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Pacific Northwest
National Laboratory
Operated by Battelle for the
U.S. Department of Energy

HWVP Iodine Trap Evaluation

L. L. Burger
R. D. Scheele

September 2004

Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RL01830

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Summary

This report details our assessment of the chemistry of the planned Hanford Waste Vitrification Plant (HWVP) off-gas system and its impact on the applicability of known iodine removal and control methods. To predict the gaseous species in the off-gas system, we completed thermodynamic calculations to determine theoretical equilibrium concentrations of the various potential chemical species. In addition, we found that HWVP pilot-plant experiments were generally consistent with the known chemistry of the individual elements present in the off gas.

Of the known trapping techniques for radioiodine, caustic scrubbing and silver-containing sorbents are, in our opinion, the most attractive methods to reduce the iodine concentration in the HWVP melter off gas (MOG) after it has passed through the high-efficiency particulate air (HEPA) filter. These two methods were selected because they 1) have demonstrated retention factors (RFs), ratio of amount in and amount out, of 10 to 1000, which would be sufficient to reduce the iodine concentration in the MOG to below regulatory limits; 2) are simple to apply; 3) are resistant to oxidizing gases such as NO_x; 4) do not employ highly hazardous or highly corrosive agents; 5) require containment vessels constructed of common materials; 6) have received extensive laboratory development; 7) and the radioactive wastes produced should be easy to handle.

On the basis of iodine trapping efficiency, simplicity of operation, and waste management, silver sorbents are superior to caustic scrubbing, and, of these sorbents, we prefer the silver zeolites. No method has been fully demonstrated, from laboratory-scale through pilot-plant testing, to be an effective iodine trap at the low iodine concentration (2×10^{-11} mol I/L) expected in the MOG of the HWVP in the presence of the other gaseous off gas components.

In terms of compatibility of the trapping technology with the components in the MOG, there is some question about the resistance of the silver zeolites' aluminosilicate matrix to the fluoride component in the off gas. The caustic scrubber has no compatibility problems with the MOG off gas; however, the acidic components such as CO_2 will increase the volume of waste produced and could affect the efficiency of the iodine trapping.

To apply these gaseous iodine trapping technologies to the HWVP, further development work would be required. Neither method has been demonstrated at the very low iodine concentrations that exist in the off gas, which are 0.01% to 1% of that found in nuclear fuel dissolver off gases for which these technologies were developed. Furthermore, the large excess of other reactive and trappable gases in

the HWVP off gas imposes a heavy load on the trapping medium, could impede iodine trapping, and could have deleterious effects on the trapping medium itself.

For silver zeolites, other trappable gases such as chlorine, which are in gross excess of the iodine in the off gas, will compete for the active sites in the silver zeolite. In applying a silver zeolite to the HWVP, 99.9% of the silver would be used to trap chlorine with less than 0.1% of the silver employed in the zeolite bed used for iodine trapping. It is also difficult to predict what will happen when the aluminosilicate framework of the zeolite is exposed to the reactive gas, HF, which is also present in the off gas and is known to attack silicates.

In the case of caustic scrubbing, because of the low iodine concentration in the off gas essentially all of the caustic will be used for CO_2 removal, a small fraction for chlorine and fluorine removal, and a trace amount for iodine removal. NO_x, which should exist largely as NO, will not be removed.

To answer questions about the effects of other trappable and reactive gases and to complete the development of this technology for application in the HWVP, an experimental testing program using gas compositions typical of the HWVP off gas will be required. For the caustic method, the efficiency at the low iodine concentration must be determined to permit design of the countercurrent column or other scrubbing device. For silver zeolite, the bed and operating parameters, such as particle size, depth, face velocity, temperature, exposure time, etc. must be studied to determine the real effect of the thousand-fold excess of other halogens.

From a regulatory standpoint, it should be noted that the predicted iodine concentration in the gas leaving the high-efficiency mist eliminator (HEME) is only 20 times the limit shown in Table 2 of 10 CFR 20 for release to an uncontrolled area, and is a factor of 5 less than can be released to a controlled (restricted) area. Thus, there is not a regulatory requirement to treat the MOG and reduce the ^{129}I concentration further to allow release of the gases to a controlled area. We expect that the HWVP will be located in a controlled area. In addition, after the MOG is mixed with the plant vent off gases (a dilution factor of 250), there would not be a regulatory requirement for additional iodine abatement to allow release to an uncontrolled area. It should also be noted that the estimated iodine concentrations at the HEME exit assumed no iodine retention in the MOG process steps. Real iodine concentrations are expected to be lower.

A further consideration is that application of iodine trapping technology to the HWVP will produce a concentrated ^{129}I form that could be a more hazardous radioactive waste than the gas stream itself. In addition, the wastes produced would be mixed hazardous and radioactive wastes because of the high pH for the spent caustic solution and the silver in the silver sorbents.

For both caustic scrubbing and silver zeolites, no known secondary wastes would be produced.

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1.0 Introduction

(Note: This report was originally issued in December 1991 with limited distribution to a restricted number of readers at the request of the Hanford Waste Vitrification Plant (HWVP) project office. The HWVP has been terminated, however, and the report is now being released with no restrictions because of interest by the U.S. Department of Energy and its contractors. As Hanford wastes are converted to stable disposal forms, such as glass, which require high-temperature processing, controlling semi-volatile radioiodine to prevent its environmental release is again of concern. We are releasing the document to support efforts to dispose of Hanford radioactive wastes.)

Westinghouse Hanford Company (Westinghouse) is considering the inclusion of a radioiodine abatement facility as part of their design effort for the Hanford Waste Vitrification Plant (HWVP). Westinghouse requested that the Pacific Northwest Laboratory (PNL)(a) evaluate, based on information in the open literature, available radioiodine control technologies and their applicability to the HWVP.

Based on the expected iodine content of the HWVP feed, the expected iodine concentration in the melter off-gas (MOG) stream will be quite low, only a factor of 5 higher than allowable release levels for an uncontrolled area (10 CFR 20). It is nonetheless desirable to examine the options and assess their impact on HWVP operation.

R. W. Goles of PNL identified the following questions as necessary to assess the iodine control options and their impact on HWVP operation:

1. Which of the demonstrated ^{129}I process treatment technologies are compatible with the composition of HWVP process exhaust?
2. How effective will the compatible technologies be?
3. Are abatement methods proven under conditions reasonably similar to those associated with HWVP, and if not, what development effort would be required to adapt the technology and verify its suitability?
4. What are the nature and approximate generation rates of secondary wastes produced by the various compatible technologies under reference process conditions?

(a) Pacific Northwest National Laboratory is operated by Battelle for the U.S. Department of Energy under Contract DE-AC06-76RL01830.

In examining these issues, this report reviews the chemistry involved in the MOG and gas treatment components, reviews the known gaseous iodine trapping and control technologies, and discusses the potential application of viable concepts and any necessary development effort for each option.

2.0 Regulatory Requirements for Iodine Control

The regulations governing radioiodine control for the nuclear industry have been published in the Code of Federal Regulations (CFR) (10 CFR 20). The U.S. Nuclear Regulatory Commission's (NRC) published concentration limits for release of ^{129}I to the environment are for soluble iodine at 2×10^{-9} mCi/L (9×10^{-11} mol/L) and 2×10^{-11} mCi/L (9×10^{-13} mol/L) for a controlled (limited access) area and uncontrolled (nonrestricted) area, respectively. For insoluble iodine the limits are less restrictive-- 3.1×10^{-9} mol/L and 9×10^{-11} mol/L, respectively.

In addition, the U.S. Environmental Protection Agency (EPA) has placed limits on total releases from the Light Water Reactor (LWR) fuel cycle (40 CFR 190). For ^{129}I the limit is 5 mCi/$GW_{(e)}$-yr (e.g., for a typical LWR and associated reprocessing facilities).

Iodine-129 comprises about 80% of the fission product iodine. Thus, the permitted release from the HWVP may be a factor of 1.25 above the molar concentration limits.

3.0 HWVP Design

Figure 1 shows the proposed HWVP flowsheet. The principal components affecting iodine control are the melter, the film cooler, the submerged bed scrubber (SBS), the high-efficiency mist eliminator (HEME), and the high-efficiency particulate air (HEPA) filter.

The film cooler will reduce the temperature of the vapors released from the melter before they enter the SBS, while maintaining a high linear gas velocity to prevent deposition of condensed matter. The SBS is an aqueous-based scrubber which will remove bulk quantities of particulates, condensibles, and soluble gases. The HEME will remove any mist that leaves the SBS. The gases are heated before passing through a roughing filter and a HEPA filter. The HEPA filter will remove any remaining particulates. If an iodine removal system is used, current plans call for inserting it after the HEPA filter. A catalytic NO_X reducing system, if needed, completes the gas treatment system.

The pertinent design data given in Table 1 for the off gas system are taken from the Preliminary Safety Analysis Report (PSAR) (1990) and the HWVP Technical Data Package (HWVP TDP) (1990).

The chemical composition range for the HWVP reference feed is given in Table 2. This table identifies the composition limits for the feeds derived from double-shell tank wastes, such as neutralized current acid wastes (NCAW), complex concentrate waste (CCW), etc. Table 3 lists the reference composition. Table 4 lists the radioactive components. Data for these tables are from the TDP.

