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Best-Basis Estimates of Solubility of Selected Radionuclides in Sludges in Hanford Single-Shell Tanks

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Abstract: The Hanford Defined Waste (HDW) model (Rev. 4) (Agnew et al. 1997) projects inventories (as of January 1, 1994) of 46 radionuclides in the Hanford Site underground waste storage tanks. To model the distribution of the 46 radionuclides among the 177 tanks, it was necessary for Agnew et al. to estimate the solubility of each radionuclide in the various waste types originally added to the single-shell tanks. Previous editions of the HDW model used single-point solubility estimates. The work described in this report was undertaken to provide more accurate estimates of the solubility of all 46 radionuclides in the various wastes.

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BEST-BASIS ESTIMATES OF SOLUBILITY OF SELECTED RADIONUCLIDES IN HANFORD SINGLE-SHELL TANK SLUDGE

October 1998

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CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF TERMS

DKPRO	Radioactive Decay and Separations Processing (computer code)
DST	Double-shell tank
HAW	High-activity waste
HDW	Hanford Defined Waste
LANL	Los Alamos National Laboratory
ORIGEN2	Oak Ridge Isotope Generation (computer code)
PUREX	Plutonium-uranium extraction (process or plant)
REDOX	Reduction and oxidation (process or plant)
SMM	Supernatant Mixing Model
SST	Single-shell tank
TLM	Tank Layer Model
WSTRS	Waste Status and Transaction Record Summary

BEST-BASIS ESTIMATES OF SOLUBILITY OF SELECTED RADIONUCLIDES IN HANFORD SINGLE-SHELL TANK SLUDGE

1.0 INTRODUCTION

The Hanford Defined Waste (HDW) model (Revision 4) (Agnew et al. 1997) provides tables indicating the projected inventory (as of January 1, 1994) of 46 radionuclides in the Hanford Site 149 single-shell tanks (SSTs) and 28 double-shell tanks (DSTs).[1] The 46 radionuclides of interest represent isotopes of 28 different elements that have been determined to be of particular importance and concern to final disposal of the Hanford tank waste (Kupfer et al. 1998).

At the end of fiscal year 1997, data concerning the total amount of the 46 radionuclides to be distributed among the 177 tanks were provided to involved Los Alamos National Laboratory (LANL) personnel by Lockheed Martin Hanford Corporation. Total inventories of the various 46 radionuclides (as of January 1, 1994) were calculated by means of the computer codes Oak Ridge Isotope Generation (ORIGEN2) and Radioactive Decay and Separations Processing (DKPRO) (Kupfer et al. 1998).

To model the distribution of the 46 radionuclides among the 177 Hanford tanks, it was necessary for the LANL scientists to estimate the solubility of each radionuclide in the various types of waste originally added to the SSTs. In previous editions of the HDW model, LANL personnel had obtained what they believed were reasonable estimates of the single-point solubility of Cs-137, Sr-90, plutonium, and uranium from reported analytical data for Hanford tank supernatants (Agnew and Watkins 1994). For isotopes of the remaining 24 elements, Agnew et al. (1997) were required to use their best judgements as to the solubility of these isotopes in the various wastes added to the SSTs. However, because of schedule constraints in fiscal year 1997, the LANL modelers were required to make radionuclide solubility estimates in a very limited time period. Thus, for some radionuclides (e.g., Eu-152, Eu-155, Ra-228, Th-229, Cm-242, etc.) the LANL modelers simply assumed, in the absence of any other basis, that 50 percent of each radionuclide precipitated and 50 percent remained in solution. Therefore, a substantial bias exists because of this modeling simplification, and this bias is reflected in the Revision 4 predictions of the radionuclide inventory in each of the 177 tanks. The magnitude and direction of this bias are not known.

The work described in this report was undertaken to provide more accurate estimates of the solubility (fraction precipitated) of all the 46 radionuclides in the various wastes added to the SSTs. With improved descriptions of the solubility behavior, more reliable predictions by the HDW model of the distribution of all radionuclides among the 177 tanks is possible,

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[1] Readers of this report are assumed to have read or, at least, have access to a copy of Revision 4 of the HDW model report. A good knowledge and understanding of the contents of Revision 4 of the HDW model report is essential to critically review and comprehend the material presented in this report.

especially for analytes that are not directly measured. Estimates of radionuclide solubilities, in various wastes, were obtained initially by critical and in-depth review of the chemistry of each of the 28 elements (46 radionuclides). Then, where available, analytical data for various radionuclides in SST and DST wastes were used to supplement and corroborate best-basis solubility estimates derived from chemistry considerations.

It is anticipated that the newly derived fraction precipitated values presented in this report will be used in a subsequent revision of the HDW model to establish updated inventories of the 46 radionuclides to the 177 tanks. Some preliminary radionuclide distribution data obtained using the new solubility (fraction precipitated) estimates for Sr-90 and Cs-137 are presented in this report. These preliminary distribution assignments are shown to be in better agreement with actual analytical data for the tanks involved than the estimates presented in Revision 4 of the HDW model report.

2.0 SUMMARY

New estimates of the solubility (fraction precipitated) of 46 radionuclides in various alkaline wastes originally added to the 149 Hanford SSTs are presented (Table 2-1). For comparison purposes, solubility estimates of the same 46 radionuclides provided in Revision 4 of the HDW model report (Agnew et al. 1997) are listed in Table 2-2.

The new solubility estimates are intended for use in a subsequent revision of the HDW model, the results of which will be used to provide estimates for unmeasured radionuclides. Some preliminary HDW model application and evaluation of the new solubility estimates for Sr-90 and Cs-137 were completed to determine the impact and quality of these revisions on the results. Inventory predictions of Sr-90 and Cs-137 for various SSTs and DSTs obtained with the new solubility estimates are compared with inventories derived from analytical data and also with the model predictions using the solubility estimates provided in Revision 4 of the HDW model. For 60 selected SSTs and DSTs for which reliable analytical data are available, the Sr-90 inventory calculated by the HDW model using the revised fraction precipitated estimates agrees much better with the analytically-determined inventory than does the Sr-90 inventory value listed in Revision 4 of the HDW model report. For the same 60 tanks, the Cs-137 inventory calculated by the HDW model using the revised fraction precipitated estimates agrees very well with both the analytically-determined radiocesium inventory and the Cs-137 inventory listed in Revision 4 of the HDW model report.

These two analytes were selected because there is sufficient analytical data across a variety of tanks to evaluate them and they represent extremes in solubility behavior (Cs-137 is nearly totally soluble in most of the tank wastes; Sr-90 is almost always precipitated).

Table 2-1. Compilation of New Best-Basis Estimates of Radionuclide Solubilities. (4 Sheets)

HDW model	Fraction of radionuclide precipitated			
Waste types[1]	Ac-227	Americium[10]	Sb-125	Ba-137m
Process HAW				
$BiPO_4$ process[2]	0.10	0.98	0.15	0.10
Other processes[3]	0.10	0.98	0.15	0.10
Cladding wastes				
Aluminum[4]	0.0	0.98	0.0	0.0
Zircaloy[5]	0.10	0.98	0.15	0.30
Miscellaneous wastes				
Solid wastes Ferrocyanide solids Other solids[7]	 0.0 0.98	 0.0 0.98	 0.0 0.98	 0.98 0.0
Complexed waste[8]	0.0	0.0	0.0	0.0
Other liquid wastes[9]	0.10	0.98	0.0	0.0

Table 2-1. Compilation of New Best-Basis Estimates of Radionuclide Solubilities. (4 Sheets)

HDW model	Fraction of radionuclide precipitated			
Waste Types[1]	Cd-113m	C-14	Cesium[11]	Co-60
Process HAW				
$BiPO_4$ process[2]	0.98	0.05	0.10	0.90
Other processes[3]	0.98	0.05	0.10	0.90
Cladding wastes				
Aluminum[4]	0.0	0.0	0.0	0.0
Zircaloy[5]	0.98	0.50	0.30	0.98
Miscellaneous wastes				
Solid wastes				
Ferrocyanide solids	0.0	0.0	0.98	0.0
Other solids[7]	0.98	0.98	0.98	0.98
Complexed waste[8]	0.0	0.0	0.0	0.0
Other liquid wastes[9]	0.0	0.0	0.0	0.0
Waste types[1]	Curium[12]	Europium[13]	H-3	I-129
Process HAW				
BiPO4 process[2]	0.98	0.75	0.0	0.50
Other processes[3]	0.98	0.75	0.0	0.50
Cladding wastes				
Aluminum[4]	0.98	0.0	0.0	0.50
Zircaloy[5]	0.98	0.75	0.0	0.50
Miscellaneous wastes				
Solid wastes				
Ferrocyanide solids	0.0	0.0	0.0	0.0
Other solids[7]	0.98	0.98	0.0	0.98
Complexed waste[8]	0.0	0.0	0.0	0.0
Other liquid wastes[9]	0.98	0.0	0.0	0.0
Waste types[1]	Np-237	Nickel[14]	Nb-93m	Plutonium[15]
Process HAW				
BiPO4 process[2]	0.85	0.98	0.98	0.97
Other processes[3]	0.85	0.98	0.98	0.97
Cladding wastes				
Aluminum[4]	0.0	0.98	0.98	0.97
Zircaloy[5]	0.85	0.98	0.98	0.97

Table 2-1. Compilation of New Best-Basis Estimates of Radionuclide Solubilities. (4 Sheets)

HDW model	Fraction of radionuclide precipitated			
Waste types[1] (Continued)	Np-237	Nickel[14]	Nb-93m	Plutonium[15]
Miscellaneous wastes				
Solid wastes				
Ferrocyanide solids	0.0	0.0	0.0	0.0
Other solids[7]	0.98	0.98	0.98	0.98
Complexed waste[8]	0.0	0.0	0.0	0.0
Other liquid wastes[9]	0.0	0.98	0.98	0.98
Waste types[1]	Pa-231	Radium[16]	Ru-106	Sm-151
Process HAW				
BiPO$_4$ process[2]	0.98	0.90	0.10	0.75
Other processes[3]	0.98	0.90	0.10	0.75
Cladding wastes				
Aluminum[4]	0.98	0.0	0.0	0.0
Zircaloy[5]	0.98	0.90	0.10	0.90
Miscellaneous wastes				
Solid wastes				
Ferrocyanide solids	0.0	0.0	0.0	0.0
Other solids[7]	0.98	0.98	0.98	0.98
Complexed waste[8]	0.98	0.0	0.0	0.0
Other liquid wastes[9]	0.98	0.0	0.0	0.0
Waste types[1]	Sr-90	Tc-99	Thorium[17]	Sn-126
Process HAW				
BiPO$_4$ process[2]	0.98	0.33	0.98	0.35
Other processes[3]	0.98	0.33	0.98	0.35
Cladding wastes				
Aluminum[4]	0.98	0.10	0.98	0.25
Zircaloy[5]	0.98	0.33	0.98	0.75
Miscellaneous wastes				
Solid wastes				
Ferrocyanide solids	0.0	0.0	0.0	0.0
Other solids[7]	0.98	0.98	0.98	0.98
Complexed waste[8]	0.0	0.0	0.0	0.0
Other liquid wastes[9]	0.98	0.0	0.98	0.0

Table 2-1. Compilation of New Best-Basis Estimates of Radionuclide Solubilities. (4 Sheets)

HDW model	Fraction of radionuclide precipitated			
Waste types[1]	Uranium[18]	Y-90	Zr-93	Se-79
Process HAW				
$BiPO_4$ process[2]	0.75	0.75	0.98	0.05
Other processes[3]	0.98	0.75	0.98	0.05
Cladding wastes				
Aluminum[4]	0.98	0.0	0.98	0.0
Zircaloy[5]	0.98	0.90	0.98	0.05
Miscellaneous wastes				
Solid wastes				
Ferrocyanide solids	0.0	0.0	0.0	0.0
Other solids[7]	0.98	0.98	0.98	0.98
Complexed waste[8]	0.0	0.0	0.0	0.0
Other liquid wastes[9]	0.98	0.0	0.98	0.0

HAW = High-activity waste
HDW = Hanford Defined Waste

Notes:

[1] After addition of NaOH

[2] Includes HDW Model (Revision 4) Waste Types: MW1, MW2, 1C1, 1C2, 2C1, 2C2, 224, and UR

[3] Includes HDW Model (Revision 4) Waste Types: R1, R2, P1, P2, P2', Th1, Th2, P3, PL1, PL2, and Z

[4] Includes HDW Model (Revision 4) Waste Types: CWR1, CWR2, CWP1, and CWP2

[5] Includes HDW Model (Revision 4) Waste Types: CWZr1, and CWZr2

[6] Includes HDW Model (Revision 4) Waste Types: PFeCN1, PFeCN2, TFeCN, and 1CFeCN

[7] Includes HDW Model (Revision 4) Waste Types: DE, CEM, and AR

[8] Includes HDW Model (Revision 4) Waste Types: HS and SSR

[9] Includes HDW Model (Revision 4) Waste Types: OWW1, OWW2, OWW3, NIT, BL, CSR, DW, N, PSAF, and B

[10] Includes Am-241 and Am-243

[11] Includes Cs-134 and Cs-137

[12] Includes Cm-242, Cm-243, and Cm-244

[13] Includes Eu-152, Eu-154, and Eu-155

[14] Includes Ni-59 and Ni-63

[15] Includes Pu-238, Pu-239, Pu-240, Pu-241, and Pu-242

[16] Includes Ra-226 and Ra-228

[17] Includes Th-232 and Th-229

[18] Includes U-232, U-233, U-234, U-235, U-236, and U-238.

