanford-Site Operations:
Its Production and Behavior During Fuel Processing, Off-Gas
Treatment, and Release to the Atmosphere

Comment Number	Commenter	Page, Paragraph	Comment Summary	Resolution
26.	BS	Pages 17, 18	When did air sparging begin?	Air sparging, including its start date, is discussed on p. 18 and mentioned again on p. 23.
27.	BS	Pages 17, 18	Which release factors will be used for the source term in the early years -- 50, 60-65, or 85%? Will all be used depending on the period?	NA - Future work.
28.	BS	Page 22, para. 2	Object to tone of "no fuel processed until radioactive decay had eliminated most of the I-131." Instead, state quantity of iodine-131 that decays relative to remaining amount.	New sentence was added.
29.	A. Slickpoo		Is iodine (as opposed to other radioactive elements) the only hazard to human life?	NA - Other airborne radionuclides will be investigated later in the project.
30.	J.E. Till		Report gives impression that iodine is our only focus. Much literature on iodine not referenced here, especially in environmental chemistry, e.g., 1) Hoffman at ORNL investigating pasture grass interception and retention of iodine-131 and 2) Chernobyl data. Only nine pages here on environmental behavior, and mostly global transport rather than near-field deposition. This information is critical to the prediction of transport and deposition. Does another HEDR report address environmental behavior of iodine in more depth?	NA - Future work.
NA = No action.				

SUMMARY OF TSP COMMENTS AND BATTELLE RESPONSES

Document Number PNL-7210 HEDRDocument Title Fission-Product Iodine During Early Hanford-Site Operations:
Its Production and Behavior During Fuel Processing, Off-Gas
Treatment, and Release to the Atmosphere

Comment Number	Commenter	Page, Paragraph	Comment Summary	Resolution
31.	JET	Page v, para. 4, 2nd sentence	Delete sentence. Iodine-131 control may have been considered, but was obviously not practiced.	Paragraph was rewritten (see comment number 4). Iodine control was practiced.
32.	JET	Page vii, last sentence	" <u>Stable</u> iodine is also a normal ..."	Sentence was revised. (See comment number 22.)
33.	JET	Page 1, last para., 1st line	Iodine is near the top of the right peak of the fission yield curve. I have never heard this distribution called the element stability curve. Add reference and fission yields for Hanford reactors.	Sentence was revised.
34.	JET	Page 1, para. 3, 3rd line	Reference this: "... processing plant designers were concerned ..."	Paragraph was rewritten.
35.	JET	Page 2, para. 3	Specify which reports will quantify release of iodine for the Phase I study -- Milestone 03-E?	NA - It will be addressed in the FY 1991 Milestone 0302A, "Documented Phase I iodine-131 releases."
NA = No action.				

SUMMARY OF TSP COMMENTS AND BATTELLE RESPONSES

Document Number PNL-7210 HEDRDocument Title Fission-Product Iodine During Early Hanford-Site Operations:
Its Production and Behavior During Fuel Processing, Off-Gas
Treatment, and Release to the Atmosphere

Comment Number	Commenter	Page, Paragraph	Comment Summary	Resolution
36.	JET	Page 3, para. 2, 2nd sentence	Explain "some concern."	Text was revised.
37.	JET	Page 3, para. 2, penultimate sentence	Reference past lack of knowledge about iodine-129 half-life.	Text was revised.
38.	JET	Page 3, para. 2, lines 6-7	"Because of the small amount produced ..." Reference or indicate it's an assumption.	Text was revised.
39.	JET	Page 8, para. 6, last sentence	How many is "several" years?	Addressed in text. (See comment number 5.)
40.	JET	Page 11	Reference info on dissolving operations.	Reference was added.
41.	JET	Page 16, para. 3, 3rd line	Add references to support statement that higher-than-expected releases were observed.	Reference was added.
42.	JET	Page 18, para. 3, line 6	State date of January 1951, as shown on Page 23. Did sparging begin in both T and B Plants in January 1951? Answer here and on page 23.	Changes were made on pages 18 and 23. (See comment number 26.)
NA = No action.				

SUMMARY OF TSP COMMENTS AND BATTELLE RESPONSES

Document Number PNL-7210 HEDRDocument Title Fission-Product Iodine During Early Hanford-Site Operations:
Its Production and Behavior During Fuel Processing, Off-Gas
Treatment, and Release to the Atmosphere

Comment Number	Commenter	Page, Paragraph	Comment Summary	Resolution
43.	JET	Page 18, para. 2, line 7	How much increase was observed for a 5-degree increase in temperature?	Sentence was revised.
44.	JET	Page 20, para. 3, last sentence	Further discuss Haller and Perkins data.	NA - Future work.
45.	JET	Page 21, 3rd sentence	Specify the radionuclides detected in particulate form.	Sentence was added.
46.	JET	Page 25, Table 1	Put data into graph (cooling time vs. filter efficiency).	NA
47.	JET	Page 27, para. 1	"After regeneration the removal efficiency ..." How long did beds last? What was minimum efficiency? Show data to support the statement, "...and in later years even lower efficiencies were often noted." Identify efficiency to be used as a function of time.	Text was revised.
48.	JET		Add conclusion.	NA - Conclusion not necessary for this report - see Summary for an overview of the work described in this report.
NA = No action.				