The waste oxides make up about 25 wt% of the feed solids or total oxides. The remaining 75 wt% is mostly borosilicate glass frit.

Using data from Tables 1 through 4, the probable MOG compositions were calculated by the authors and are listed in Table 5. If all of the potentially volatile components escape, the MOG will be of the composition presented in column 1 of the table. Assuming the recommended retention factor (RF) values, the ratio of the amount entering to the amount exiting [as taken

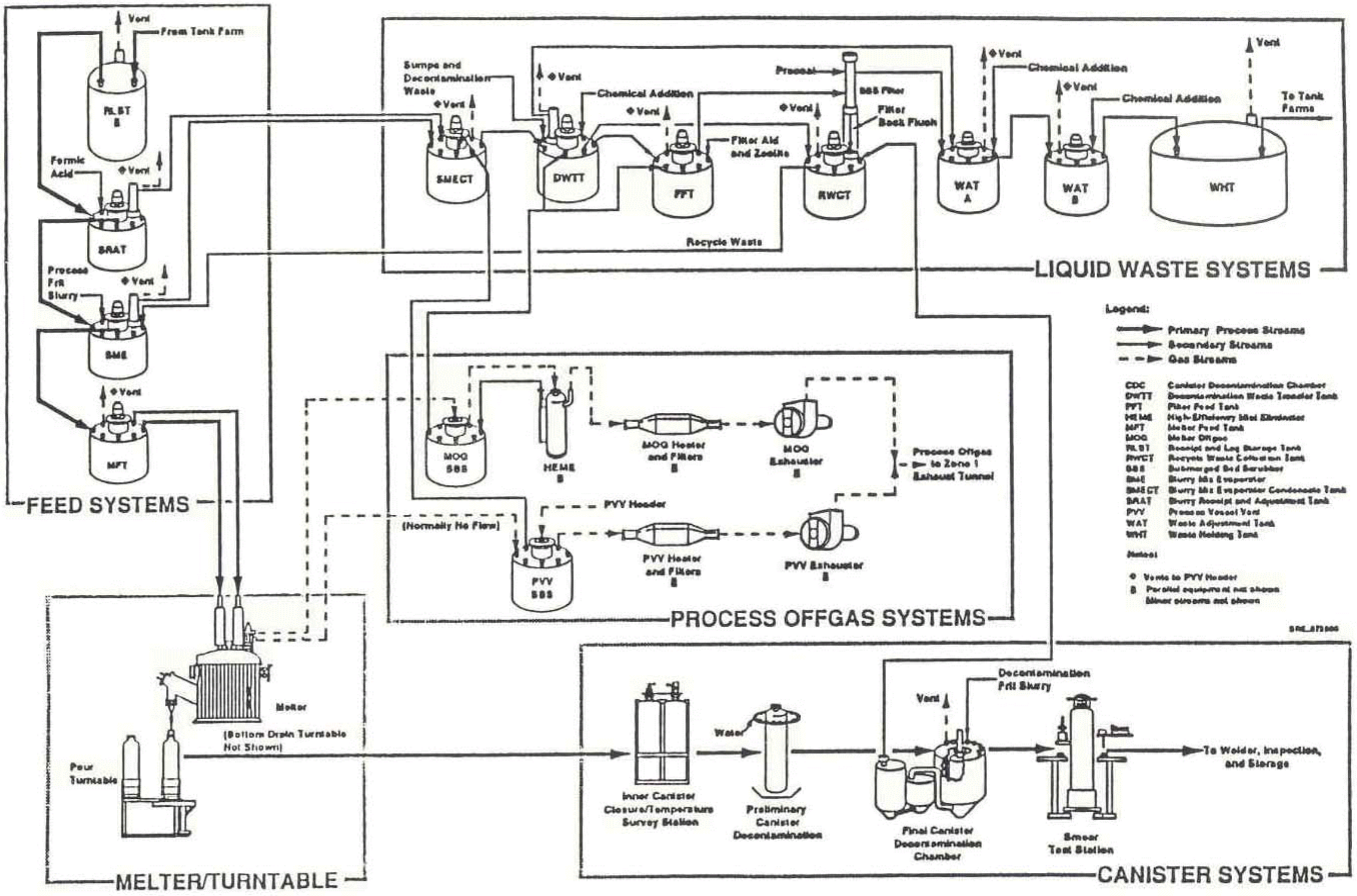

Figure 1. Hanford Waste Vitrification Plant

Table 1. HWVP Design Data Pertinent to Gas Scrubbing(a,b)

Design Parameter	Level
Feed Rate to melter	3.3 L/min
Glass Temperature	1050 to 1170EC
Melter Plenum Temperature	650 to 1150EC
Plenum Volume	2230 L
Flow Rate from Plenum, MOG	5820 L/min
Flow Rate to SBS	13870 L/min
Flow Rate to HEME	12600 L/min
Feed Water Content	800 g/L
Feed Solids Oxide Basis Content	400 to 600 g/L
Approximate Gas Composition, MOG	
H_2O	0.55 mol fraction
O_2	0.086
N_2	0.345
CO_2	0.011
NO_X	0.003
Quenched off-gas temperature	50EC
HEME Packing	Glass Fiber

(a) All gas data at standard temperature and pressure (STP).

(b) Data from *HWVP Technical Data Package (TDP)*, WHC-SD-NWV-DP-001, Rev 5; and *Preliminary Safety Analysis Report Rev B (PSAR)*, WHC-EP-0250, July 1990.

from the *Melter Pilot Scale Test Report* by Goles et al. (1989)], the MOG will be of the composition presented in column 2.

Section 5 provides a thermodynamic consideration of the actual chemical species judged to be present at each point in the process. Gaseous residence times at the various conditions, i.e., reaction kinetics, may drastically affect some of the computed (equilibrium) concentrations.

Table 2. Chemical Compositional Range for the HWVP Reference Feed (TDP)

Chemical Compositional Range Limits (oxide basis)	Wt% of Total Nonvolatile Oxides	
	Minimum	Maximum
Al_2O_3	2.02	6.0
BaO	0.0	20.0
CaO	0.0	20.0
CdO	0.0	10.0
Fe_2O_3	8.0	60.0
$(La, Nd)_2O_3$	0.0	8.0
MnO_2	0.0	20.0
MoO_3	0.0	8.0
Na_2O	4.5	22.0
NiO	0.0	8.0
SiO_2	0.0	17.5
TiO_2	0.0	4.0
U_3O_8	0.0	32.0
ZrO_2	0.0	40.0
Cr_2O_3	0.0	2.0
Noble metals (PdO, Rh_2O_3, Ru_2O_3)	0.0	1.0
P_2O_5	0.0	4.0
SO_3	0.0	2.0
F	0.0	6.9
Fission product elements and minor components	0.0	5.0(a)

Volatile Components	Wt%	Total Waste Oxides
Cl	0.0	0.3
CO_3	2.4	30.0
NO_x (as NO_3)	0.0	36.0
TOC	0.0	11.0

Overall Waste Loading Limits		
g total nonvolatile oxides/L	18	100

(a) Maximum value for the sum of fission product elements and trace components is 5.0 wt%. Maximum wt% for individual fission products and trace components not shown individually above should be assumed to be equal to the nominal values given in Table 3 or converted from curie values given in Table 4, whichever is greater.

TOC = Total organic carbon.

Table 3. Nominal Chemical Composition for the HWVP Reference Feed (TDP 1990)

Nonvolatile Oxides(a)	Wt% Oxides	Nonvolatile Oxides(a)	Wt% Oxides
Ag_2O	1.0 E-02	MoO_3	1.2 E+00
As_2O_3	4.3 E-05	Na_2O	1.8 E+01
Al_2O_3	9.0 E+00	Nb_2O_3	1.0 E-02
Am_2O_3	2.0 E-02	Nd_2O_3	1.6 E+00
B_2O_3	1.0 E-01	NiO	2.3 E+00
BaO	4.0 E-01	NpO_2	1.0 E-01
BeO	1.0 E-01	P_2O_5	8.8 E-01
CaO	3.0 E-01	PbO_2	5.0 E-02
CdO	3.0 E+00	PdO	2.0 E-01
CeO_2	6.0 E-01	Pm_2O_3	1.0 E-01
Cr_2O_3	5.0 E-01	Pr_2O_3	4.0 E-01
Cs_2O	6.0 E-01	PuO_2	2.0 E-02
CuO	6.0 E-01	Rb_2O_3	2.0 E-01
Dy_2O_3	1.0 E-04	Rh_2O_3	2.0 E-01
Eu_2O_3	2.0 E-02	Ru_2O_3	6.0 E-01
F^-	1.2 E+00	SO_3	6.5 E-01
Fe_2O_3	2.8 E+01	Sb_2O_3	5.9 E-03
Gd_2O_3	1.0 E-02	SeO_2	3.0 E-02
GeO_2	1.6 E-04	SiO_2	4.0 E+00
Ho_2O_3	5.3 E-06	Sm_2O_3	2.0 E-01
I	4.5 E-06	SnO	4.0 E-02
In_2O_3	1.3 E-03	SrO	4.0 E-01
K_2O	5.0 E-02	Ta_2O_5	3.0 E-02
La_2O_3	2.9 E+00	Tb_2O_3	2.3 E-04
MgO	2.0 E-01	Tc_2O_7	4.0 E-01
MnO_2	6.0 E-01	TeO_2	1.0 E-01
TiO_2	1.0 E-02	Tm_2O_3	1.7 E-10
U_3O_8	4.7 E+00	Y_2O_3	2.0 E-01
ZrO_2	1.5 E+01		

Miscellaneous Feed Components

Volatiles	Wt% Oxides
NO_3^-	1.9 E+01
NO_2^-	2.4 E+00
Cl^-	3.0 E-01
OH_3^-	1.5 E+00
CO^{--}	1.7 E+01
TOC	2.0 E+00

(a) Listing of "nonvolatile components" includes semi-volatiles.