Table 2-2. Hanford Defined Waste Model (Revision 4) Values for Fraction of Radionuclides Precipitated in Various Waste Types (Agnew et al. 1997). (10 Sheets)

			HDW Revision 4 fraction precipitated solids by defined waste type									
Radionuclide	MW1	MW2	1C1	1C2	2C1	2C2	224	UR/TBP	PFeCN1	PFeCN2	TFeCN	1CFeCN
H-3	0	0	0	0	0	0	0	0	0	0	0	0
C-14	0.381681	0.479089	0	0	0	0	0	0	0	0	0	0
Ni-59	0	0	0	0	0	0	0	0	0.645494	0.64551	0.820251	0.82063
Ni-63	0	0	0	0	0	0	0	0	0.645494	0.64551	0.820251	0.82063
Co-60	0	0	0	0	0	0	0	0	0	0	0	0
Se-79	0	0	0	0	0	0	0	0	0	0	0	0
Sr-90	0	0	0	0	0	0	0	0	0.98	0.98	0.98	0.55
Y-90	0	0	0	0	0	0	0	0	0.98	0.98	0.98	0.55
Zr-93	0	0	0	0	0	0	0	0	0	0	0	0
Nb-93m	0	0	0	0	0	0	0	0	0	0	0	0
Tc-99												
Ru-106	0	0	0	0	0	0	0	0	0	0	0	0
Cd-113m	0	0	0	0	0	0	0	0	0	0	0	0
Sb-125	0	0	0	0	0	0	0	0	0	0	0	0
Sn-126	0	0	0	0	0	0	0	0	0	0	0	0
I-129												
Cs-134	0	0	0	0	0	0	0	0.01	0.97	0.97	0.97	0.55
Cs-137	0	0	0	0	0	0	0	0.01	0.97	0.97	0.97	0.55
Ba-137m	0	0	0	0	0	0	0	0.01	0.97	0.97	0.97	0.55
Sm-151	0	0	0	0	0	0	0	0	0	0	0	0
Eu-152	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5

Table 2-2. Hanford Defined Waste Model (Revision 4) Values for Fraction of Radionuclides Precipitated in Various Waste Types (Agnew et al. 1997). (10 Sheets)

				HDW Revision 4 fraction precipitated solids by defined waste type							
Radionuclide	MW1	MW2	1C1	1C2	2C1	2C2	224	UR/TBP	PFeCN1	PFeCN2	TFeCN	1CFeCN
Eu-154	0	0	0	0	0	0	0	0	0	0	0	0
Eu-155	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Ra-226	0.190533	0	0	0	0	0	0	0	0	0	0	0
Ra-228	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Ac-227	0.067272	0	0	0	0	0	0	0	0	0	0	0
Pa-231	0	0	0	0	0	0	0	0	0	0	0	0
Th-229	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Th-232	0	0	0	0	0	0	0	0	0	0	0	0
U-232	0.982639	0.983068	0.877168	0.872172	0.042157	0	0	0	0	0	0	0.867604
U-233	0.982639	0.983068	0.877168	0.872172	0.042157	0	0	0	0	0	0	0.867604
U-234	0.982639	0.983068	0.877168	0.872172	0.042157	0	0	0	0	0	0	0.867604
U-235	0.982639	0.983068	0.877168	0.872172	0.042157	0	0	0	0	0	0	0.867604
U-236	0.982639	0.983068	0.877168	0.872172	0.042157	0	0	0	0	0	0	0.867604
U-238	0.982639	0.983068	0.877168	0.872172	0.042157	0	0	0	0	0	0	0.867604
U-Total	0.982639	0.983068	0.877168	0.872172	0.042157	0	0	0	0	0	0	0.867604
Np-237												
Pu-238	0	0.350336	0.139189	0.448065	0.32874	0.213264	0	0	0	0	0	0.428657
Pu-239	0	0.350336	0.139189	0.448065	0.32874	0.213264	0	0	0	0	0	0.428657
Pu-240	0	0.350336	0.139189	0.448065	0.32874	0.213264	0	0	0	0	0	0.428657
Pu-241	0	0.350336	0.139189	0.448065	0.32874	0.213264	0	0	0	0	0	0.428657
Pu-242	0	0.350336	0.139189	0.448065	0.32874	0.213264	0	0	0	0	0	0.428657
Radionuclide	R1	R2	CWR1	CWR2	P1	P2	P2'	PL1	CWP1	CWP2	CWZr1	OWW1
Pu-Total	0	0.350336	0.139189	0.448065	0.32874	0.213264	0	0	0	0	0	0.428657
Am-241	0	0	0	0	0	0	0	0	0	0	0	0

Table 2-2. Hanford Defined Waste Model (Revision 4) Values for Fraction of Radionuclides Precipitated in Various Waste Types (Agnew et al. 1997). (10 Sheets)

				HDW Revision 4 fraction precipitated solids by defined waste type							
Am-243	0	0	0	0	0	0	0	0	0	0	0	0
Cm-242	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Cm-243	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Cm-244	0	0	0	0	0	0	0	0	0	0	0	0
H-3	0	0	0	0	0	0	0	0	0	0	0	0
C-14	0	0	0	0	0	0	0	0	0	0	0	0
Ni-59	0.55939	0.55353	0	0	0.55157	0.55338	0	0.55286	0	0	0	0.551
Ni-63	0.55939	0.55353	0	0	0.55157	0.55338	0	0.55286	0	0	0	0.551
Co-60	0	0	0	0	0	0	0.92438	0.5	0	0	0	0.5
Se-79	0	0.24381	0	0	0.34224	0.68364	0.98159	0.5	0	0	0	0.5
Sr-90	0.55163	0.87526	0	0	0.88035	0.94918	0.99729	0	0	0	0	0
Y-90	0.55163	0.87526	0	0	0.88035	0.94918	0.99729	0	0	0	0	0
Zr-93	0	0.21128	0	0	0.30181	0.66463	0.98063	0.5	0	0	0	0.5
Nb-93m	0	0.26846	0	0	0.37717	0.6804	0.98027	0.5	0	0	0	0.5
Tc-99												
Ru-106	0	0	0	0	0	0.74824	0.99906	0.5	0	0	0.16251	0.5
Cd-113m	0	0	0	0	0	0.58466	0.97938	0.5	0	0	0	0.5
Sb-125	0	0	0	0	0	0	0	0.5	0	0	0	0.5
Sn-126	0	0.21212	0	0	0.36312	0.69222	0.98199	0.5	0	0	0	0.5

Table 2-2. Hanford Defined Waste Model (Revision 4) Values for Fraction of Radionuclides Precipitated in Various Waste Types (Agnew et al. 1997). (10 Sheets)

				HDW Revision 4 fraction precipitated solids by defined waste type								
Radionuclide	R1	R2	CWR1	CWR2	P1	P2	P2'	PL1	CWP1	CWP2	CWZr1	OWW1
I-129												
Cs-134	0.005	0.005	0	0	0	0	0	0.03077	0	0	0	0
Cs-137	0.005	0.005	0	0	0	0		0.03077	0	0	0	0
Ba-137m	0.005	0.005	0	0	0	0	0	0.03077	0	0	0	0
Sm-151	0	0.24854	0	0	0.36012	0.69732	0.98023	0.5	0	0	0	0.5
Eu-152	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Eu-154	0	0	0	0	0	0.35218	0.98352	0.5	0	0	0	0.5
Eu-155	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Ra-226	0.43702	0.69501	0	0	0.74566	0.82333	0.9843	0.5	0	0	0	0.5
Ra-228	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Ac-227	0.36835	0.63618	0	0	0.72089	0.81219	0.98279	0.5	0	0.9303	0	0.5
Pa-231	0	0.2527	0	0	0.38725	0.63424	0.96994	0.5	0	0.77983	0	0.5
Th-229	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Th-232	0	0	0	0	0	0	0	0.5	0	0	0	0.5
U-232	0	0	0.78841	0.78044	0	0	0.86289	0	0.7365	0.55274	0.66829	0.69225
U-233	0	0	0.78841	0.78044	0	0	0.86289	0	0.7365	0.55274	0.66829	0.69225
U-234	0	0	0.78841	0.78044	0	0	0.86289	0	0.7365	0.55274	0.66829	0.69225
U-235	0	0	0.78841	0.78044	0	0	0.86289	0	0.7365	0.55274	0.66829	0.69225
U-236	0	0	0.78841	0.78044	0	0	0.86289	0	0.7365	0.55274	0.66829	0.69225
U-238	0	0	0.78841	0.78044	0	0	0.86289	0	0.7365	0.55274	0.66829	0.69225
U-Total	0	0	0.78841	0.78044	0	0	0.86289	0	0.7365	0.55274	0.66829	0.69225

Table 2-2. Hanford Defined Waste Model (Revision 4) Values for Fraction of Radionuclides Precipitated in Various Waste Types (Agnew et al. 1997). (10 Sheets)

				HDW Revision 4 fraction precipitated solids by defined waste type							
Radionuclide	R1	R2	CWR1	CWR2	P1	P2	P2'	PL1	CWP1	CWP2	CWZr1	OWW1
Np-237												
Pu-238	0.70817	0.76116	0.93784	0.94532	0.8557	0.91646	0.99786	0.80571	0.933	0.89584	0.96754	0
Pu-239	0.70817	0.76116	0.93784	0.94532	0.8557	0.91646	0.99786	0.80571	0.933	0.89584	0.96754	0
Pu-240	0.70817	0.76116	0.93784	0.94532	0.8557	0.91646	0.99786	0.80571	0.933	0.89584	0.96754	0
Pu-241	0.70817	0.76116	0.93784	0.94532	0.8557	0.91646	0.99786	0.80571	0.933	0.89584	0.96754	0
Pu-242	0.70817	0.76116	0.93784	0.94532	0.8557	0.91646	0.99786	0.80571	0.933	0.89584	0.96754	0
Pu-Total	0.70817	0.76116	0.93784	0.94532	0.8557	0.91646	0.99786	0.80571	0.933	0.89584	0.96754	0
Am-241	0	0.58214	0	0	0.41908	0.83339	0.99763		0	0	0	
Am-243	0	0.58214	0	0	0.41908	0.83339	0.99763	0	0	0	0	0
Cm-242	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Cm-243	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Cm-244	0	0.75628	0	0	0	0.76341	0.99878	0.5	0	0	0.59372	0.5
Radionuclide	OWW2	OWW3	Z	HS	TH1	TH2	AR	B	BL	SRR	CSR in	CSR
H-3	0	0	0	0	0	0	0	0	0	0	0	0
C-14	0.00217	0	0	0	0	0	0	0	0	0	0	0
Ni-59	0.55095	0.55101	0.55466	0.55094	0.5517	0.5517	0.70421	0.10069	0.82041	1	1	0.63056
Ni-63	0.55095	0.55101	0.55466	0.55094	0.5517	0.5517	0.70421	0.10069	0.82041	1	1	0.63056
Co-60	0.5	0.5	0.5	0	0.5	0.5	0	0	0	0	0.5	0
Se-79	0.5	0.5	0.5	0	0	0	0.43204	0.38794	0	0.81519	0.5	0.47962
Sr-90	0	0	0	0.7413	0	0.10644	0.91895	0.54931	0.59769	0.64472	0.07649	0
Y-90	0	0	0	0.7413	0	0.10644	0.91895	0.54931	0.59769	0.64472	0.07649	0

Table 2-2. Hanford Defined Waste Model (Revision 4) Values for Fraction of Radionuclides Precipitated in Various Waste Types (Agnew et al. 1997). (10 Sheets)

				HDW Revision 4 fraction precipitated solids by defined waste type								
Radionuclide	OWW2	OWW3	Z	HS	TH1	TH2	AR	B	BL	SRR	CSR in	CSR
Zr-93	0.5	0.5	0.5	0	0	0	0.38788	0.35585	0	0.79215	0.5	0.4783
Nb-93m	0.5	0.5	0.5	0	0	0	0.45284	0.34379	0	0.82377	0.5	0.48141
Tc-99												
Ru-106	0.5	0.5	0.5	0	0	0	0.05208	0.96872	0.68444	0.93192	0.5	0
Cd-113m	0.5	0.5	0.5	0	0	0	0.04856	0.31419	0	0.57247	0.5	0.44075
Sb-125	0.5	0.5	0.5	0	0	0	0	0	0	0	0.5	0
Sn-126	0.5	0.5	0.5	0	0	0	0.45325	0.40115	0	0.82551	0.5	0.48022
I-129												
Cs-134	0	0	0	0	0	0	0	0	0	0	0	0
Cs-137	0	0	0	0	0	0	0	0	0	0	0	0
Ba-137m	0	0	0	0	0	0	0	0	0	0	0	0
Sm-151	0.5	0.5	0.5	0	0	0	0.45576	0.34255	0	0.82511	0.5	0.48012
Eu-152	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Eu-154	0.5	0.5	0.5	0	0	0	0	0.45193	0	0.26884	0.5	0.1582
Eu-155	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Ra-226	0.5	0.5	0.5	0.65206	0.87621	0.96984	0.78192	0.47785	0.40757	0.94511	0.5	0.50729
Ra-228	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Ac-227	0.5	0.5	0.5	0.61214	0.99997	0.99999	0.7628	0.42767	0.34073	0.93885	0.5	0.52169
Pa-231	0.5	0.5	0.5	0	0.99988	0.99998	0.43707	0	0	0.80448	0.5	0.50502
Th-229	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Th-232	0.5	0.5	0.5	0	0	0.51744	0	0	0	0	0.5	0

Table 2-2. Hanford Defined Waste Model (Revision 4) Values for Fraction of Radionuclides Precipitated in Various Waste Types (Agnew et al. 1997). (10 Sheets)

			HDW Revision 4 fraction precipitated solids by defined waste type									
Radionuclide	OWW2	OWW3	Z	HS	TH1	TH2	AR	B	BL	SRR	CSR in	CSR
U-232	0.3375	0.3032	0	0	0	0	0	0	0	0	0.77264	0.23034
U-233	0.3375	0.3032	0	0	0	0	0	0	0	0	0.77264	0.23034
U-234	0.3375	0.3032	0	0	0	0	0	0	0	0	0.77264	0.23034
U-235	0.3375	0.3032	0	0	0	0	0	0	0	0	0.77264	0.23034
U-236	0.3375	0.3032	0	0	0	0	0	0	0	0	0.77264	0.23034
U-238	0.3375	0.3032	0	0	0	0	0	0	0	0	0.77264	0.23034
U-Total	0.3375	0.3032	0	0	0	0	0	0	0	0	0.77264	0.23034
Np-237												
Pu-238	0	0	0.9871	0.8362	0	0	0	0.92873	0.77646	0.90504	0	0
Pu-239	0	0	0.9871	0.8362	0	0	0	0.92873	0.77646	0.90504	0	0
Pu-240	0	0	0.9871	0.8362	0	0	0	0.92873	0.77646	0.90504	0	0
Pu-241	0	0	0.9871	0.8362	0	0	0	0.92873	0.77646	0.90504	0	0
Pu-242	0	0	0.9871	0.8362	0	0	0	0.92873	0.77646	0.90504	0	0
Pu-Total	0	0	0.9871	0.8362	0	0	0	0.92873	0.77646	0.90504	0	0
Am-241			0.95763	0.33202	0	0	0.63163	0.92125	0.47974	0.92599		0.48479
Am-243	0	0	0.95763	0.33202	0	0	0.63163	0.92125	0.47974	0.92599	0	0.48479
Cm-242	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Cm-243	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Cm-244	0.5	0.5	0.5	0	0	0	0.18003	0.95955	0.608	0.92015	0.5	0.06708

Table 2-2. Hanford Defined Waste Model (Revision 4) Values for Fraction of Radionuclides Precipitated in Various Waste Types (Agnew et al. 1997). (10 Sheets)

Radionuclide	DE	CEM	NIT	Salt Slurry	DW	N	P3	PL2	CWZr2	BP /Cplx	BP /NCplx	PASF	Solubility Limit (Ci/L except as noted)
H-3	0	0	0	0	0	0	0	0	0	0	0	0	
C-14	0	0	0	0.664	0	0	0	0	0	0	0	0	
Ni-59	0	0	0	1	0.5513	0.5513	1	0.551	1	0	0	1	
Ni-63	0	0	0	1	0.5513	0.5513	1	0.551	1	0	0	1	
Co-60	0.5	0.5	0.5	0.5	0.5	0.5	0.9473	0.5	0	0.5	0.5	0.5	1.00E-04
Se-79	0.5	0.5	0.5	0.5	0.5	0.5	0.8701	0.5	0	0.5	0.5	0.5	2.00E-06
Sr-90				1	1	1	0.9859	0	0			1	0.034
Y-90	0	0	0	1	1	1	0.9859	0	0	0	0	1	
Zr-93	0.5	0.5	0.5	0.5	0.5	0.5	0.8653	0.5	0	0.5	0.5	0.5	1.00E-05
Nb-93m	0.5	0.5	0.5	0.5	0.5	0.5	0.7767	0.5	0	0.5	0.5	0.5	7.00E-06
Tc-99													
Ru-106	0.5	0.5	0.5	0.5	0.5	0.5	1	0.5	0.9999	0.5	0.5	0.5	5.00E-09
Cd-113m	0.5	0.5	0.5	0.5	0.5	0.5	0.9251	0.5	0	0.5	0.5	0.5	6.00E-05
Sb-125	0.5	0.5	0.5	0.5	0.5	0.5	0.5868	0.5	0	0.5	0.5	0.5	1.90E-02
Sn-126	0.5	0.5	0.5	0.5	0.5	0.5	0.8764	0.5	0	0.5	0.5	0.5	3.00E-06
I-129													
Cs-134	0	0	0	0.16	0.16	0.16	0.01	0	0	0	0	0	
Cs-137				0.16	0.16	0.16	0.01	0	0			0	
Ba-137m	0	0	0	0.16	0.16	0.16	0.01	0	0	0	0	0	
Sm-151	0.5	0.5	0.5	0.5	0.5	0.5	0.8685	0.5	0	0.5	0.5	0.5	0.007
Eu-152	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	
Eu-154	0.5	0.5	0.5	0.5	0.5	0.5	0.9648	0.5	0	0.5	0.5	0.5	5.00E-04
Eu-155	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	

Table 2-2. Hanford Defined Waste Model (Revision 4) Values for Fraction of Radionuclides Precipitated in Various Waste Types (Agnew et al. 1997). (10 Sheets)

Radionuclide	DE	CEM	NIT	Salt Slurry	DW	N	P3	PL2	CWZr2	BP /Cplx	BP /NCplx	PASF	Solubility Limit (Ci/L except as noted)
Ra-226	0.5	0.5	0.5	0.5	0.5	0.5	0.5003	0.5	0	0.5	0.5	0.5	6.20E-11
Ra-228	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	
Ac-227	0.5	0.5	0.5	0.5	0.5	0.5	0.4954	0.5	0	0.5	0.5	0.5	3.60E-10
Pa-231	0.5	0.5	0.5	0.5	0.5	0.5	0.5088	0.5	0	0.5	0.5	0.5	2.00E-09
Th-229	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	
Th-232	0.5	0.5	0.5	0.5	0.5	0.5	0	0.5	0	0.5	0.5	0.5	7.00E-07
U-232				0	0	0	0.6902	0.2085	0.493			0	
U-233				0	0	0	0.6902	0.2085	0.493			0	
U-234				0	0	0	0.6902	0.2085	0.493			0	
U-235				0	0	0	0.6902	0.2085	0.493			0	
U-236				0	0	0	0.6902	0.2085	0.493			0	
U-238				0	0	0	0.6902	0.2085	0.493			0	
U-Total				0	0	0	0.6902	0.2085	0.493			0	0.004 M
Np-237													
Pu-238				0.8	0.8	0.8	0.9845	0.8421	0.9247			0.8	
Pu-239				0.8	0.8	0.8	0.9845	0.8421	0.9247			0.8	
Pu-240				0.8	0.8	0.8	0.9845	0.8421	0.9247			0.8	
Pu-241				0.8	0.8	0.8	0.9845	0.8421	0.9247			0.8	
Pu-242				0.8	0.8	0.8	0.9845	0.8421	0.9247			0.8	
Pu-Total				0.8	0.8	0.8	0.9845	0.8421	0.9247			0.8	0.000148 g/L
Am-241							0.9968		0				3.00E-05
Am-243				0	0	0	0.9968	0	0			0	
Cm-242	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	

Table 2-2. Hanford Defined Waste Model (Revision 4) Values for Fraction of Radionuclides Precipitated in Various Waste Types (Agnew et al. 1997). (10 Sheets)

Radionuclide	DE	CEM	NIT	Salt Slurry	DW	N	P3	PL2	CWZr2	BP /Cplx	BP /NCplx	PASF	Solubility Limit (Ci/L except as noted)
Cm-243	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	
Cm-244	0.5	0.5	0.5	0.5	0.5	0.5	0.9973	0.5	0	0.5	0.5	0.5	1.00E-07

3.0 APPROACH

3.1 BACKGROUND

In the following sections, the radionuclides of interest are identified; modeling considerations, bases, and assumptions are defined; selection of fraction precipitated estimates is discussed; and the evaluation of estimates using analytical data is explained.

3.1.1 Radionuclides of Interest

Table 3-1 provides a list of the 46 radionuclides whose distribution among the 177 Hanford SSTs and DSTs has been determined to be important for future management, especially with respect to tank waste disposal. Also listed in Table 3-1 are the half-lives (in seconds) and specific activities (curies/gram) of all the 46 radionuclides. Some information is provided in Table 3-1 concerning the origin of all the 46 radionuclides; additional information on this latter topic is provided in the expanded discussion on each radionuclide in Appendix A.

The best-basis global inventory as of January 1, 1994, of the 46 radionuclides that was generated at the Hanford site is listed in Table 3-1 (Kupfer et al. 1998). The inventories for certain activation products, e.g., C-14, etc., have been updated, reflecting better production information. For certain radionuclides, e.g., C-14, Tc-99, and I-129, not all the inventory shown in Table 3-1 was disposed to the Hanford tanks. Some C-14 volatilized (as CO_2) during fuel dissolution, some Tc-99 was extracted during REDOX and PUREX process operation and was sent offsite as an impurity in the recovered uranium product, and some I-129, as well as I-131, evolved during fuel dissolution operations, but was mostly trapped on the silver reactors during downstream processing. Some of the sorbed I-129 was eventually washed from the silver reactors, and the wash solution was sent to one or more SSTs.

An accurate knowledge of the total inventory of radionuclides in all Hanford tanks is necessary in planning and performing disposal of the waste in these tanks. However, such knowledge is not necessary to make estimates of the fraction of each radionuclide that precipitated when various neutralized wastes were added to the SSTs. Solubility (fraction precipitated) estimates apply to whatever percent of the total amount of each radionuclide that found its way into the SSTs.

Table 3-1. Radionuclides of Concern to Disposal of Hanford Site Tank Wastes. (2 Sheets)

Half-life		Ci per gram	Type	Total inventory[1]
Radionuclide	Sec			
H-3	3.897E+08	9.6513E+03	3	3.40E+04
C-14	1.808E+11	4.458E+00	1	4.81E+03
Ni-59	2.525E+12	7.575E-02	3	9.34E+02
Co-60	1.663E+08	1.131E+03	1	1.3E+04
Ni-63	2.903E+09	6.169E+01	3	9.20E+04
Se-79	2.540E+13	5.623E-03	3	7.73E+02
Sr-90	9.190E+08	1.364E+02	3	7.16E+07
Y-90	2.304E+05	5.441E+05	3	7.16E+07
Zr-93	4.828E+13	2.513E-03	3	3.63E+03
Nb-93m	5.081E+08	2.388E+02	3	2.69E+03
Tc-99	6.722E+12	1.696E-02	3	3.26E+04
Ru-106	3.181E+07	3.346E+03	3	1.04E+05
Cd-113m	4.604E+08	2.169E+02	3	1.69E+04
Sb-125	8.741E+07	1.033E+03	3	2.08E+05
Sn-126	7.890E+12	1.135E-02	3	1.19E+03
I-129	4.950E+14	1.766E-04	3	6.30E+01
Cs-134	6.507E+07	1.294E+03	3	8.89E+04
Cs-137	9.467E+08	8.700E+01	3	4.64E+07
Ba-137m	1.531E+02	5.380E+08	3	4.39E+07
Sm-151	2.840E+09	2.631E+01	3	2.75E+06
Eu-152	4.292E+08	4.370E+02	3	1.48E+03
Eu-154	2.714E+08	2.700E+02	3	1.47E+05
Eu-155	1.565E+08	4.652E+02	3	1.36E+05
Ra-226	5.049E+10	9.888E-01	2	6.31E-02
Ac-227	6.871E+10	7.234E+01	2	8.76E+01
Ra-228	2.114E+08	2.341E+02	2	7.71E+02
Th-229	2.316E+11	2.127E-01	2	1.18E+00
Pa-231	1.034E+12	4.724E-02	2	1.56E+02
Th-232	4.434E+17	1.097E-07	2	2.11E+00
U-232	2.272E+09	2.141E+01	2	1.23E+02
U-233	5.002E+12	9.682E+03	2	4.76E+02

Table 3-1. Radionuclides of Concern to Disposal of Hanford Site Tank Wastes. (2 Sheets)

Half-life		Ci per gram	Type	Total inventory[1]
Radionuclide	Sec			
U-234	7.716E+12	6.299E-03	2	3.46E+02
U-235	2.221E+16	2.162E-06	2	1.45E+01
U-236	7.389E+14	6.471E-05	2	9.57E+00
Np-237	6.753E+13	7.050E-04	2	1.41E+02
U-238	1.410E+17	3.362E-07	2	3.22E+02
Pu-238	2.769E+09	1.712E+01	2	2.77E+03
Pu-239	7.594E+11	6.217E-02	2	2.91E+04
Pu-240	2.063E+11	2.279E-01	2	8.93E+03
Pu-241	4.544E+08	1.030E+02	2	2.29E+05
Am-241	1.364E+10	3.433E+00	2	6.99E+04
Pu-242	1.221E+03	3.819E-03	2	1.16E+00
Am-242	1.410E+07	3.307E+03	2	7.70E+01
Am-243	2.329E+11	1.999E-01	2	9.34E+00
Cm-243	8.894E+08	5.163E+01	2	1.00E+01
Cm-244	5.715E+08	8.092E+01	2	2.42E+02

Notes:
1 = activation product
2 = actinides and daughters
3 = fission product

[1] Data from Kupfer et al. (1998).

3.2 HANFORD DEFINED WASTE MODEL CONSIDERATIONS

The revised solubility values devised in this report are intended for use within the present HDW model framework. A good working knowledge of the essentials of the HDW model is a requirement for appreciation of the new radionuclide solubility estimates presented in this report.

3.2.1 Model Synopsis and Highlights

Figures 3-1 and 3-2 (Agnew et al. 1997) together with the accompanying text provide a brief introduction to the construction of the HDW model. The text is paraphrased from that provided on page 3 of Revision 4 of the HDW model report.

The HDW model begins with a process and transaction data set derived from a variety of sources. A balanced tank-by-tank quarterly summary transaction spreadsheet is derived called the Waste Status and Transaction Record Summary (WSTRS). Using these fill records, the Tank Layer Model (TLM) provides a definition of the sludge and saltcake layers within each tank. The TLM is a volumetric and chronological description of tank inventory based on a defined set of waste solids layers. Each solids layer is attributed to a particular waste addition. Finally, the Supernatant Mixing Model (SMM) calculates the supernatant concentration within each tank using information from WSTRS and the TLM.