NOTE: Nominal overall waste loading of 0.031 kg nonvolatile oxides/L.

TOC = Total organic carbon.

Table 4. Nominal Radionuclide Composition for the HWVP Reference Feed (TDP 1990)

Isotope	Ci/gal	Isotope	Ci/gal	Isotope	Ci/gal
^{3}H	2.09 E-05	^{113}Sn	2.84 E-11	^{147}Pm	1.47 E+00
^{14}C	2.04 E-06	^{115m}Cd	9.03 E-22	^{148m}Pm	1.76 E-22
^{55}Fe	5.07 E-03	^{119m}Sn	1.92 E-06	^{151}Sm	1.97 E-01
^{59}Ni	3.08 E-05	^{121m}Sn	2.19 E-05	^{152}Eu	3.94 E-04
^{60}Co	4.24 E-04	^{123}Sn	1.03 E-08	^{153}Gd	3.81 E-09
^{63}Ni	3.42 E-03	^{126}Sn	1.03 E-04	^{154}Eu	4.09 E-02
^{79}Se	8.90 E-07	^{124}Sb	3.26 E-18	^{155}Eu	3.88 E-02
^{89}Sr	1.51 E-16	^{126}Sb	1.44 E-05	^{160}Tb	2.68 E-16
^{90}Sr	8.42 E+00	^{126m}Sb	1.03 E-04	^{234}U	1.29 E-06
^{90}Y	8.42 E+00	^{125}Sb	7.16 E-02	^{235}U	5.40 E-08
^{91}Y	3.91 E-14	^{125m}Te	1.75 E-02	^{236}U	1.19 E-07
^{93m}Nb	1.74 E-04	^{127}Te	1.85 E-09	^{238}U	9.91 E-07
^{93}Zr	2.96 E-04	^{127m}Te	1.88 E-09	^{237}Np	4.41 E-05
^{95}Zr	8.24 E-13	^{129}Te	8.86 E-27	^{238}Pu	1.25 E-04
^{95}Nb	1.90 E-12	^{129m}Te	1.36 E-26	^{239}Pu	3.31 E-04
^{99}Tc	2.12 E-03	^{129}I	3.64 E-09	^{240}Pu	1.11 E-04
^{103}Ru	9.51 E-22	^{134}Cs	2.63 E-02	^{241}Pu	3.55 E-03
^{103m}Rh	8.58 E-22	^{135}Cs	5.71 E-05	^{242}Pu	2.15 E-08
^{106}Ru	1.18 E-02	^{137}Cs	1.02 E+01	^{241}Am	8.02 E-02
^{106}Rh	1.18 E-02	^{137m}Ba	9.61 E+00	^{242}Am	6.24 E-05
^{107}Pd	8.54 E-06	^{141}Ce	8.27 E-26	^{243}An	1.07 E-05
^{110m}Ag	6.26 E-07	^{144}Ce	2.26 E-02	^{242}Cm	5.14 E-05
^{113m}Cd	2.41 E-03	^{144}Pr	2.26 E-02	^{244}Cm	1.42 E-03
^{113m}In	2.84 E-11	^{144m}Pr	2.71 E-04		

Total Activity (Ci/gal) 3.89 E+01

Decay heat (w/gal) 1.09 E-01

NOTE: Radionuclide composition values given in this table are based on the "nominal" overall waste loading as defined by Table 3 (i.e., 0.031 kg nonvolatile oxides/L).

The RF achieved in the melter depends first on the volatility of the compounds, and second on the formation and stability of aerosols (particulates) of the different species. Although all the compounds in Table 4 have appreciable volatility, it is likely that the last six entries in the table

Table 5. Predicted Concentrations of Important Components in the Melter Off Gas

Component	Concentration, mol/L	
	No RF	With RF
Cl(a)	6.0 E-06	2.0 E-06
F	4.4 E-05	1.1 E-05
I	2.4 E-11	2.4 E-11
CO_3(b)	3.1 E-04	3.1 E-04
NO_x	2.5 E-04	2.5 E-04
SO_3	5.8 E-06	1.2 E-06
H_2O	2.5 E-02	2.5 E-02
P_2O_5	4.4 E-06	8.8 E-09
Sb_2O_5	1.4 E-08	2.8 E-11
Cs_2O(c)	7.4 E-07	5.3 E-08
H_3BO_3(d)	--	1.3 E-03
SeO_2	1.9 E-07	1.9 E-8
TeO_2	4.4 E-07	8.8 E-10

(a) Halogen content includes all compounds.
(b) Includes carbonate and TOC.
(c) Cs should be present as CsCl rather than Cs_2O. See text.
(d) Boron and silicon are present.

are carried in the off-gas stream largely as particulates as the gases cool. The appreciable temperature range (see Table 1) of the melter will also affect the volatility of the different species.

Based on pilot-plant experience (Goles et al. 1989), a large fraction of both Si and B apparently exists as large particle aerosols that are rapidly deposited. For the other components, over one half of the aerosols have diameters of less than 1 μm (Goles et al. 1989). Particles, including fogs, with diameters of the order of 0.5 Fm or less are not efficiently removed by washing and a small fraction of these will pass through the SBS and the HEME filters. For example, it is known that SO_3 is very difficult to trap in H_2O in spite of its very high affinity for H_2O (Ephraim, Thorne and Roberts 1947). Details of aerosol carryover from pilot-plant experience are discussed in the melter test report (Goles et al. 1989).

Volatility of the compounds in the melt depends on more than just the relative vapor pressures of the pure chemical compounds; it depends also on miscibility in the melt and complex interactions among the dissolved species. It is therefore difficult at present to accurately predict the composition of the MOG because these interactions in the melt are not well understood.

4.0 Review of Gaseous Iodine Trapping Technologies

The pertinent work on gaseous radioiodine trapping has been done in support of nuclear fuel reprocessing. Several technologies have been developed for the removal of radioiodine from gaseous streams in a nuclear fuel reprocessing plant (NFRP). These have been reviewed in some detail in recent papers (Holladay 1979; MacKay, Miquel and White 1982; Brown, Christian, and Thomas 1983; Burger and Scheele 1983; Scheele, Burger, and Soldat 1984). The technologies fall into two basic groups, liquid scrubbers and solid absorbers. The following discussion briefly reviews the important features of each.

The Hanford PUREX (Plutonium-Uranium Extraction) silver reactor was a solid absorber employed primarily to retain ^{131}I long enough to permit its decay. It utilized beds of Berl saddles or other similar packing over which concentrated silver nitrate was poured and evaporated. It was operated at a temperature of around 190EC. Typically, a new bed achieved a RF of 1000, but over time an average of 100 was more realistic. In principle the device is simple and, aside from the cost of silver, inexpensive. In practice, operating problems existed, including difficulties with temperature control. Although the silver reactor could be regenerated with fresh silver nitrate solution, the reactor's efficiency tended to degenerate with each successive regeneration. The silver reactor has not been tested for ^{129}I control, long-term iodine retention, or under conditions expected with the HWVP.

The mercurex process is a liquid scrubber technology that uses mercuric nitrate-nitric acid scrubbing to complex the iodine and hold it in solution. If the nitric acid is greater than 8 M, then methyl iodide is removed in addition to elemental iodine, which is trapped effectively at lower nitric acid concentrations. The proposed treatment of the waste involved precipitation of mercuric iodate as a first step. However, no suitable method for handling the mixed radioactive and hazardous waste was ever developed. There is some question about the relative hazards of mercury and ^{129}I, and these potential hazards should be evaluated before the mercurex process is considered further for use in the HWVP. The process was tested at the Belgium Nuclear Research Center (Collard et al. 1980) and was planned for the Barnwell NFRP (Benedict, Pigford and Levi 1981).

Iodox is another liquid scrubbing method. It employs hyperazeotropic nitric acid (20 to 22 M), which oxidizes all iodine species to the iodate or to HI_3O_8, which can be recovered by evaporation of the nitric acid. The RFs obtained are high, 1000 to 10000, but the difficulty of working with the highly corrosive liquid has discouraged application. No large-scale testing has been done.

Another liquid scrubbing method, electrolytic scrubbing, employs chemical oxidation to accomplish the same result as the Iodox process, only this method uses an electrolytically generated oxidant such as Co(III). Very little development work was done with this method.