The WSTRS, TLM, and SMM together determine the waste inventory of each tank as a linear combination of sludge and supernatant inventories. The TLM and SMM compositions describe each waste stream based on process historical information.

Revision 4 of the HDW model report should be studied for further details of the construction and utilization of the HDW model.

3.2.2 Hanford Defined Waste Model Waste Types

One of the important features of the HDW model is that it provides a basis set of wastes that can be used to define all of the wastes that were introduced into the SSTs or, in the case of PUREX process wastes generated in the period 1983 through 1988, directly into DSTs. Appendix A of Revision 4 of the HDW model report provides a list of the Hanford defined wastes; this list, with a modified format, is reproduced in this report as Table 3-2.

For use in this report, Table 3-3 provides a greatly simplified list of Hanford waste types. The waste types listed in Table 3-3 include all the 44 waste types listed in Appendix A of Revision 4 of the HDW model report.

Figure 3-1. Schematic of Overall Hanford Defined Waste Model Strategy. (Reproduced from Agnew et al. 1997)

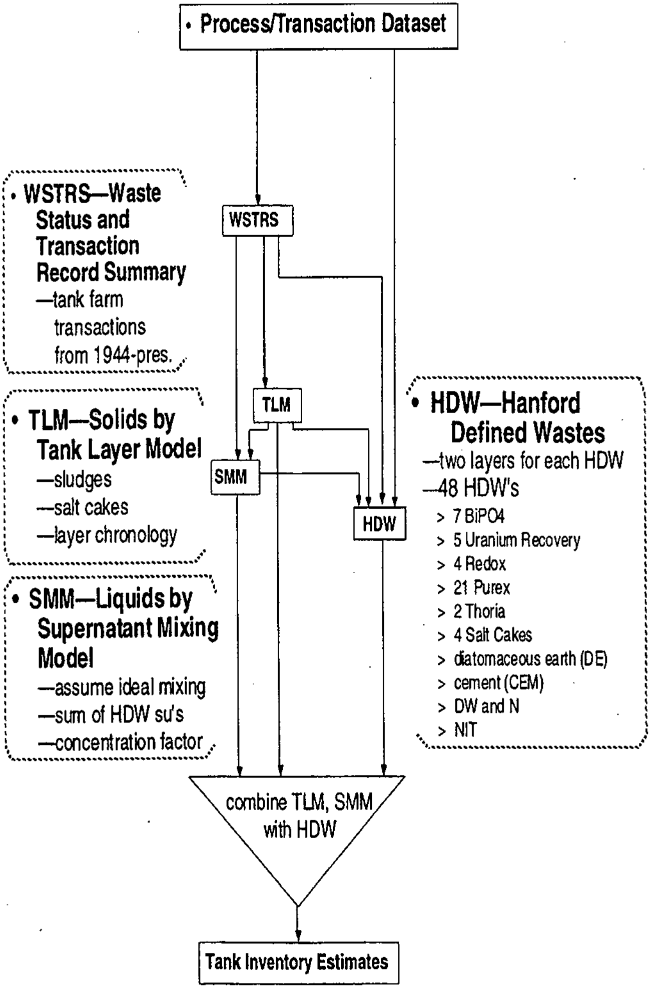


Figure 3-2. Block Diagram of Hanford Defined Waste Model Spreadsheet. (Reproduced from Agnew et al. 1997)

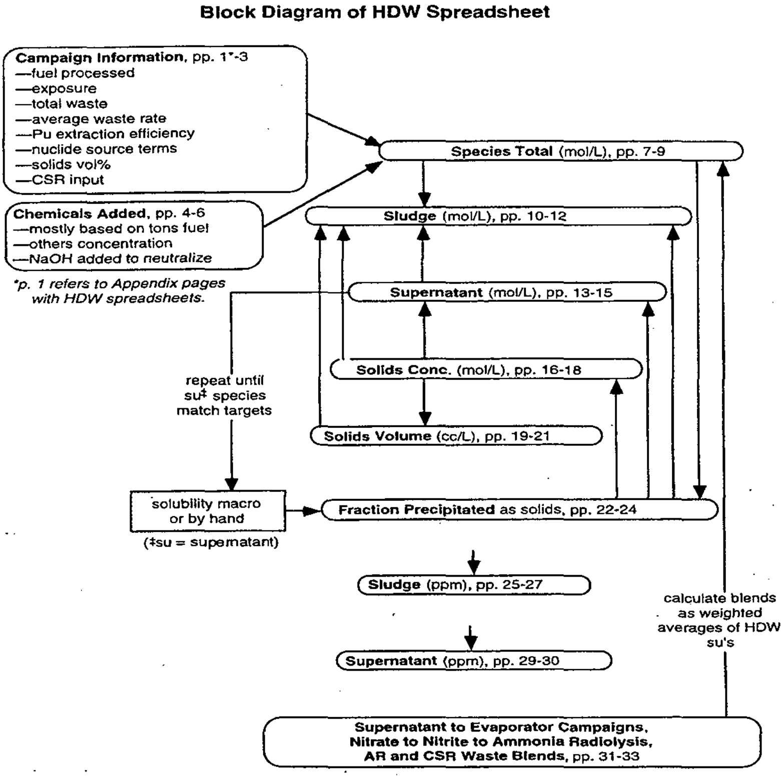


Table 3-2. Hanford Defined Wastes. (2 Sheets)

Waste type	Comments
$BiPO_4$ and uranium recovery process wastes	
MW1	1944 to 1949
MW2	1950 to 1956
1C1	1944 to 1949, includes cladding waste
1C2	1950 to 1956, includes cladding waste
2C1	1944 to 1949
2C2	1950 to 1956
224	Lanthanum fluoride finishing waste, U plant waste
UR	Uranium recovery plant waste
PFeCN1	In-plant ferrocyanide scavenged waste
PFeCN2	In-plant ferrocyanide scavenged waste
TFeCN	AR vault ferrocyanide scavenged waste
1CFeCN	1C scavenged waste
REDOX and PUREX process wastes	
R1	1955 to 1962
R2	1958 to 1966
P1	1955 to 1962
P2	1963 to 1967
P2'	1968 to 1972
Th1	1966
Th2	1970
P3	1983 to 1988
PL1	1956 to 1976
PL2	1987 to 1988
Z	Derived from analysis of Tank 241-SY-102
CWR1	Al clad fuel, 1952 to 1960
CWR2	Al clad fuel, 1961 to 1972
OWW1	1956 to 1962
OWW2	1963 to 1967
OWW3	1968 to 1972
AR	"Washed" PUREX process sludge

Table 3-2. Hanford Defined Wastes. (2 Sheets)

Waste type	Comments
REDOX and PUREX Process Wastes (Continued)	
B	PUREX acid waste
BL	Low Level waste from B Plant
SRR	Strontium recovery waste
CSR	Cesium recovery waste
PASF	PUREX ammonia scrubber feed
HS	Strontium semiworks waste
Other wastes	
DE	Diatomaceous earth
CEM	Cement
NIT	Partial neutralized feed
DW	Decontamination waste
N	N-Reactor decontamination waste
Saltcakes	
BSltCk	Saltcake from 242-B operation
T1SltCk	Saltcake from 242-T operation
RSltCk	Saltcake from S and SX farm operation
BYSltCk	Saltcake from in-tank solidifications

Notes:

PUREX = Plutonium-uranium extraction
REDOX = Reduction and oxidation

[1] Agnew et al. (1997).

Table 3-3. Classification of Hanford Defined Waste Model Waste Types.

Class	HDW model waste types
Process high-activity waste	
$BiPO_4$ process	MW1, MW2, 1C1, 1C2, 2C1, 2C2, 224, and UR
Other processes	R1, R2, P1, P2, P2', Th1, Th2, P3, PL1, PL2, and Z
Cladding wastes	
Aluminum	CWR1, CWR2, CWP1, and CWP2
Zircaloy	CWZr1 and CWZr2
Miscellaneous wastes	
Solid wastes	
Ferrocyanide solids	PFeCN1, PFeCN2, TFeCN, and 1CFeCN
Other solids	DE, CEM, and AR
Complexed waste	HS and SRR
Other liquid wastes	OWW1,OWW2, OWW3, NIT, BL, CSR, DW, N, PASF, and B

In addition to the 44 waste types called out in Table 3-3, Appendix A of Revision 4 of the HDW model report also lists four saltcakes designated as waste types not calculated by the SMM: BSltCk, BYSltCk, T1SltCk, and RSltCk. Saltcakes originated as the result of evaporation of supernatant liquids from wastes previously introduced into the SSTs. They are not included in the suite of waste types addressed in Appendix A of this report that provides detailed consideration of the chemical behavior of the 46 radionuclides of interest.

3.3 BASES AND ASSUMPTIONS

Bases and assumptions used to achieve the objectives of this study included the following:

1. The majority of radionuclides introduced into SSTs were from neutralized ($pH > 10$) high-activity waste (HAW) resulting from the Hanford site $BiPO_4$, Uranium Recovery, REDOX, and PUREX processes operated in the period 1943 to 1988.

2. In general, insoluble radionuclides in the SSTs reported to the sludge phase while those radionuclides which were soluble in the alkaline media in the SSTs remained in the supernatants.

3. Radionuclides that reported to the sludge phase initially generally remained there and were not removed during the many and various transfers into and out of any particular SST.

4. Radionuclides that were soluble in the alkaline supernatant resulting after settling of insoluble solids (sludge) remained soluble when supernatants were transferred from tank to tank and also during evaporation operations. The soluble radionuclides partitioned between the saltcake and the highly alkaline concentrate produced from the evaporator-crystallizer operations. Thus, saltcake now stored in many SSTs contains soluble radionuclides.

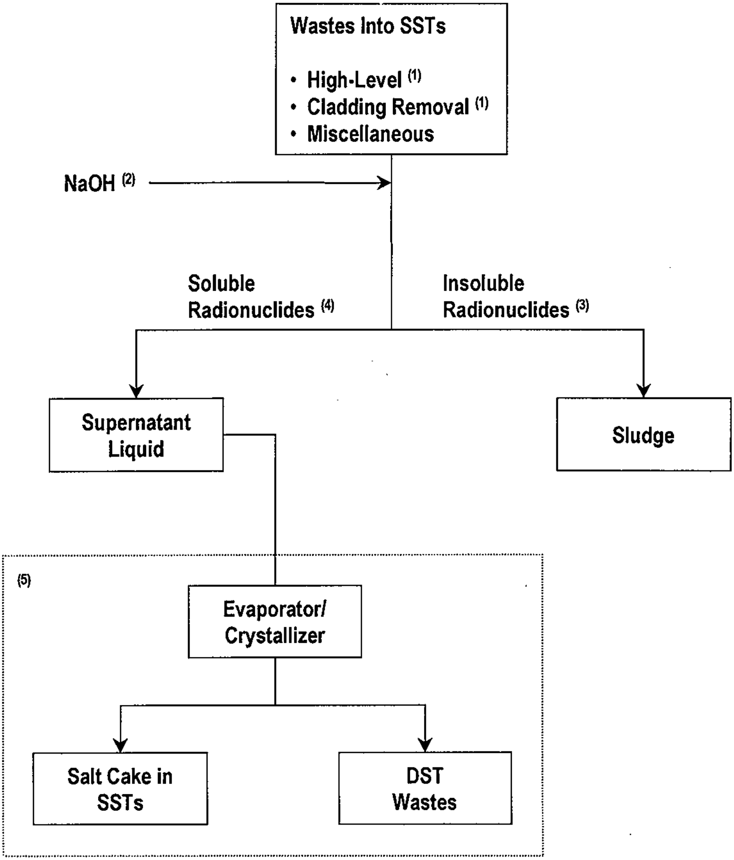
5. Revised radionuclide solubility estimates for SSTs are considered separately from those for DSTs. This is because all of the wastes in the 28 DSTs have been sampled (some many times) and analyzed for various (not all) radionuclides. In those cases where analytical data are available, radionuclide inventories calculated from the actual analytical data obviate the need for any estimation of radionuclide solubilities and can be used to estimate solubilities in unsampled tanks with similar wastes.

3.4 SELECTION OF FRACTION PRECIPITATED ESTIMATES

Figure 3-3 is provided to aid in describing and clarifying the approach taken in this report to provide what are presently believed to be best-basis estimates of the fraction of each of the 46 radionuclides that precipitated when various wastes were added to the 149 SSTs. As illustrated in Figure 3-3, known or inferred chemistry of each of 28 elements (46 radionuclides) in the alkaline media in SSTs is the primary tool used to arrive at solubility estimates. To the extent suitable analytical data were available, such data were used to empirically quantify solubility estimates, rather than using those obtained from theoretical considerations.

The resulting new fraction precipitated (solubility) estimates are intended to be used in refining the HDW model to arrive at new predicted inventories of radionuclides in Hanford tank sludges.

Figure 3-3. Logic Followed in Deriving Radionuclide Solubility Estimates.



Notes:

1. From fuel reprocessing
2. If needed to make alkaline
3. Estimated from chemistry and available waste analysis
4. One minus insoluble fraction
5. HDW model predictions

It is clear from Figure 3-3 and the immediately preceding discussion that, in this report, consideration of the detailed chemistry of the 46 radionuclides is exclusively focused on estimating the fraction of each radionuclide that reported to the sludge phase in all 149 SSTs. But, what of the radionuclide content of saltcakes and the wastes in the DSTs? Obviously, it is desirable and necessary to predict the radionuclide content of these latter wastes. For this goal, two important points need to be recalled and discussed.

Firstly, both saltcakes and the majority[1] of the DST wastes resulted from simple evaporation and concentration of supernatants in the SSTs. These supernatants, by definition, contained soluble radionuclides. Thus, the general expectation is that radionuclides in saltcakes and DST wastes continue to be soluble. One exception to this expectation is that radionuclides which precipitated from complexed concentrates as the result of radiolytic and/or thermal degradation of organic materials in complexed wastes, which as the name implies, form strong complexes with radionuclides such as actinides and Sr-90 as well as with various nonradioactive metals ions, e.g., Fe(III), Ni(II), etc., and prevented their precipitation even at high NaOH concentrations. As the organic complexants were destroyed, the complexed metal ions, both inert and radioactive, were released and precipitated as a sludge similar to those in many SSTs. Another, somewhat trivial, exception is that when dissolved in water some saltcakes appear to contain some insoluble radionuclides. Such radionuclides are really associated with the small amounts of sludges which are often entrained in the saltcake.

Secondly, the HDW model, as presently developed, is already configured to calculate and predict the way soluble radionuclides in concentrated SST supernatants were split between saltcake and DST wastes. Thus, any change in the specification of the solubility (fraction precipitated) of a radionuclide as it was introduced into the SSTs is reflected immediately in the amount, i.e., more or less, available to be partitioned to saltcakes and DSTs.

Other than providing new starting inventories of soluble radionuclides, no effort was made in this report to change the way in the which the HDW model presently partitions soluble radionuclides between saltcakes and DST wastes. Such changes might have included, for example, "force fitting" the model to predict exactly the inventories of Cs-137 and Sr-90 now believed from analytical data to be in each of the 28 DSTs. Changes to the basic framework of the HDW model were deemed outside the scope of this report.

3.5 RELEVANT ANALYTICAL DATA

In the discussion in Section 3.4, it was noted that, where available, relevant data from analysis of tank wastes were used to evaluate radionuclide best-basis solubility estimates based on known chemistry. Utilization of analytical data to determine fraction precipitated factors is a departure from the practice followed in the HDW model (Revision 4) report to establish radionuclide solubility estimates.

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[1] Some PUREX process wastes were added directly to DSTs 241-AW-103, 241-AW-105, 241-AZ-101, and 241-AZ-102. Solids (sludges) in these tanks contain various insoluble radionuclides.

At the time this report was prepared (September 1998), wastes in all the DSTs and in many SSTs have been sampled and analyzed. Thus, it appears that abundant analytical data are available to aid in making best-basis estimates of the solubility of all radionuclides in wastes added to the SSTs. Closer inspection and evaluation of the available analytical data shows that very few of them are of any direct use in establishing best-basis radionuclide solubility estimates.

This is because the majority of the radionuclide analytical data for SST sludge samples tell what is in a given tank now. The data are not at all helpful in determining the soluble and insoluble fractions of radionuclides at the time the waste was introduced into any particular SST. In addition, for many radionuclides there are no data at all, or, at least, only fragmentary, scattered analyses.

The analytical data for waste solids now in DSTs 241-AW-103, 241-AW-105, 241-AZ-101, and 241-AZ-102 are an exception to that portrayed in the preceding paragraph. The former two DSTs still contain, almost exclusively, solids deposited when neutralized zircaloy cladding wastes were introduced into them. And, DSTs 241-AZ-101 and 241-AZ-102 still contain, almost exclusively, sludges laid down when neutralized PUREX process HAW was introduced into them. PUREX process wastes added to these DSTs were generated in the period 1983-1988. Alkaline supernatants in some of these four DSTs have been removed and evaporated; the concentrates were not returned to the same tanks.

The solid wastes in DSTs 241-AW-103, AW-105, AZ-101, and AZ-102 have all been core sampled and analyzed for some, unfortunately not all, radionuclides. Liquid supernatants in these tanks were also sampled before they were removed; supernatants were analyzed for only very few radionuclides. Radionuclide inventories calculated from the analytical data are summarized here in Tables 3-4, 3-5, 3-6, and 3-7. Complete analytical data for wastes in the four DSTs of interest are reported in Kupfer et al. (1998). This reference should be consulted, particularly concerning limitations on the accuracy of tank inventories calculated from the existing analytical data.

Table 3-4. Radionuclide Inventory Data for Wastes in Tank 241-AW-103.[1]

Radionuclide	Ci		% in supernatant
	Sludge	Supernatant	
C-14	1.25E+00	NA	
Sr-90	1.96E+04	1.29E-01	0.00066.
Y-90	1.96E+04	1.29E-01	0.00066
Cs-137	1.20E+05	1.22E+04	9.24
Ba-137m	1.14E+05	1.15E+04	9.20
Np-237	<8.82E-01	NA	
Pu-239/240	1.35E+03	<6.67E-03	<4.94E-05
Am-241	2.38E+02	<9.68E-01	4.10E-01

Notes:

NA = not analyzed

[1] Data taken from Kupfer et al. (1998).

Table 3-5. Radionuclide Data for Wastes in Double-Shell Tank 241-AW-105.[1]

Radionuclide	Ci		% in supernatant
	Sludge	Supernatant	
H-3	1.36E+01	NA	
C-14	2.26E+00	NA	
Co-60	4.86E+02	3.17E-01	0.07
Sr-90	2.63E+05	2.67E+01	0.01
Y-90	2.63E+05	2.67E+01	0.01
Tc-99	1.08E+02	NA	
Sb-125	1.86E+03	NA	
Cs-134	9.58E+01	NA	
Cs-137	5.32E+05	1.36E+03	2.4
Ba-137m	5.03E+05	1.23E+03	2.4
Eu-154	2.73E+02	NA	
Eu-155	1.99E+02	NA	
Pu-238	6.91E+02	NA	
Pu-239/240	8.31E+02	9.65E-02	0.01
Am-241	4.72E+02	5.81E-02	0.01
Cm-243/244	1.84E+02	NA	

Notes:

NA = not analyzed

[1] Data taken from Kupfer et al. (1998).

Table 3-6. Radionuclide Data for Waste in Double-Shell Tank 241-AZ-101.[1]

Radionuclide	Total added to tank Ci[2]	Inventory[3]		Percent of radionuclides in[4]	
		Sludge Ci	Supernatant Ci	Sludge	Supernatant
H-3	2.59E+04	4.0E+00	NA	0.015	
C-14	3.34E+02	4.33E-01	NA	0.13	
Co-60	4.61E+03	3.57E+03	NA	77	
Se-79	4.13E+01	5.53E-01	NA	1.3	
Sr-90	6.36E+06	7.38E+06	NA	116	
Tc-99	1.10E+03	5.81E+02	1.23E+03	53	112
Ru-106	1.06E+05	3.65E+03	NA	3.4	
Sb-125	1.31E+05	1.95E+04	NA	15	
I-129	2.78E+00	7.14E+00	NA	260	
Cs-134	4.34E+04	4.58E+02	NA	1.1	
Cs-137	7.43E+06	2.82E+05	5.37E+05	3.8	75
Eu-154	5.76E+04	1.02E+04	NA	18	
Np-237	1.96E+01	1.26E+01	NA	64	
Pu-239	1.50E+03	9.58E+02	1.47E-01	64	0.01
Pu-240	4.60E+02	2.72E+02	NA	59	
Am-241	2.26E+04	8.20E+02	<1.05E+01	303	<0.046
Cm-242	2.54E+01	1.16E+03	NA	4,600	

Notes:

NA = not analyzed

[1] The tank contains neutralized PUREX process HAW produced in the period 1983 to 1988
[2] Calculated from fuel irradiation history and ORIGEN code
[3] Calculated from analytical data reported in Kupfer et al. (1998)
[4] Percent of calculated total amount added to tank.

Table 3-7. Radionuclide Data for Wastes in Double-Shell Tank 241-AZ-102.[1]

Radionuclide	Total in tank Ci[2]	Inventory[3]		Percent of radionuclides in[4]	
		Sludge Ci	Supernatant Ci	Sludge	Supernatant
C-14	8.30E-01	8.00E-01		96	
Sr-90	7.22E+06	6.37E+06	5.80E+03	88	0.08
Tc-99	5.99E+02	2.20E+02	3.55E+02	38	59
Cs-137	4.03E+06	3.43E+05	3.37E+06	8.5	84
Np-237	6.01E+01	4.92E+01		82	
Pu-238	1.81E+02	1.75E+02		97	
Pu-241	1.71E+04	1.64E+04		96	
Am-241	3.77E+04	3.61E+04	<1.53E+01	96	<0.04
Uranium[5,6]	9.58E+03	4.70E+03	4.88E+03	49	52

Notes:

[1] Data taken from Kupfer et al. (1998)
[2] Calculated from analyses of core samples
[3] Actual analytical data
[4] Of total calculated to be in tank
[5] Sum of all uranium isotopes
[6] In kilograms.

The analytical data presented in Tables 3-4 through 3-7 offer convincing evidence that >99 percent of Sr-90, americium, and plutonium all precipitated from neutralized PUREX process HAW and zircaloy cladding waste. Such evidence strongly supports the expectations from known chemistry of strontium and actinides in alkaline tank waste.

The analytical data listed in Tables 3-4 through 3-7 have certain failings that limit their utility in estimating radionuclide solubilities. For example, the paucity of analytical data for radionuclides in supernatant phases is a major shortcoming. There are also minor difficulties with the recorded inventories of radionuclides in sludge phases due to the presence of a small, but not insignificant, heel of solids resulting from wastes introduced into the DSTs 241-AW-103, 241-AW-105, 241-AZ-101, and 241-AZ-102 prior to the introduction, in 1983 through 1988, of alkaline PUREX process HAW and cladding wastes. Finally, ORIGEN code computations (Table 3-6) of inventories for certain radionuclides added to any particular tank are uncertain due to partial losses that occurred during final seperations processing. But, in spite of all these shortcomings, the analytical data listed in Tables 3-4 through 3-7 are the only data available and that are relevant to the determination of radionuclide solubility behavior and were used in preparing this report.

In addition to the data cited in Tables 3-4 through 3-7, some use was made in this study of data obtained by Lumetta et al. (1998) concerning water and dilute NaOH treatment of actual tank sludges. In particular, these latter data were used to (a) illustrate that all SST sludges examined contained at least some Cs-137 and Tc-99, and (b) that, in most instances, simple washing with water and/or dilute NaOH solutions removed most of the radiocesium and radiotechnetium.

4.0 APPLICATION AND EVALUATION OF NEW RADIONUCLIDE SOLUBILITY ESTIMATES

The HDW model (Revision 4) was varied using Cs-137 and Sr-90 fraction precipitated solids values selected for each HDW type based on process chemistry. The model normally calculates these values from a single solubility limit defined for each species. Three cases were examined with different sets of fraction precipitated solids values. The model variations are called Case 1, Case 2 and Case 3. Comparisons are made to the HDW model (Revision 4) as well as to tank sample data. The sample data resulted from the analysis of from one to eight cores from each of 47 SSTs and 13 DSTs. The DSTs chosen were those with little or no waste transfers between sampling and 1994, the date of final transactions used in the model. The criterion for judging the quality of model predictions is the degree to which predictions agree with inventories determined from analysis of actual tank waste.

4.1 LIMITATIONS AND EVALUATION APPROACH

The new best-basis radionuclide solubility estimates provided in this report are intended specifically for use in the present HDW model to obtain revised predictions of the inventory of the 46 radionuclides of interest in all 177 Hanford tanks. The quality of such revised inventory predictions is of obvious interest. The accepted criterion for judging the quality of model predictions in this report is the degree to which such predictions agree with inventories determined from analyses of actual tank wastes.

4.1.1 Limitations

There are important factors to be considered in comparing analytically-determined radionuclide inventories to those predicted by the HDW model, even using the revised radionuclide solubility estimates given in this report. These considerations derive from limitations both of the analytical data and of the HDW model itself.

The principal limitation of the HDW model, in its present form, center around two faults: (a) Missing waste transaction data, and, (b) misidentification of waste types in a given SST. Agnew et al. (1997) explicitly recognized in Revision 4 of the HDW model report that incomplete historical records prevented them from recording all waste transactions in the WSTRS report. That Agnew et al. 1997 apparently misidentified both the type and amount of certain wastes introduced into some SSTs came to light during the recently completed independent major effort to provide best-basis estimates of the inventory of nonradioactive components in all 177 Hanford tanks (Kupfer et al. 1998).

There are many significant limitations to the existing analytical data base for radionuclides in SST and DST wastes. Probably the most important are as follows:

1. Not all SST wastes have been sampled.
2. Wastes in the SSTs are very heterogeneous, both vertically and horizontally, as the result of having been deposited in discrete layers over long time periods. Tank inventories calculated from analyses of a limited number of core samples, usually two, taken at random positions within the tank may be biased by these heterogenities.
3. Sample-based inventories are also potentially biased because of analysis errors, such as instrument limitations, and errors in analytical procedures.
4. There are no analytical data for many radionuclides, e.g., Pa-231, Ac-227, etc.
5. For many radionuclides, there are only scattered and fragmentary analytical data, e.g., Se-79, I-129, C-14, etc.

But, on the positive side:

1. Wastes in the 13 DSTs used in this analysis have been sampled and analyzed for Cs-137 and Sr-90.
2. Samples taken from the 47 SSTs used in this analysis have been analyzed for Cs-137 and Sr-90.

4.1.2 Evaluation Approach

Given the particulars just detailed, it is not surprising that the initial evaluation of newly-formulated radionuclide solubility estimates has focused on comparing analytically-derived tank inventories of Cs-137 and Sr-90 with HDW model predictions using both the original (Agnew et al. 1997) and the new solubility estimates. Three different sets of fraction precipitated estimates were evaluated for both Sr-90 and Cs-137. These data sets, termed Case 1, Case 2 and Case 3 are presented in Tables 4-1 and 4-2. These cases represent different estimates of the fractions of Cs-137 and Sr-90 that precipitated when various alkaline wastes were added to the SSTs. The Case 3 estimates are the best-basis estimates listed in Table 2-1. The Case 1 and Case 2 fraction precipitated estimates were made to help judge the sensitivity of calculated Cs-137 and Sr-90 inventories to selected changes in estimates of fractions of these two radionuclides that precipitated in the SSTs.