Organic liquids also have been proposed as scrubs because of iodine's high solubility in organic liquids. Organics ranging from fluorocarbons at low temperatures to tributyl phosphate at ambient temperatures have been suggested. The complexity of the systems, including recovery of the organic and disposal methods for iodine, apparently have made the methods unattractive.

Organic solids such as macroreticular resins have also been proposed as iodine sorbers. Most organic polymers have a high affinity for iodine, but the iodine is easily desorbed. In addition, waste treatment of radioactive organic materials is difficult. Neither organic liquids nor solids have been employed on a plant scale.

Carbon filters have been the standard method for gaseous iodine control in reactor containment systems. Various activated charcoals with and without additives such as KI, or organic amines to improve methyl iodide sorption, have been intensively studied for many years. We briefly discuss the method for the HWVP application because it is a developed technology and has been demonstrated to be effective at low iodine concentrations.

Unfortunately, there are serious problems with the application of carbon filter technology to the HWVP. Carbon filters work best when few impurities are present in the gas stream. They demonstrate loss of efficiency as a result of poisoning or aging brought on by a variety of compounds such as ozone or oxides of nitrogen. They are also subject to fires, including those caused by NO_2 absorption (Rodger and Reese 1969). For these reasons we believe carbon filters are not applicable to the HWVP.

Two developed or partially developed methods remain which do appear attractive and may provide the necessary iodine retention factor while still being compatible with the various constituents in the HWVP off gas requiring treatment. These are a liquid scrubber using sodium or potassium hydroxide (the caustic scrubber) and silver-containing sorbents. Silver-substituted zeolites and silver-nitrate-impregnated amorphous silica are best examples of the latter, and have been extensively investigated and demonstrated to be effective in laboratory- and pilot-scale experiments. Because of their potential for application in the HWVP, both the caustic scrubber and the silver-impregnated solids are discussed in more detail in Section 5.

5.0 Chemical Reactions

To determine which iodine control technology or technologies would be applicable to the HWVP, it is necessary to know the physical and chemical nature of the gas stream to be treated. To know the nature of the gas stream, it is necessary to know the reactions that occur in the melter, in the immediate off-gas system, and in the trapping systems under consideration.

The chemistry of the melter and the off-gas treatment systems determines the species for which the iodine trapping system must be designed. The chemistry of the gaseous species and the iodine trap will determine whether the trap is compatible with or resistant to the HWVP MOG, and will also determine the necessary design capacity. The following section discusses the predicted chemistry based on thermodynamic properties. The selection of elements for discussion was based on potential impact on iodine trapping, known volatility, and results from the pilot-plant melter test (Goles et al. 1989).

5.1 Thermodynamic Data and Chemical Reactions

To provide a basis for predicting the nature of the gas stream to be treated to remove the radioiodine released from the melter, Gibbs free energy (G) data for some 75 chemical species potentially involved in significant gaseous reactions have been compiled from Barin, Knacke, and Kubachewski (1973, 1977), from the National Bureau of Standards (NBS) (Wagman et al. 1982), and from Barin (1989). From these the free energies of the important reactions were calculated for temperatures between 298 and 1000K. These data are tabulated in the appendix of this report. Where pertinent, equilibrium constants and partial pressures were computed.

5.1.1 Melter, Melter Plenum, and Film Cooler Chemistry

The melter chemistry determines the nature of the compounds introduced into the MOG, and the melter plenum chemistry determines the nature of the species introduced into the MOG gaseous cleaning system. Although reducing agents (e.g., sugar, formic acid) are added to the melter feed, the off-gas conditions are oxidizing; NO_2 and excess air are present in the plenum at a temperature of about 700EC. The residence time in the plenum calculated from Table 1 data is about 25 seconds. Equilibrium should be reached with respect to the important species by the time the gases leave the plenum, and calculations show that the following compounds should predominate for each of the volatile elements:

<u>Chlorine</u>. Possible Cl species produced by the melter include HCl, Cl_2, NOCl, NO_2Cl, CsCl, and chloride aerosols. Hydrogen chloride is readily oxidized by O_2, HNO_3, and NO_2 at the temperatures involved (the Deacon Process). Oxygen from the air is expected to be the principal oxidant and the equilibrium

$$K = (Cl_2)(H_2O)/(HCl)^{1/2}(O_2)$$

would determine the HCl/Cl_2 ratio. At 1000K K is about 0.085, at 500K about 380, and at 400K about 1.26×10^4. Partial pressures of water and oxygen calculated from Table 1 are 0.55 and 0.086 atm, respectively. Thus, if the plenum vapors are acid, HCl would predominate at the high temperature, and as the vapor cools Cl_2 should form. The equilibrium is also concentration dependent, and at 400K about 90% should be Cl_2 if the Cl species are at 1×10^{-5} atm, but only 10% if the partial pressure is 1×10^{-7} atm. However, equilibrium is approached slowly at lower temperatures and it is possible that a large fraction of the chlorine will enter the SBS as HCl before it is oxidized.

In addition to HCl and Cl_2, both NOCl and NO_2Cl will be formed in the plenum. As the gas leaves the plenum and the temperature drops, NOCl is the more thermodynamically stable and at low oxygen concentrations NOCl would be the predominant species. However, in the oxygen-rich environment of the MOG, it should react with oxygen to form NO_2 and Cl_2 with a free energy of -3.62 kcal at 298K and -2.91 kcal at 500K. Since O_2 is present in great excess, and the reaction is apparently quite rapid (Mellor 1967), the NOCl should be short lived with little of either NOCl or NO_2Cl leaving the film cooler.

Thus, either Cl_2 or HCl should be the predominant gaseous chlorine species leaving the film cooler, depending on the total concentration of chlorine in the MOG. The Cl_2 would be the principal gaseous chlorine compound at moderate concentrations of Cl, while HCl should predominate at very low concentrations. Any NOCl remaining in the MOG should hydrolyze to HCl and HNO_2 in the water scrubbers following the film cooler and be removed. In other reactions it may behave similarly to Cl_2.

Chlorine will also leave the melter and be carried as aerosols (particulates) such as CsCl and NaCl. Cesium chloride, existing largely as the dimer, is moderately volatile. Vapor pressures of the pertinent alkali halides are listed in Table 6. Any alkali chlorides should be removed downstream of the plenum by the SBS, HEME, and HEPA and therefore would not interfere with iodine trapping.

Because of uncertain reaction kinetics and the rapidly changing temperature as the gases escape, the ratios of the various chlorine species cannot be fixed with much certainty. The chlorine exiting the film cooler will exist as gaseous Cl_2 or HCl or as the particulates CsCl or NaCl.

Fluorine. HF is by far the most stable gaseous fluorine species and is expected to be the principal gaseous form released from the melter. However, fluorides may also exist as aerosols.

Of the potential aerosols, NaF is the most stable of the alkali halides, and some of the fluorine may be tied up in that form. CsCl is more stable than CsF; however, because of the large amount of F present some of the F may exist as CsF. The alkali fluorides should be efficiently removed by the SBS, HEME, and HEPA and should not interfere with iodine trapping.

As with chlorine, because of uncertain reaction kinetics, the ratios of the various fluorine species escaping from the melt and from the plenum cannot be fixed with much certainty. Fortunately all are very soluble in water, the impact of which will be discussed in the section on the SBS and HEME.

Table 6. Vapor Pressures of Alkali Halides, torr

Compound	700EC	1000EC
CsI	3.0	70
CsCl	1.7	42
NaI	1.2	35
NaCl	0.24	7.8
CsF	<0.1	2.0

Iodine. The principal gaseous iodine species in the plenum and exiting the film cooler should be ICl because of the presence of a large excess of chlorine relative to iodine and the favorable thermodynamics relative to I_2 formation, $\hat{I}G_f$ = -4.05 kcal at 700K and -4.33 kcal at 900K.

If it were not for the great excess of other halogens, CsI rather than ICl or I_2 would be the principal iodine species released from the melter. In addition to its exceptional chemical stability, CsI is the most volatile of the alkali halides and thus may escape to the plenum gas.

The other form of iodine that will be present in the MOG is particulates containing iodine. There is a remote possibility that HI and organic iodides (principally CH_3I) may be present in the gas leaving the film cooler; however, the thermodynamics and plenum conditions such as high temperatures do not favor their existence. A considerable amount of iodine will be in particulate form as metal iodides and iodates and as iodine absorbed on other particles. The iodine-containing particulates should be efficiently removed by the SBS, HEME, and HEPA systems before reaching the iodine trap, as discussed in detail later.

Nitrogen. Nitrogen will be present in the MOG as N_2, NO, NO_2, and HNO_3. The N_2 will be present in a large excess from air dilution, the oxides of nitrogen will arise from the thermal decomposition of the nitrate and nitrite, and the HNO_3 will arise from the acidic nature of the melt and the nitrate in the melt. N_2 will act as an inert diluent and the oxides of nitrogen (NO_x) will affect the oxidizing strength of the MOG. Because of the reactivity of the oxides of nitrogen, they are potentially important in the iodine trapping system.

The principal NO_x species that will be evolved from the melt should be NO_2; however, at the temperature of the plenum the equilibrium ratio NO/NO_2 is about 20. As the gas cools on leaving the plenum, the NO_2 concentration will increase. Both NO and NO_2 will leave the film cooler and enter the SBS.

The NO_x species that exit the film cooler will be controlled by the concentrations of the species themselves and the kinetics. NO is oxidized very rapidly at high concentrations in air, but as discussed later at low concentrations the rate becomes very slow (Yost and Russell 1944). The species that leave the film cooler will determine the amount of NO_x that enters the iodine trapping system. If NO_2 is the predominant species leaving the film cooler, it will slowly be removed by a water scrub (SBS) leaving, and also producing NO in the sorption reaction. Thus, as the overall concentration of NO_X is reduced the principal species becomes NO.

Sulfur. The predominant gaseous sulfur species released from the melter should be SO_3, which is very soluble in water. However, since it tends to form a fog, it is not easily trapped by aqueous scrubbers. SO_2 also should be present in lesser quantities, and as the gas is cooled as it leaves the plenum, the SO_2 should be oxidized to SO_3 based on thermodynamics. Since the reaction is slow, a small amount of the less soluble SO_2 may pass through the plenum and film cooler and enter the SBS.

Antimony. Antimony was found in the gas samples taken during the pilot-plant melter test (Goles et al. 1989). Based on thermodynamics, the predominant antimony compound formed in the melt should be Sb_2O_5. Some Sb_2O_3 and the mixed valence oxide Sb_2O_4 also may be present. Thermodynamic data for antimony compounds from Barin, Knacke, and Kubaschewski (1973, 1977) do not agree well with NBS

(Wagman et al. 1982) data. It is certain that Sb_2O_5 is the most stable compound between 25 and 300EC, but the literature states that Sb_2O_5 decomposes at 380EC. Probably Sb_2O_5, Sb_2O_4, and Sb_2O_3 aerosols will be present in the MOG. Of these compounds only Sb_2O_3 is slightly volatile, having a vapor pressure of about 1 torr at 850K, and as the gases cool any gaseous Sb_2O_3 will condense and join the other antimony compounds as an aerosol.

Tellurium and Selenium. Tellurium and selenium were found in the off gas samples taken during the pilot-plant melter test. In the melt both tellurium and selenium should be present as the dioxides. SeO_2 should volatilize from the melter because of its moderate volatility (sublimes 602K). For the non-volatile TeO_2 the vapor pressure at 1000K is calculated to be about 0.1 torr, therefore any TeO_2 that leaves the melter will leave as an aerosol. As the gases cool while passing through the plenum, the SeO_2 should condense and leave the film cooler as an aerosol. The MOG will contain little of these two elements as gases as it exits the film cooler.

Cesium. As noted above, CsCl should be the principal form of cesium released from the melter and it will exist as both a solid and gaseous form in the MOG, the latter primarily as Cs_2Cl_2. Cs_2O is not a stable compound in this environment. The particulate control systems downstream of the film cooler should remove most of the cesium compounds that are not scrubbed out with water in the SBS, e.g., the HEME and HEPAs.

Kinetics will play a very significant role in fixing the proportion of the chemical species (for example, during the rapid cooling of the plenum gases and during aqueous scrubbing).

The greatly different concentrations of the elements Cs, Cl, F, and I from each other and compared, for example, to that of oxygen markedly influence the equilibrium positions with respect to the molecular species. The probable gas phase concentrations at the melter surface are in the order $Cl > F >> Cs >> I$. The concentrations, partial pressures, of these species are very small, and it is emphasized that slow reaction rates may not permit many of the equilibria discussed here to be reached.

General. Although many other metals in the melt form stable halide salts or complexes, there still should be an adequate amount of HCl or Cl_2 released to satisfy the equilibria involved among the species discussed above.

It should be emphasized that the chemical species leaving the melt surface are really unknown, as is much of the melt chemistry, and although there is theoretical basis for the predictions about chemical speciation, considerable speculation is also involved.

Actually, the form of many elements leaving the melter is a moot point. For example, it is relatively unimportant whether cesium is in the form of a salt or an oxide or that CsO_2 is the most stable oxide. Likewise, the fact that the cesium compounds are probably dimers in the gas phase is probably irrelevant, since aerosols may make up the bulk of these contaminants as the plenum gas is cooled. For the chlorine species all except Cl_2 should be efficiently removed by the SBS and HEME. The combination of the SBS and HEME will remove much of the aerosol and particulate matter. Final cleanup of particulates is achieved with the HEPA filter.

5.1.2 Chemistry of the Submerged Bed Scrubber and High Efficiency Mist Eliminator

The gases from the melter are diluted with about three volumes of air upon passing through the film cooler and the SBS. The SBS is an aqueous scrubber which removes soluble gases and aerosols from the cooled gases. The temperature in the SBS is low, about 30EC to 50EC, and the extent to which Cs, Sb, S, P, B, Se, and Te are removed depends largely on aerosol trapping efficiency. To some extent the iodine may be removed by the same mechanism, since it has a tendency to absorb on all particulate matter.

An unknown in the nature of the iodine leaving the SBS and HEME system is how much of the iodine reacts with the trace organics after the gas cools. Iodine is notorious for reacting with any organics (for example, greases) in a plant to form organic iodides such as CH_3I. Typically, the iodine in the off-gas in nuclear fuel reprocessing plants is 1% to 10% organic iodides, and its composition in the HWVP may be similar.

The solubility and partial pressures of the true gases listed in Table 4 are also very important in determining the decontamination in the SBS and in the subsequent HEME filter. About two-thirds of the water carried out of the melter should condense in the scrubber.

Mists carried from the SBS and a portion of any remaining particulates are trapped on the fiberglass fibers of the HEME. In the event that equilibrium solubility is not reached in the SBS, there is also a chance for further decontamination in the HEME. A possibly unwelcome RF is also expected for fluorine from the reaction of HF with the fiberglass filter.

Compounds of Cs, Sb, B, Si, Te, and Se are reduced to very low concentrations by the SBS and HEME. They are subsequently not particularly significant with regard to subsequent iodine chemistry, and are no longer considered in this report.

The gas phase concentrations of the halogen species exiting the SBS and HEME should be dictated largely by their solubilities in water. Any HI entering the SBS should be completely removed because of its high solubility, based on data from the International Critical Tables (Washburn 1928). The equations presented here were generated by a linear least squares fit of the data from the pertinent reference.

The solubility of HCl gas in water, expressed in terms of partial pressure (P), is given by Equation (1) based on the lower concentration points of Zeisber et al. (1933).

$$\begin{array}{lll} \text{HCl} & \text{25EC} & P(\text{torr}) = 3.64 \text{ x } 10^{-04}\ \underline{M}^{2.63} \\ & 40 & \quad 1.87 \text{ x } 10^{-03}\ \underline{M}^{2.44} \\ & 80 & \quad 7.76 \text{ x } 10^{-02}\ \underline{M}^{2.02} \end{array} \tag{1}$$

The lowest concentration that Zeisber et al. used was 0.6 $\underline{M}$, and extrapolation to very low values may be unreliable because of the ionization of the HCl in the aqueous phase. The calculated P at these lower concentrations can be considered an upper limit.

Equation (2) provides the vapor pressure of HF as a function of HF concentration at three temperatures. The HF data come close to following Henry's law,(a) which states that partial pressure is proportional to concentration in the aqueous phase. Since neither appreciable ionization nor radical change in polymerization occurs for HF in an aqueous solution, extrapolation of Equation (2) to lower concentrations is reasonable. However, even for HF, Equation (2) probably will predict erroneously high pressures at very low concentrations.

$$\begin{array}{lll} \text{HF} & \text{25EC} & P(\text{torr}) = 4.16 \text{ E-02 } \underline{M}^{1.05} \\ & 40 & \quad 1.2 \text{ E-01 } \underline{M}^{1.05} \\ & 80 & \quad 1.0 \text{ E 00 } \underline{M}^{1.05} \end{array} \tag{2}$$

The equations fit data from Seidel (1953) and Vdovenko, Lazarev, and Shirvinskaya (1965) reasonably well.

Equation (3) for iodine is derived using data from Eggleton (1967) and is also for higher concentrations.

(a) Common forms of Henry's law are H = P/$\underline{M}$ or the reciprocal form, Conc = kP. Gas solubility is also commonly expressed as a partition ratio, K = (mol/L in aq)/(mol/L in gas).

I_2 25EC P(torr) = 2.1 E 02 $\underline{M}$ (3)
40 4.4 E 02 $\underline{M}$
80 1.3 E 03 $\underline{M}$

For iodine, experimental vapor pressure data exist in the range of interest to HWVP. A Henry's law plot given by Lin (1981) suggests that P/$\underline{M}$ at 21EC is about 170 torr/$\underline{M}$ for concentrations of iodine above 4 x 10^{-4} $\underline{M}$. At 0.1 mg/L, 3.94 x 10^{-6} $\underline{M}$, P/$\underline{M}$ is 1.7 torr/$\underline{M}$ and decreases by a factor of 0.01 for each decrease by a factor of 0.1 in aqueous iodine concentration.

Chlorine data used to generate Equation (4) are from Seidel (1953) and Lange (1973) and also are for higher aqueous concentrations, approaching saturation.