Table 4-1. Estimates of Sr-90 Fraction Precipitated Solids for Hanford Defined Wastes.

HDW model waste types[1]	Fraction of Sr-90 precipitated case 1	Fraction of Sr-90 precipitated case 2	Fraction of Sr-90 precipitated case 3
Process HAW			
$BiPO_4$ process[2]	0.98	0.85	0.98
Other processes[3]	0.98	0.85	0.98
Cladding wastes			
Aluminum[4]	0.98	0.85	0.98
Zircaloy[5]	0.98	0.85	0.98
Miscellaneous wastes			
Solid wastes			
Ferrocyanide solids[6]	0.0	0.0	0.0
Other solids[7]	1.0	0.85	0.98
Complexed waste[8]	0.0	0.0	0.0
Other liquid wastes[9]			

Notes:

HAW = High-activity waste
HDW = Hanford Defined Waste

[1] After addition of NaOH
[2] Includes HDW Model (Revision 4) Waste Types: MW1, MW2, 1C1, 1C2, 2C1, 2C2, 224, and UR
[3] Includes HDW Model (Revision 4) Waste Types: R1, R2, P1, P2, P2', Th1, Th2, P3, PL1, PL2, and Z
[4] Includes HDW Model (Revision 4) Waste Types: CWR1, CWR2, CWP1, and CWP2
[5] Includes HDW Model (Revision 4) Waste Types: CWZr1 and CWZr2
[6] Includes HDW Model (Revision 4) Waste Types: PFeCN1, PFeCN2, TFeCN, and 1CFeCN
[7] Includes HDW Model (Revision 4) Waste Types: DE, CEM, and AR
[8] Includes HDW Model (Revision 4) Waste Types: HS and SSR
[9] Includes HDW Model (Revision 4) Waste Types: OWW1, OWW2, OWW3, NIT, BL, CSR, DW, N, PASF, and B.

Table 4-2. Estimates of Cs-137 Fraction Precipitated Solids for Hanford Defined Wastes.

HDW model waste types[1]	Fraction of Cs-137 precipitated case 1	Fraction of Cs-137 precipitated case 2	Fraction of Cs-137 precipitated case 3
Process HAW			
$BiPO_4$ process[2]	0.25	0.1	0.1
Other processes[3]	0.25	0.1	0.1
Cladding wastes aluminum[4]	0.0	0.1	0.0
Zircaloy[5]	0.95	0.1	0.3
Miscellaneous wastes			
Solid wastes			
Ferrocyanide solids[6]	1.0	0.98	0.98
Other solids[7]	1.0	0.0	0.98
Complexed waste[8]	0.0	0.0	0.0
Other liquid wastes[9]	0.0	0.0	0.0

Notes:

HAW = High-activity waste
HDW = Hanford Defined Waste

[1] After addition of NaOH
[2] Includes HDW Model (Revision 4) Waste Types: MW1, MW2, 1C1, 1C2, 2C1, 2C2, 224, and UR
[3] Includes HDW Model (Revision 4) Waste Types: R1, R2, P1, P2, P2', Th1, Th2, P3, PL1, PL2, and Z
[4] Includes HDW Model (Revision 4) Waste Types: CWR1, CWR2, CWP1, and CWP2
[5] Includes HDW Model (Revision 4) Waste Types: CWZr1 and CWZr2
[6] Includes HDW Model (Revision 4) Waste Types: PFeCN1, PFeCN2, TFeCN, and 1CFeCN
[7] Includes HDW Model (Revision 4) Waste Types: DE, CEM, and AR
[8] Includes HDW Model (Revision 4) Waste Types: HS and SSR
[9] Includes HDW Model (Revision 4) Waste Types: OWW1, OWW2, OWW3, NIT, BL, CSR, DW, N, PASF, and B.

Performance measures were defined to provide a basis of comparison among the models. Conventional scatter diagrams of model versus sample values were tried initially to compare model performance. When applied to the 60 tanks, the results were inconclusive due to the high degree of randomness; but the diagrams provided a basis for a refined approach. The next performance measures that were examined included model to sample ratio diagrams and log of model to sample ratio diagrams with the sixty sampled tanks ordered on the horizontal axis. Again, these results were difficult to interpret due to random variations among tanks. The next step was to sort the sampled tanks in order of increasing performance measure. This "sorted log ratio" performance measure was then used to compare several models on same graph.

Since the sorted log ratio is weighted equally for all sampled tanks, an additional performance measure was developed to compare model performance weighted by cumulative curie inventory. Tables were used to accumulate curie inventories with model-to-sample curie ratios less than 2, 4, 8 and 10.

4.2 STRONTIUM-90 INVENTORY COMPARISONS

Sr-90 inventory predictions from each case are compared with HDW (Revision 4) and with analytical data.

4.2.1 Strontium-90 Comparison with Hanford Defined Waste (Revision 4) Predictions

The Sr-90 inventory predictions of Case 1, 2 and 3 are compared to HDW (Revision 4) by ordering the tanks by increasing HDW (Revision 4) inventory. Figure 4-1 presents the results. The Case 1 results are essentially identical to Case 3 and are not plotted for clarity. The fraction precipitated solids adjustments raised the Sr-90 prediction for almost every low inventory tank and lowered the prediction for almost every tank with over 100,000 curies Sr-90 inventory.

4.2.2 Strontium-90 Comparison with Analytical Data

The sorted log ratio measure was used to compare the Sr-90 performance relative to analytical data for the cases. Figure 4-2 presents the results for HDW (Revision 4), Case 2 and Case 3. The Case 1 results are essentially identical to Case 3 and are not plotted for clarity.

A goal is to have all predictions at least within a factor of ten of the analytical data; points with a performance measure between minus one and plus one meet this criterion. Note at the left side of the graph that nearly all of the tanks that had very low HDW (Revision 4) Sr-90 predictions relative to analytical data now have predictions within the criteria. For very high Sr-90 predictions relative to analytical data, one additional tank now exceeds the criteria.

Table 4-3 compares HDW (Revision 4) and Case 3 by categorizing the Sr-90 predictions by proximity to sample values. The categories are model-to-sample ratio range between one-half and two, between one-fourth and four, between one-eighth and eight, and between one-tenth and ten. The results are expressed as fraction of sampled tank Sr-90 inventory (all sampled tanks) and percent of sampled tanks. Case 3 increases from 75 percent to 84 percent the fraction of sampled tank inventory with predictions within a factor of four of sample. Case 3 reduces the fraction of sampled tanks outside the one-tenth to ten range from 25 percent to 12 percent.

Figure 4-1. Comparison of Different Hanford Defined Waste Model Predictions of Strontium-90 for All Sampled Tanks.

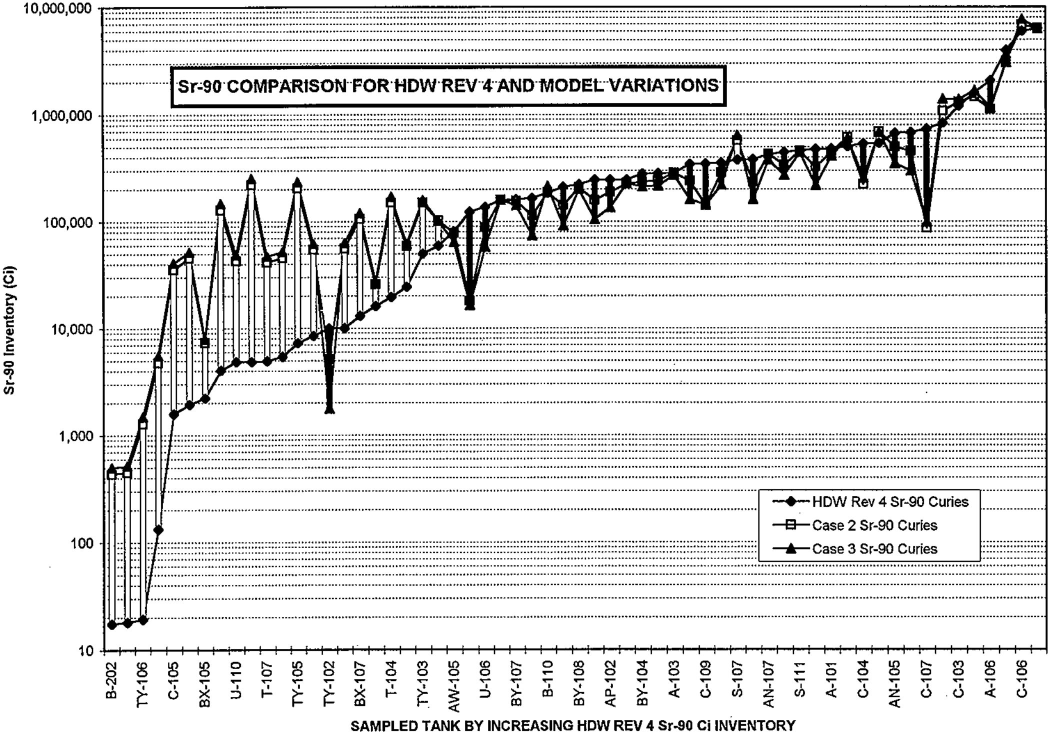


Figure 4-2. Hanford Defined Waste Model Comparison for Strontium-90 for All Sampled Tanks.

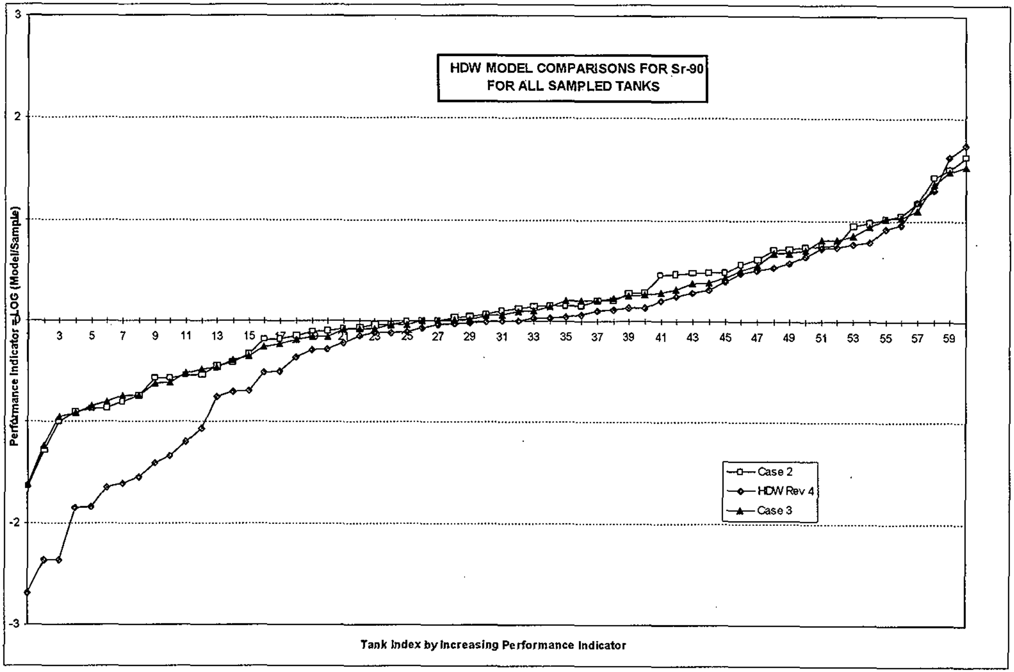


Table 4-3. Comparison of Stronium-90 Performance for Hanford Defined Waste Revision 4 and Case 3.

Model to sample ratio range	HDW Revision 4		Case 3	
	Fraction of sampled tank Ci inventory	Percent of sampled tanks	Fraction of sampled tank Ci inventory	Percent of sampled tanks
Model one half to two times sample	0.629	43.3%	0.636	45.0%
Model one quarter to four times sample	0.749	60.0%	0.842	70.0%
Model one eighth to eight times sample	0.918	71.7%	0.903	85.0%
Model one tenth to ten times sample	0.920	75.0%	0.916	88.3%
Beyond (outlier)	0.080	25.0%	0.084	11.7%

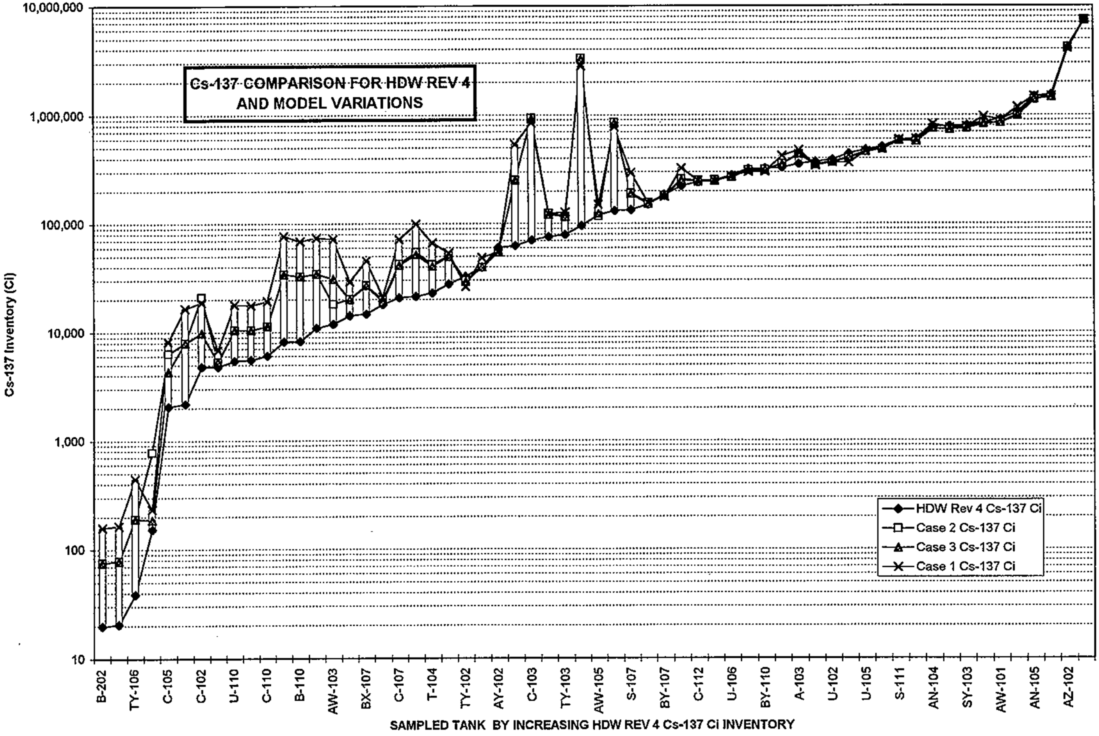
4.3 CESIUM-137 INVENTORY COMPARISONS

Cs-137 inventory predictions from each case are compared with HDW (Revision 4) and with analytical data.