Cl_2 25EC P(torr) = 1.95 E 05 $\underline{M}^{1.70}$ (4)

Both chlorine and iodine follow Henry's law at high concentrations but, at the very low concentrations where ionization and hydrolysis predominate, the linear relation is not valid. No data were found for ICl, which is likely the predominant iodine species.

The four sets of vapor pressure equations serve mostly to illustrate the behavior of four uniquely different compounds, one which is nearly completely ionized (HCl), one which is un-ionized but tends to polymerize and also form exceptionally strong hydrogen bonds (HF), and the two elemental halogens which react similarly with water but have greatly different vapor pressures. As noted earlier, HI falls in the same category (ionized) as HCl. The data also suggest relative potential efficiencies and possible limitations of the SBS and the HEME filters.

The composition of the gas stream entering the iodine trapping system is dependent on the solubilities and subsequent vapor pressures of the gases over the solutions. As the MOG passes through the SBS and the HEME, soluble gases will be removed. HI, HCl, SO_3 and P_2O_5 are very soluble and, except for mist formation, all four compounds should be nearly completely removed by the combined SBS and HEME filter. The removal of HF and perhaps NOCl is predicted to be less efficient, and an even lower scrubbing efficiency is predicted for Cl_2, ICl, I_2, CO_2, NO_x and any remaining SO_2 that might have formed in the plenum.

In the case of NO_x, by the time the gas reaches the HEME it is probably mostly insoluble NO, much of the NO_2 having been removed in the SBS. At the concentrations in the MOG, the oxidation rate of NO to the more soluble NO_2 is negligible. Using data from Yost and Russell (1944), the half time for the reaction at a concentration of 0.01% NO in air is 60 minutes, and the reaction rate is proportional to the square of the concentration! An additional chemical reaction step would be required to significantly reduce the concentration of the remaining NO entering the iodine control system.

In the case of the elemental halogens, a further point should be noted. The important aqueous reactions,

$$X_2 + H_2O = HOX + X^- + H^+ \tag{5}$$

and

$$3HOX = 2X^- + 3H^+ + XO_3^- \tag{6}$$

increase the solubility of the halogens, but at low halogen concentrations the slow kinetics limit the scrubbing efficiency. (The same reactions, of course, can increase efficiency even more if a caustic wash is used.) Taylor (1959) found appreciable liquid phase resistance to iodine transfer to water in contrast to chemically reactive systems such as caustic or thiosulfate, which were gas phase controlled. It is interesting to note that if chlorine actually existed as NOCl rather than Cl_2 it might be easier to remove with water, since the former apparently hydrolyzes rapidly, forming HCl.

The significant reactive gases likely to leave the HEME and be introduced into the iodine trapping system are HF, Cl_2, ICl, CO_2, and NO.

5.1.3 Results from the Pilot-Plant Test

The RF values observed by Goles et al. (1989) are generally consistent with the solubility and vapor pressure data. However, more conservative values were recommended for use, resulting in somewhat higher estimated concentrations in the exiting gas streams. Table 7 lists the latter values for gases of interest.

Comparison of the calculated gas phase concentrations, using Equa-tions (1) through (4), and the measured halide content of the HEME drainage liquid observed in the pilot-plant study with the estimated gas concentrations exiting the HEME filter shown in Table 7 provides an interesting insight into the chemistry of the system.

It may be noted that the iodine concentration exiting the HEME is 2.4×10^{-11} mol/L (Table 7) assuming no retention in the SBS or HEME. This corresponds to about 2.0×10^{-11} mol ^{129}I/L or about 20 times greater than the 10 CFR 20 (1983) limit for an uncontrolled (unrestricted) area but a factor of 5 below that permitted for a controlled area, similar to the Hanford Area. As discussed earlier an appreciable amount of iodine may exist as aerosols and may be removed. Also I_2 (or ICl) itself is slightly soluble in water and some will be removed in the SBS and HEME. The entire MOG stream will be greatly diluted before discharge from the plant.

Table 7. Estimated Concentrations of Important Species in Melter Off Gas, mol/L[(a)]

	Melter Off Gas		
Compound	Exit from Film Cooler	Exit from SBS	Exit from HEME
ICl	2.4×10^{-11}	2.4×10^{-11}	2.4×10^{-11}
Cl_2, HCl[(b)]	2.0×10^{-06}	4.0×10^{-07}	1.0×10^{-08}
HF	1.1×10^{-05}	2.2×10^{-06}	5.5×10^{-08}
NO_x	2.5×10^{-04}	2.5×10^{-04}	2.5×10^{-04}
CO_2	3.1×10^{-04}	3.1×10^{-04}	3.1×10^{-04}
SO_3, SO_2	1.2×10^{-06}	2.4×10^{-07}	4.8×10^{-08}
P_4O_{10}	4.4×10^{-09}	9.8×10^{-10}	1.8×10^{-11}

(a) Using DF (RF) values recommended in the Melter Test Report (Goles 1989).

(b) As Cl.

At an HF concentration of 400 wppm in the SBS drain liquid or 2×10^{-2} M (Goles et al. 1989), Equation (2) predicts a vapor pressure of 6.8×10^{-4} torr or 4.0×10^{-8} mol HF/L in the vapor (STP). The agreement is surprising since the table value may be high.

The Cl concentration in the HEME drain liquid is about 220 wppm and, if the species in solution is HCl, the calculated P would be 5.9×10^{-10} torr or 3.5×10^{-14} mol HCl/L gas. If the solute is pure Cl_2, the calculated P would be 11 torr or 6.6×10^{-4} mol Cl_2/L gas. The calculated vapor phase concentrations for HCl and Cl_2 are factors of six orders of magnitude lower and five orders of magnitude higher, respectively, than the concentration computed from estimated RFs. This suggests that the Cl species are predominantly HCl but include considerable Cl_2.

It can also be estimated that if the gaseous iodine shown in Table 7 existed as I_2 and if aqueous equilibria exist, the concentration of iodine in the HEME exit liquid would be 1.0×10^{-9} mol I_2/L. It is unknown how the total iodine is divided between the species ICl, I_2, HI, CH_3I, and particulates as the gas leaves the HEME, but ICl is probably still the major component.

6.0 Iodine Scrubbing

Assuming the concentrations of iodine and other reactive gases indicated in Table 6, we can now examine the feasibility of further reducing the iodine concentration. The methods that we believe offer promise for application to the HWVP off gas stream are caustic scrubbing and silver-containing sorbents.

6.1 Caustic Scrubbing

Caustic scrubbing of iodine from gases is an inexpensive and well-established method for trapping gaseous iodine. Several nuclear fuel reprocessing facilities have treated dissolver off gas by this method, including those in France, Great Britain, and the United States. The Idaho National Engineering Laboratory (INEL) has had considerable experience with the process, and their waste management reference document (Brown, Christian, and Thomas 1983) briefly summarizes the applicability. MacKay, Miquel, and White (1982) also describe the application of caustic scrubbing to gaseous iodine control in an NFRP.

The concentration of iodine in the vapor in an NFRP is several orders of magnitude higher than that expected in the HWVP. The major question regarding caustic scrubbing and its application to the HWVP is the scrubbing efficiency at the very low concentration of ICl or I_2 and CH_3I that remains after passing through the SBS and HEME. It is also possible that some iodine exists absorbed on particulate matter, since iodine has a tendency to absorb on most surfaces.

No information has been found regarding scrubbing efficiency at concentrations as low as that in Table 7. In support of the effort of Rockwell Hanford, a previous Hanford Site contractor, to design the Process Facility Modification, Burger and Scheele found RFs of greater than 1×10^{-3} with a feed of 4×10^{-6} mol I/L. The concentrations in the exit gas in those tests were still three orders of magnitude above that of Table 7. Since the kinetics will be controlled by the gas phase, it is predicted that a steadily declining efficiency will result as the iodine concentration goes down.

The equipment envisioned is a packed tower with countercurrent flow of about 1 M NaOH. Such a contractor is efficient for scrubbing soluble gases, but possibly not for particulates of very small diameter. Particulates having diameters of a few tenths of a micron or less are not efficiently removed by sprays (Griffiths 1963), and probably not by a countercurrent liquid. If a significant fraction of iodine is associated with particulates on the order of 0.1 μm in size, there may be little iodine removal.

Organic iodine, generated by interaction between iodine and organics (such as greases) in/on the off gas system, will be removed by contact with caustic solutions only to the extent that it is soluble in water. Hasty (1967) reported that the partition coefficient--the ratio of the concentration in water to the concentration in the gas phase--for methyl iodide was 2.75 at 30EC.

Other compounds such as thiosulfate or hydrazine (Row 1968) have been added to improve the efficiency of caustic, but their performance has not been tested under HWVP conditions. The tendency for thiosulfate to release sulfur on to radiolysis make its use questionable.

Depletion of the caustic by the other acid gases creates another set of problems. First is the competition between the large excesses of the other acidic gases and the iodine as they pass through the scrubber. Second is the large volume of waste that will be generated. As an example we will consider CO_2, the major acidic gas in the HEME effluent. Using the gas flow from Table 1 and the CO_2 concentration of Table 7, it is seen that 2.1 mol/min or about 1×10^5 mol per month of hydroxide would be neutralized. Another problem exists: if NaOH is used, the limited solubility of sodium carbonate and the large amount of CO_2 could result in large quantities of solids, traced with radioiodine and radiocarbon, which would have to be dealt with by the designers and operators of the HWVP. The precipitation problem could be solved by substituting KOH for NaOH, at somewhat greater cost.

Perhaps the worst aspect of caustic depletion is disposal of the estimated 50 t/month of liquid radioactive waste. In addition to ^{129}I and ^{14}C, the scrub liquid will contain chloride, hypochlorite, fluoride, nitrate, nitrite, sulfate, phosphate, and carbonate salts, as well as smaller amounts of iodide, hypoiodite, and iodate. Grouting the liquid waste is a potential disposal technology, but this treatment adds another process to the HWVP. If it is necessary to prepare the waste for disposal in grout, preliminary neutralization could be done in the presence of added hydroxyl amine to prevent I_2 formation, but with this operation there is always the hazard of inadvertent excess acid addition to the caustic waste, thus releasing iodine.

The current "state-of-the-art" and politically acceptable disposal strategy for ^{129}I is to convert the iodine to an insoluble iodide or iodate, encapsulate the form in cement, and place the cement waste form in a geologic repository. However, there is no land-based strategy which can guarantee the necessary time to ensure decay of the ^{129}I, the half-life of which is 1.6×10^7 y. An alternative strategy involves deep ocean disposal, which provides isolation and isotopic dilution to reduce the hazard associated with the radioiodine (Burger 1980; Burger, Scheele, and Wiemers 1981). MacKay, Miquel, and White (1982) suggest direct disposal of the liquid to the ocean and rely on isotopic dilution to reduce the hazard from the radioiodine. The topic of a disposal strategy is discussed briefly here since the iodine trapping process would concentrate a nearly acceptable, on a regulatory basis, iodine concentration.

Caustic scrubbing can likely achieve some reduction in iodine release from the HWVP. The gas exiting the scrub could possibly meet regulatory limits for an uncontrolled area, RF of 20 required, without taking into account the dilution that will occur when the remainder of the HWVP vent system gases are mixed with the cleaned MOG. The reduction by scrubbing may be small as it is predicted to be an inefficient process at the low iodine concentrations involved for very fine particulates and for organic iodides. An actual test of the method would be required under the expected HWVP conditions to determine the trapping efficiency, bed sizing, volume of waste generated, and several other operating parameters.

6.2 Silver-Containing Sorbents

Three silver-containing solids have been successfully tested for iodine trapping: silver mordenite (AgZ); silver faujasite (AgX); and the European-developed amorphous silica, which contains silver nitrate (AgSi). The silver zeolites are made by treating the respective zeolites with a silver nitrate solution to replace sodium sites in the framework with silver ions. The AgSi is prepared using a proprietary process.

Silver zeolites have been investigated in many laboratories, most recently by Scheele, Burger, and Halko (1988). Wilhelm and Schuettelkopf (1970) demonstrated the effectiveness of AgSi in their studies. The recent testing of the three materials at PNL found AgZ and AgX to be superior to the AgSi when used to remove 1 x 10^{-7} mol/L iodine from a simulated NFRP off-gas stream (Scheele, Burger, and Halko 1988). We believe that the relatively poor performance of the AgSi was caused by condensation of water on the beds, which solubilized the silver nitrate and then blocked the pores when the material dried after our experimental difficulties were overcome. The zeolite beds tested in parallel and exposed to similar conditions did not suffer in performance. Although European experience with the AgSi has been and continues to be good (personal communication by J. Fürrer of Karlsruhe), we prefer zeolites based on our experience.

The iodine concentrations used in testing silver-containing sorbents have normally been of the order of 1 x 10^{-6} mol I/L, although Scheele, Burger and Halko (1988) found that 36 wt% silver AgX made a satisfactory analytical trap for iodine at a nominal 1 x 10^{-12} mol I/L level.

The silver-containing beds are operated at an elevated temperature, typically 150EC to 200EC. Under these conditions, Scheele, Burger, and Matsuzaki (1983) found that methyl iodide is decomposed and trapped along with other iodine species.

As with caustic scrubbing, an unanswered question is the operating efficiency of silver zeolite beds at the 10^{-13} to 10^{-11} mol I/L concentration level. The early laboratory work of Pence and Maeck (1969) and Pence, Duce, and Maeck (1972) indicated that AgX was effective in reducing iodine concentrations at feed concentrations comparable to those expected with the HWVP. They used methyl iodide concentrations ranging from 1×10^{-16} to 4×10^{-13} mol I/L and were able to obtain RFs of 1×10^{4} to 1×10^{3} for a 10-cm-long bed at 90EC. No operating experience with plant-scale absorbers has been reported.

A second factor to be considered is the presence of the other reactive gases of which nearly all are in much higher concentrations than the iodine. The small amount of NO_x should not be a problem; iodine removal has been demonstrated at levels up to 18% NO_x. Likewise, water at 40EC dew point caused no problem in the recent PNL tests (Scheele, Burger, and Halko 1988). However, it must again be emphasized that these experiments were done at much higher iodine concentrations.

From a purely equilibrium (thermodynamic) standpoint with respect to iodine trapping, the only species that could prevent trapping and retention of iodine by the silver-containing sorbents is chlorine. The data in the appendix show that silver iodide is sufficiently stable that at the concentrations of SO_2, SO_3, HF, and P_4O_{10} in the HEME effluent, the formation of silver sulfate, fluoride, and phosphate will not preclude iodine trapping or retention. In contrast, AgCl is much more stable than is AgI and coupled with the large excess of chlorine in the gas, chlorine would be predicted to prevent the trapping and retention of any iodine by the silver-containing sorbents.

Experimental evidence indicates that any chlorine species will negatively impact retention of iodine by silver zeolites. Burchsted, Kahn, and Fuller (1976) report in the <u>Nuclear Air Cleaning Handbook</u> that a silver zeolite bed exposed to HCL was almost immediately rendered ineffective for iodine control. Ackley and Combs (1973) found that Cl_2 loaded onto an AgX bed reduced the RF for iodine. They found that 10-cm-deep beds loaded to 0.4 mmol Cl/mL AgX and 0.8 mmol/mL provided RFs of 20 and 14, respectively, as opposed to 1×10^{3} in the absence of Cl. It may be noted that 0.8 mmol/mL is only 25% silver utilization.

It is worth noting that experience with the "silver reactor" used at the Hanford PUREX plant confirmed the replacement of iodine by chlorine, the latter apparently coming from impurities in process chemicals (duPlessis and Sutter 1969; Strachan 1978).

The use of AgX or AgZ would require sizing the trap to take care of the chloride concentration in the gas. It is also likely that a lower face velocity (greater residence time) would be desired.

The known thermodynamics of iodine indicate iodine should be trapped in the silver zeolites as both silver iodide and silver iodate. Our own experience suggests that elemental iodine is retained by silver zeolites, possibly as a complex. The operational temperature of the silver-containing sorbents could have an effect on the concentration of the iodine species in the silver-containing sorbent. The free energy data indicate that the stability of AgI with respect to $AgIO_3$ increases as the temperature increases up to a crossover point, where AgI becomes more stable and the $AgIO_3$ decomposes to AgI; this temperature in the presence of NO_x is at about 190EC.

The equilibrium reaction for iodine in the silver-based system also predicts that the partial pressure of iodine above the system is proportional to the square of the NO_2 concentration. This imposes a theoretical limit on iodine removal at high NO_x concentrations, but would be of little consequence at the NO_2 levels of the HEME exit gases.

The formation of silver iodide and silver iodate in silver zeolites have been experimentally confirmed at macro concentrations of iodine (Patil et al. 1967), but no work has been done at very low iodine concentrations.

Although HF, P_4O_{10}, SO_3 or SO_2, and CO_2 may not compete with iodine in an equilibrium sense, it is quite likely that the diffusion process within the zeolite pores may be impeded by these large molecules; i.e., one might expect to see kinetic effects that lower the efficiency of iodine absorption. Even water at high concentrations was found by Pence and coworkers to have a negative influence on iodine removal if the bed is operated at high face velocity (Pence and Maeck 1969). They later reported that, under different conditions, neither 10 vol% NO_2 nor CO_2 had a deleterious effect (Pence, Duce, and Maeck 1972).

Although HF should not compete with iodine for silver in the zeolites, HF could attack and destroy the aluminosilicate framework of the zeolite. This attack could reduce the useful lifetime of the zeolite.

Before implementing silver zeolites in the HWVP, laboratory testing would be required primarily to determine their effectiveness at the iodine concentrations expected in the HWVP and to determine the effects of the other reactive gases. Other important parameters including bed size, particle size, temperature, and flow rate (face velocity) should also be studied. Tracer iodine would be employed with concentrations in the 1 x 10^{-14} to 1 x 10^{-12} mol I/L range. The experiments would determine the loading characteristics of iodine at extremely low concentrations and, perhaps more importantly, whether the excess of chlorine and other reactive gases can be accommodated simply by making the bed larger.