4.3.1 Cesium-137 Comparison with Hanford Defined Waste (Revision 4) Predictions

The Cs-137 inventory predictions of Cases 1, 2 and 3 are compared to HDW (Revision 4) by ordering the tanks by increasing HDW (Revisoin 4) inventory. Figure 4-3 presents the results. The fraction precipitated solids adjustments raised the Cs-137 prediction for almost every low inventory tank and left the prediction essentially unchanged for every tank with over 200,000 curies Cs-137 inventory. In general, the Case 1 solubility parameters resulted in the greatest increase in predicted Cs-137 inventories. Case 2 and Case 3 gave essentially the same results.

Figure 4-3. Comparison of Different Hanford Defined Waste Model Predictions of Cesium-137 Inventory for All Sampled Tanks.



4.3.2 Cesium-137 Comparison with Analytical Data

The sorted log ratio measure was used to compare the Cs-137 performance relative to analytical data for the cases. Figure 4-4 compares the HDW (Revision 4) predictions with those of Cases 1, 2 and 3.

A goal is to have all predictions at least within a factor of ten of the analytical data; points with a performance indicator between minus one and plus one meet this criteria. For all modified models, the tanks that had very low HDW (Revision 4) Cs-137 predictions relative to analytical data now have all but one or two predictions within the (factor of 10) criteria. Unfortunately, four tanks were pushed over the criteria at the high prediction end (see right side of Figure 4-4, tank index 54 and higher).

Table 4-4 compares HWD (Revision 4) and Case 3 by categorizing the Cs-137 predictions by proximity to sample values. The categories are the same as used for Sr-90. The results are essentially the same for HDW (Revision 4) and Case 3 with 98 percent of sampled tank inventory having predictions within a factor of four of sample. Also, 87 percent of the sampled tanks have predictions within a factor of eight of sample. Only one percent of the sampled tank inventory had predictions outside the one-eighth to eight model-to-sample ratio range.

Figure 4-4. Hanford Defined Waste Model Comparison for Cesium-137 for All Sampled Tanks.

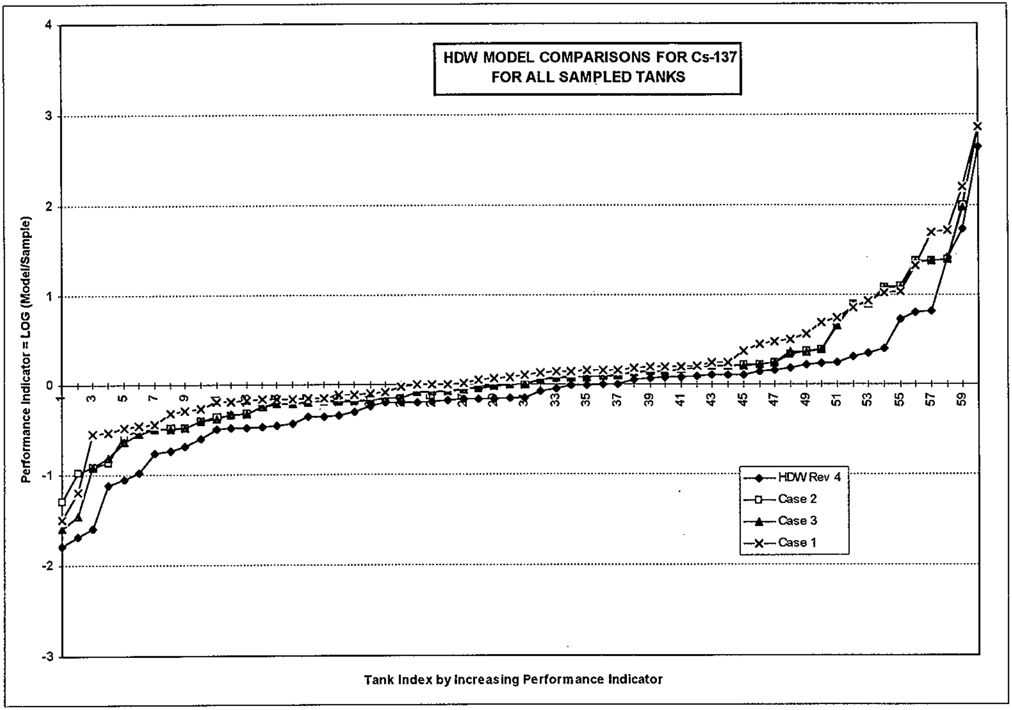


Table 4-4. Comparison of Cesium-137 Performance for Hanford Defined Waste Revision 4 and Case 3.

Model to sample ratio range	HDW Revision 4		Case 3	
	Fraction of sampled tank Ci inventory	Percent of sampled tanks	Fraction of sampled tank Ci inventory	Percent of sampled tanks
Model one half to two times sample	0.761	53.3%	0.763	58.3%
Model one fourth to four times sample	0.982	76.7%	0.975	76.7%
Model one eighth to eight times sample	0.99	86.7%	0.99	86.7%
Model one tenth to ten times sample	0.99	88.3%	0.99	86.7%
Beyond (outlier)	0.010	11.7%	0.015	13.3%

5.0 REFERENCES

Agnew, S. F., and J. G. Watkins, 1994, *Estimation of Limiting Solubilities for Ionic Species in Hanford Waste Tank Supernates*, LAUR-94-3590, Los Alamos National Laboratory, Los Alamos, New Mexico.

Agnew, S. F., J. Boyer, R. A. Corbin, T. B. Duran, J. R. Fitzpatrick, K. A. Jurgensen, T. P. Ortiz, and B. L. Young, 1997, *Hanford Tank Chemical and Radiochemical Inventories: HDW Model Rev. 4.*, LA-UR-96-3860, Los Alamos National Laboratory, Los Alamos, New Mexico.

Agnew, S. F., 1998, "Comparisons of Historical Process Estimates with Tank Waste Assays," in *Science and Technology for Disposal of Radioactive Tank Waste*, W. W. Schulz and N. J. Lombardo, Eds., Plenum Press Pub., New York, New York.

Ames, L. L., Jr., D. R. Fullerton, and D. W. Pearce, 1964, *Process of Removing Ruthenium from Aqueous Solution*, U.S. Patent 3, 136, 715.

Bryan, S. A., K. H. Pool, S. L. Bryan, S. V. Forbes, F. V. Hoopes, B. D. Lerner, G. M. Mong, P. T. Nguyen, G. F. Schiefelbein, R. L. Sell, and L. M. P. Thoms, 1995, *Ferrocyanide Safety Program Cyanide Speciation Studies Final Report*, PNL-10696, Pacific Northwest Laboratory, Richland, Washington.

Cotton, F. A., and G. Wilkinson, 1966, *Advanced Inorganic Chemistry*, 2nd Ed. Interscience Pub. Co., New York, New York.

Eller, G. F., and R. A. Penneman, "Curium," in *Chemistry of the Actinide Elements*, 2nd Ed., Vol 1, J. J. Katz, G. T. Seaborg, and L. Morss, Eds, Gordon and Breach, New York, New York.

Heslop, R. B., and K. Jones, 1976, *Inorganic Chemistry. A Guide to Advanced Study*, Elsevier Scientific Pub. Co., New York, New York.

James, W. L., and G. E. Stoner, 1963, *J. Amer. Chem. Soc., 85,* 1354.

Keller, C., 1971, *The Chemistry of the Transuranium Elements*, Verlag Chemie, Weinheim, Germany.

Kepak, F., 1979, "Contribution to the Study of the Sorption of Radionuclides of Hydrated Oxides," *J. Radioanal. Chem., 51,* 307.

Kirby, H. W., 1959, *The Radiochemistry of Protactinium*, NAS-NS-3016, National Academy of Sciences, National Research Council, Washington, D.C.

Kirby, H. W., 1986, "Actinium," in *The Chemistry of the Actinide Elements*, Vol. 1, 2nd Ed., J. J. Katz, G. T. Seaborg, and L. Morss, Chapman and Hall, New York, New York.

Kupfer, M. J., A. L. Boldt, B. A. Higley, K. M. Hodgson, L. W. Shelton, B.C. Simpson, R. A. Watrous, M. D. LeClair, G. L. Borsheim, R. T. Winward, R. M. Orme, N. G. Colton, S. L. Lambert, D. E. Place, and W. W. Schulz, 1998, *Standard Inventories of Chemicals and Radionuclides in Hanford Site Tanks*, HNF-SD-WM-TI-740, Rev. 0B, Lockheed Martin Hanford Corporation, Richland, Washington.

Lilga, M. A., E. V. Alderson, R. T. Hallam, M. O. Hogan, T. L. Hobler, G. L. Jones, D. J. Kowalski, M. R. Lumetta, G. F. Schiefelbein, and M. R. Telander, 1995, *Ferrocyanide Safety Project Management Hexacyanoferro(II) Aging Studies FY 1995 Annual Report*, PNL-10713, Pacific Northwest Laboratory, Richland, Washington.

Lumetta, G. J., B. M. Rapko, J. Liu, and D. J. Temer, 1998, "Enhanced Sludge Washing for Pretreating Hanford Tank Sludges," in *Science and Technology For Disposal of Radioactive Tank Wastes*, W. W. Schulz and N. J. Lombardo, Eds, Plenum Press Pub., New York, New York.

Music, S., M. Gessner, and R. H. H. Wolf, 1979, "Sorption of Ruthenium-97 on Fe2O3, Fe(OH)2, and Fe(OH)3 Precipitates," *Mikrochim . Acta,* 1, 95.

Nabivanets, B. I., 1964, *Russ J. Inorg Chem., 9,* 590.

Neumann, G., 1964, *Acta. Chem. Scand., 18,* 278.

Novikov, A. I., and V. I. Ruzankin, 1972, "Coprecipitation of Fission Products with Magnesium Hydroxide. I. Coprecipitation of Cs, Sr, Y, Mo, Sb, Se, As, Nb, Zr, Ru, Zn, Cd, and Ce," *Radiokhimya, 13,* 134; *Sov. Radiochem. (Eng. Transl.), 14,* 521.

Noyes, A. A., and W. C. Bray, 1948, *A System for Qualitative Analysis for the Rare Elements*, MacMillan Co., New York, New York.

Pruett, D. J., 1990, "Extraction Chemistry of Fission Products," in *Science and Technology of Tributyl Phosphate*, Vol III. W. W. Schulz, L. L. Burger, and J. D. Navratil, Eds, CRC Press, Boca Raton, Florida.

Schroeder, N. C., S. D. Radzinski, K. R. Ashley, A. P. Troung, and P. A. Szczepaniak, 1998, "Technetium Oxidation State Adjustment for Hanford Waste Processing," in *Science and Technology for Disposal of Radioactive Tank Waste*, W. W. Schulz and N. J. Lombardo, Eds., Plenum Press Pub., New York, New York.

Schulz, W. W., and G. E. Benedict, 1972, *Neptunium-237: Production and Recovery*, U.S. Atomic Energy Commission, Oak Ridge, Tennessee.

Schulz, W. W., 1976, *The Chemistry of Americium*, United States Energy Research and Development Administration, Oak Ridge, Tennessee

Schulz, W. W., and R. A. Penneman, "Americium," in *The Chemistry of the Actinide Elements*, 2nd Ed., Vol 1, J. J. Katz, G. T. Seaborg, and L. Morss, Eds, Chapman and Hill, New York, New York.

Schulz, W. W., S. G. Metcalf, and G. S. Barney, 1984, *Radiochemistry of Ruthenium*, NAS-NS-3029, National Technical Information Center, Springfield, Virginia.

Strohal, P., K. Molnar, and I. Bacic, 1972, "Preconcentration of Trace Elements by Aluminum Hydroxide," *Mikrochim. Acta, 5,* 586.

Walrafen, G. E., 1962, *J. Chem. Phys., 36,* 90.

Weaver, B., and R. R. Shoun, 1971, "Bascicities of Trivalent Actinides and Lanthanides and Solubilities of their Hydroxides," in *Proceedings of the 9th Rare Earth Research Conference*, Oct. 10-14, 1971, Blacksburg, Virginia, USAEC Report CONF-711001, (Vol. 1), p 232.

Weigel, F., 1986, "Plutonium," in *The Chemistry of the Actinide Elements*, 2nd Ed., Vol. 2, J. J. Katz, G. T. Seaborg, and L. Morss, Eds., Chapman and Hill, New York, New York.