The quantity of AgX that would be required for HWVP operation can be estimated from the data in Table 7. On the basis of 1 x 10^{-8} g atoms Cl/L and 30% silver utilization, 7.9 kg of AgX/month would be required. The approximately 1000 troy ounces of silver involved represents about $5000, based on silver prices in the summer of 1991.

Disposal of iodine-loaded silver zeolites has been studied at PNL (Burger, Scheele, and Wiemers 1981). Incorporation in concrete was identified as the "best" available disposal technique but, as mentioned in the section on caustic scrubbing, there is no practical containment method that will prevent iodine release after a period of a few hundred years. The disposal of the iodine-loaded silver zeolites is complicated by classification of silver as a hazardous material requiring treatment of this waste form as a mixed hazardous radioactive waste.

It is our belief that of the two potential methods for iodine removal in the HWVP, caustic scrubbing and silver zeolite trapping, the latter has the most hope of success and requires a less complex waste disposal operation. Other advantages include safety (little chance of accidental iodine release), no effect of variable operating conditions, and fewer overall process steps. However, the method's efficiency at the low iodine concentration and in the presence of a large excess of other halogens is unknown.

Although both methods do offer some promise for HWVP off-gas treatment, we must conclude that the technology cannot be considered developed for application in the HWVP at the present time.

If, after laboratory and pilot-scale testing, it is decided to employ the silver zeolite bed as an iodine cleanup, any additional Cl removal prior to the iodine trap is a bonus. Obtaining maximum efficiency in the SBS and the HEME is an important goal regardless of that decision.

7.0 References

10 CFR 20. U.S. Nuclear Regulatory Commission. *U.S. Code of Federal Regulations*. Appendix B.

40 CFR 190. U.S. Environmental Protection Agency. *U.S. Code of Federal Regulations*. "Environmental Radiation Protection Standards for Nuclear Power Operations."

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Appendix

Gibbs Free Energy (Barin, Knacke, and Kubachewski 1973, 1977)

Appendix

Gibbs Free Energy (Barin, Knacke, and Kubachewski 1973, 1977)

		G, kcal/mol(a)				
Compound	mp, K	298K	500K	700K	900K	1000K
Ag	1234	-3.04	-5.45	-8.35	-11.64	-13.40
AgF	708	-54.46	-59.22	-65.04		
AgCl	728	-37.16	-42.54	-49.04	-57.16(l)	-61.55
AgI	831	-23.03	-29.68	-37.84	-46.96(l)	-51.94
Ag_2O		-17.83	-26.02(B)	-36.36(B)	-48.03(C)	-54.37(C)
Ag_2SO_4	933	-185.38	-196.93	-211.40	-229.38(B)	-239.50(l)
$AgNO_3$		-38.85	-47.26(l)			
$AgIO_3$		-51.5	-59.9	-68.0		
Ag_3PO_4		-183.4(a)				
^{C}(gr)		-0.409	-0.830	-1.53	-2.48	-3.04
CO(g)		-40.50	-50.43	-60.86	-71.73	-77.30
CO_2(g)		-109.27	-120.13	-131.77	-144.09	-150.44
CCl_4(l)		-47.82	-62.91(g)	-80.87	-100.24	-110.35
Cl_2(g)		-15.89	-27.12	-38.95	-51.29	-57.61
Cs	302	-6.01	-10.85(l)	-16.28	-22.15	(-23.84 at 955 K)
CS_2(g)		+5.16	-9.05	-23.90	-39.29	-47.15
CsF	976	-138.86	-143.84	-149.86	-156.71	-160.51(l)
CsF(g)		-102.52	-114.74	-127.58	-140.94	-147.77
Cs_2F_2(g)		-237.78	-255.84	-275.35	-295.99	-306.65
CsCl	918	-113.05	-118.66	-125.34	-133.05(B)	-137.55(l)
Cs_2Cl_2(g)		-185.01	-204.62	-225.67	-247.87	-259.31
CsI(s)	894	-89.44	-96.20	-103.97	-112.62	-117.84
Cs_2O	763	-84.99	-92.22	-101.04	(-104.10 at dec 763 K)	
CsO_2		-86.44	-94.63	-104.4	(-104.74 at 705 K)	
F		-14.46	-24.69	-35.50	-46.80	-52.60
H_2(g)		-9.30	-16.00	-23.20	-30.82	-34.75
HF(g)		-77.52	-86.29	.55	-105.23	-110.19
HC1(g)		-35.37	-44.78	-54.68	-64.99	-70.27
H_2O(g)		-71.24	-80.81	-90.99	-101.69	-107.20
N_2(g)		-13.65	-23.28	-33.42	-43.99	-49.41
NH_3(g)		-24.71	-34.51	-45.04	-50.23	-62.05
NOCl(g)		-6.21	-19.49	-33.55	-48.28	-55.86
NO_2Cl(g)		-16.48	-30.38	-45.42	-61.43	-69.74
NO(g)		+6.57	-4.00	-15.09	-26.62	-32.52

		G, kcal/mol(a)				
Compound	mp, K	298K	500K	700K	900K	1000K
N_2O(g)		+3.94	-7.22	-19.16	-31.81	-38.35
NO_2(g)		-9.19	-21.29	-34.14	-47.64	-54.60
N_2O_4(g)		-19.51	-35.31	-52.86	-71.92	-81.93
HNO_3(g)		-51.08	-64.73	-79.62	-95.64	-104.01
NaF	1269	-140.76	-143.89	-147.98	-152.82	-155.46
NaF(g)		-85.60	-96.56	-108.15	-120.24	-126.45
NaCl	1074	-103.40	-107.58	-112.79	-118.79	-122.04
Na_2F_2(g)		-218.00	-233.61	-250.67	-268.86	-278.29
NaCl(g)		-59.73	-71.30	-63.50	-96.22	-102.73
Na_2Cl_2(g)		-158.50	-175.28	-193.52	-212.91	-222.94
NaI	933	-75.81	-81.27	-87.77	-95.06	-99/36(l)
Na_2O	1548 subl	-105.25	-109.87	-116.03	-123.41	-127.49
NaOH	593	-106.89	-110.85	-116.87(l)	-124.89	-128.65
Na	371	-3.65	-6.74(l)	-10.53	-14.72	-16.94
O_2(g)		-14.61	-24.91	-35.73	-47.00	-52.78
I_2	387	-8.28	bp458			
I_2(g)		-3.65	-16.72	-30.41	-44.63	-51.90
ICl(a)(g)		-13.38	(-25.75)	(-38.74)	(-52.28)	(-59.21)(b)
P(red)		-1.62	-3.03	-4.90	(-6.78 at 870 K)	
P_4O_6(g)		-537.13	-556.00	-578.40	-603.64	-617.16
P_4O_{10}		-729.51	-743.70	-763.48	(-780.89 at 843 K)	
P_4O_{10}(g)		-706.17	-728.52	-755.56	-786.53	-803.26
S	388	-2.72m	-4.32(l)	-7.17	(bp 718 K)	
S6(g)		-1.62	-20.29	-41.24	-63.98	-75.88
SO_2(g)		-88.62	-101.16	-114.50	-128.52	-135.75
SO_3(g)		-112.88	-126.01	-140.26	-155.47	-163.38
$SOCl_2$(g)		-72.69	-88.50	-105.61	-123.80	-133.22
SO_2Cl_2		-108.38	-124.52			
Sb	904	-3.24	-5.79	-8.83	-12.26	-14.61(l)
Sb_2O_3	929	-178.17	-185.53	-195.10	-206.56(B)	214.02(l)
Sb_2O_5		-249.71	-257.72	>500 K dec		
SbO_2		-112.98	-116.86	-121.96	-128.05	-131.41
$SbCl_3$(g)		(-99.93)(c)	-116.77	-135.35	-155.07	-165.27
$SbCl_3$(s)	346	-104.63				
SbI_3(s)	444	-38.36				
SbI_3(l)			-50.85			
SbI_3(g)			(-46.83)(b)	-68.20	-90.78	-102.42
Se	494	-3.01	-5.43l	-9.01	-13.07	-14.32 at bp 958 K

Compound	mp, K	G, kcal/mol(a)				
		298K	500K	700K	900K	1000K
Se_5(g)		-5.54	-14.44	-36.32	-59.68	-71.80
SeF_4		-215.12	-230.51	-247.54	-265.91	-275.52
SeF_6(g)		-289.50	-306.14	-325.42	-345.70	-357.95
$SeCl_2$(g)		-29.06	-44.07	-60.04	-76.81	-85.44
Te	723	-3.53	-6.28	-9.60	-14.42(l)	-17.06
TeO_2		-82.58	-87.05	-92.86	-99.70	-103.44
I_2O_5(d)						
HIO_3(d)						

(a) Reference state is crystalline solid unless otherwise indicated. (l) = liquid; (g) = gas; (B), (C), etc. = different solid states. Reference state for all iodine compounds is the ideal gas.

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

(c) Computed from vapor pressure data and G at normal boiling point.

Note that the table values are not free energies of formation. The latter can be calculated from

$$- G_f = G(\text{compound}) - \Sigma G(\text{elements})$$

Equilibrium constants are given by the relation

$$\text{in } K = - RT[\Sigma G(\text{products}) - \Sigma G(\text{reactants})].$$