Weigel, F., 1986a, "Uranium," in *The Chemistry of the Actinide Elements*, 2nd Ed., Vol. 2, J. J. Katz, G. T. Seaborg, and L. Morss, Eds., Chapman and Hill, New York, New York.

Yost, D. M., H. Russell, Jr., and C. S. Garner, 1947, *The Rare Earth Elements and their Compounds*, John Wiley & Sons, New York, New York.

Zeidan, Z., 1980, "Etude Bibliographique Des Differentes Especes Du Ruthenium En Solution Aqueuse," French Report CEA-R-5051, Centre d'Etudes Nucleaires de Fontenay-aux-Roses, Paris, France.

Ziv, D. M., and I. A. Shestakova, 1965, *Sov. Radiochem. 7,* 168.

APPENDIX A

BEST-BASIS RADIONUCLIDE SOLUBILITY ESTIMATES

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APPENDIX A

BEST-BASIS RADIONUCLIDE SOLUBILITY ESTIMATES

Appendix A provides for each of the 46 radionuclides of interest a detailed description of the chemistry and, where available, supporting analytical data used to derive a Best-Basis estimate of its solubility (fraction precipitated) in the various alkaline wastes added to the 149 single-shell tanks (SSTs). The contents of Appendix A are arranged alphabetically by element. Adequate and relevant references to the chemical literature are also provided.

A1.0 ACTINIUM

A1.1 PRODUCTION, HALF-LIFE, AND INVENTORY

Isotope Mass Number	Half Life
227	21.7 y

Actinium-227 occurs in nature to the extent of 5.7E-10 ppm. Its presence there is as one of the decay products of U-235:

U-235------>Th-231------>Pa-231------>Ac-227

As a matter of interest, Ac-227 can also be synthesized by irradiating Ra-226 with thermal neutrons:

Ra-226(n,gamma)Ra-227------->Ac-227

Actinium-227 in Hanford tanks arises as a decay product of U-235. As of January 1, 1994, only 72.3 Ci (1.21 g) of Ac-227 were believed to be present in all 177 tanks.

A1.2 EXPECTED BEHAVIOR DURING FUEL DISSOLUTION

Irradiated uranium metal fuel readily and completely dissolved when exposed to hot nitric acid solution. The small amount of U-235 decay product Ac-227 was solubilized at the same time.

A1.3 PREDICTED OXIDATION STATE

A1.3.1 In Nitric Acid Solution

Kirby (1986) states, "All available evidence supports the conclusions based primarily from tracer and co-precipitation studies that actinium is a higher and more basic homolog of lanthanum." All investigators concur that the only stable oxidation state of actinium in aqueous solution is +3. Thus, nitric acid solutions produced by dissolution of irradiated uranium metal contained Ac-227 in the trivalent oxidation state.

A1.3.2 In Alkaline Media

Ac-227 remained in the +3 oxidation state when acidic high-activity wastes were neutralized with sodium hydroxide prior to storage in the SSTs.

A1.4 CHEMISTRY IN ALKALINE MEDIA

As described in Kirby (1986), Ac(III), like La(III), forms an insoluble hydroxide. From the activity product in various concentrations of aqueous NH_4NO_3, Ziv and Shestakova (1965) calculated the solubility of aged $Ac(OH)_3$ in water to be 0.74 mg/L compared with 0.31 mg/L for $La(OH)_3$. Kirby (1986) states, "At the tracer level actinium is carried down quantitatively by any quantitative lanthanum precipitate, as well as by a wide variety of isomorphous and nonisomorphous carriers." Thus, reported actinium chemistry suggests that Ac-227 in various neutralized process high-activity wastes would have largely reported to the sludge phase as a result of scavenging by hydrated iron oxide, nickel hydroxide, rare earth hydroxides, and other solids.

A1.5 BEST-BASIS SOLUBILITY ESTIMATES

A1.5.1 From Chemistry Considerations

Known actinium chemistry strongly supports the belief that Ac-227 in neutralized waste streams added to the SSTs would have largely reported to the sludge phase. But, the chemical evidence must be balanced against the likely behavior of about 1 gram of Ac-227 dispersed over 177 tanks containing tens of millions of liters of waste. Certainly, the very small amount of Ac-227 introduced into any of the 149 SSTs did not exceed the solubility of $Ac(OH)_3$ in water. Very likely, some, perhaps 10%, of the Ac(III) was carried down with the large amounts of solids, e.g., $Fe_2O_3 \cdot nH_20$, $Ni(OH)_2$, rare earth hydroxides, etc. which precipitated in the SSTs. But, it is believed most of the Ac-227 remained soluble and eventually reported to either the DSTs or the salt cake in some SSTs.

A1.5.2 From Analytical Considerations

As far as is known, there are no analytical data for Ac-227 in any of the 177 tanks.

A1.5.3 Tabulated Best-Basis Solubility Estimates

Table A-1 lists Best-basis estimates of the fraction of Ac-227 precipitated when various alkaline waste solutions and solids were introduced into the SSTs. In the absence of any analytical data, the estimates shown in Table A-1 derive solely from the chemistry considerations discussed in Section A1.4. It is well recognized, of course, that not all wastes added to the SSTs contained Ac-227. But, for those that did, the solubility estimates in Table A-1 apply.

A1.6 REFERENCES

Kirby, H. W., 1986, "Actinium," in *The Chemistry of the Actinides*, 2nd Ed, Vol 1, J. J. Katz, G. T. Seaborg, and L. R. Morss, Eds, Chapman and Hill, New York, New York.

Ziv, D. M., and I. A. Shestakova, 1965, Sov. Radiochem., 7, 168-175.

Table A-1. Best-Basis Solubility Estimates for Ac-227.

Hanford Defined Waste Model Waste Type[1]	Fraction Insoluble Ac-227
Process High Activity Waste	
$BiPO_4$ process[2]	0.10
Other processes[3]	0.10
Cladding Waste	
Aluminum[4]	0.0
Zircaloy[5]	0.10
Miscellaneous Wastes	
Solid Wastes	
Ferrocyanide solids[6]	0.0
Other solids[7]	0.98
Complexed waste[8]	0.0
Other liquid wastes[9]	0.10

Notes:

[1] After addition of NaOH

[2] Includes HDW Model (Rev 4) Waste Types: MW1, MW2, 1C1, 1C2, 2C1, 2C2, 224, and UR

[3] Includes HDW Model (Rev 4) Waste Types: R1, R2, P1, P2,P2', Th1, Th2, P3, PL1, PL2 and Z

[4] Includes HDW Model (Rev 4) Waste Types: CWR1, CWR2, CWP1, and CWP2

[5] Includes HDW Model (Rev 4) Waste Types: CWZr1 and CWZr2

[6] Includes HDW Model (Rev 4) Waste Types: PFeCN1, PFeCN2, TFeCN and 1CFeCN

[7] Includes HDW Model (Rev 4) Waste Types: DE, CEM, and AR

[8] Includes HDW Model (Rev 4) Waste Types: HS and SRR

[9] Includes HDW Model (Rev 4) Waste Types: OWW1, OWW2, OWW3, NIT, BL, CSR, DW, N, PASF, and B

A2.0 AMERICIUM

A2.1 PRODUCTION AND HALF-LIFE

Isotope Mass Number	Half Life
241	4.329E+02 y
243	7.380E+03 y

Americium-241 in Hanford tank wastes resulted primarily from beta decay of Pu-241 produced during neutron irradiation of uranium:

Pu-241-------> Am-241

However, some Am-241 was also produced during fuel irradiation via the nuclear reaction:

Pu-241(n, gamma)Am-241

Americium-243, the longest-lived americium isotope in irradiated uranium fuel, resulted from two successive neutron captures by Am-241.

A2.2 EXPECTED BEHAVIOR DURING FUEL DISSOLUTION

Americium isotopes were likely dispersed on an atomic scale in irradiated uranium fuel. Since nitric acid solutions containing ionic americium are quite stable, both Am-241 and Am-243 dissolved completely during the fuel dissolution process.

A2.3 PREDICTED OXIDATION STATE

A2.3.1 In Nitric Acid Solution

From Schulz (1976) we have the following information, "The stability of the higher oxidation states of the transuranium elements typically decreases with increasing atomic number. In agreement with this, the trivalent state of americium is its most stable oxidation state and is the state resulting when americium metal dissolves in acids." Hence, without doubt, Am-241 and Am-243 in nitric acid dissolver solutions were present as Am(III).

A2.3.2 In Alkaline Media

Oxidation of Am(III) to Am(IV) or Am(VI) requires very special oxidizing conditions (Schulz and Penneman 1986). Such conditions are not present in non-complexed waste. Therefore, americium in non-complexed waste is present as Am(III). Note that non-complexed waste refers to those wastes which either contain no organic complexants or contain complexants at a concentration below that which is considered necessary to change the valence of the species in question.

A2.3.3 In Complexed Waste

Some complexed waste in the Hanford waste tanks contains very high concentrations of organic materials; conditions in these wastes are still not sufficient to oxidize Am(III) to either Am(IV) or Am(VI). Therefore, americium in complexed concentrate waste is considered present as an Am(III) species.

A2.4 CHEMISTRY IN ALKALINE MEDIA

In the absence of aqueous soluble organic compounds which complex Am(III) strongly, the chemistry of americium in alkaline solutions is essentially the chemistry of insoluble americium hydroxide. Weaver and Shoun (1971) report that Am(III) can be completely precipitated from chloride or nitrate media at an NaOH/americium ratio of 2.4. For this latter stoichiometry, they calculate, at NaOH/americium ratios of 1.0 to 1.5, that K_{sp} is $[Am]+[3(OH)^{-1}] = (3.4+0.3)\text{x } 10^{-18}$ and that the solubility in water is $2.9 \text{ x } 10^{-6}$ M.

At pHs ranging from 7 to 9, Am(III) forms only very weak complexes with inorganic anions typically present in non-complexed wastes, e.g., chloride, nitrate, sulfate, carbonate, etc. None of the weak complexes are strong enough to prevent an equilibrium shift upon addition of excess NaOH to cause the precipitation of $Am(OH)_3$. Note that the total mass of americium isotopes present in any waste tank is very small. Hence, even though $Am(OH)_3$ may have precipitated, in the absence of a carrier precipitate, the hydroxide particles may not have agglomerated sufficiently to have settled out in the alkaline waste solution, thus very small particles containing Am(III) may have remained in suspension.

However, in almost every instance when a waste stream containing even a very small amount of americium was added to a single-shell tank, a large mass of solids precipitated. Such solids included, among others, rare earth hydroxides, sodium diuranates, hydrated aluminum oxide, and, especially, hydrated iron oxide.

Because of its extensive use as a plutonium reductant in Hanford site plutonium separations processes, Fe(II) was invariably present in all high-activity wastes (HAW) routed to underground storage tanks. Of course, when such waste solutions were neutralized by addition of sodium hydroxide all the Fe(III) precipitated as an amorphous hydrated iron oxide. Freshly precipitated $Fe_2O_3 \cdot nH_20$, because of its great surface area and other properties, has a great affinity for the hydroxides of actinide elements including americium, the hydroxides of the lanthanides, and also strontium ion and/or its insoluble compounds. As the amorphous iron oxide aged and converted to crystalline minerals such as hematite, goethite, etc., the trapped or scavenged actinides, lanthanides, and strontium appear to have become part of the crystalline lattice and are, thus bound very tightly in an insoluble form. Indeed, the results of Lumetta et al. (1998), indicate washing Hanford sludges with either water or dilute NaOH solutions does not solubilize americium.

Hence, the net effect of the presence of an efficient co-precipitator or scavenger agent such as hydrated iron oxide was to efficiently agglomerate insoluble $Am(OH)_3$ and make americium water-insoluble.

A2.5 BEST-BASIS SOLUBILITY ESTIMATES

A2.5.1 From Chemistry Considerations

Evaluation of the americium chemistry described in Section A2.4 clearly demonstrates that Am-241 and Am-243 in alkaline media, especially in the presence of hydrated iron oxide, precipitated quantitatively. Thus, chemistry considerations show that 98-100% of Am-241 and Am-243 in SST wastes, as generated, are in insoluble form in the sludge phases.

A2.5.2 From Analytical Considerations

Relevant analytical data for Am-241 in neutralized PUREX process zircaloy cladding and HAW were presented and discussed earlier. These data, with appropriate reservations concerning their limited availability and sufficiency, clearly support the conclusion drawn in Section A5.2.1 to the effect that 98-100% of the americium, both Am-241 and Am-243, in SST neutralized process waste precipitated as an insoluble form in the sludge phase.

There are no analytical data from which to ascertain the behavior of americium which may have been present in miscellaneous liquid and solid wastes added to the SSTs. In the absence of such data, the assumption made here is that, except for aqueous wastes containing high concentrations of organic complexants and for ferrocyanide-type solids, americium in these miscellaneous wastes was nearly completely precipitated. Americium in neutralized waste resulting from Sr-90 solvent extraction operations in the Hanford B plant is assumed to have been strongly complexed and completely soluble.

A2.5.3 Tabulated Best-Basis Solubility Estimates

Table A-2 provides best-basis solubility (fraction precipitated) estimates for Am-241 and Am-243 in various neutralized types of waste added to the SSTs. Even though limited, analytical data indicate greater than 99.9% of the americium in process HAW-type and decladding wastes precipitated when such solutions were neutralized with sodium hydroxide, the best-basis solubility estimate is set at 98%. This lower conservative value allows for some errors in the analytical data and also acknowledges that americium is present in various salt cakes and in some DSTs.

A2.6 REFERENCES

Schulz, W. W., 1976, *The Chemistry of Americium*, Energy Research & Development Administration, Oak Ridge, Tennessee.

Schulz, W. W., and R. A. Penneman, 1986, "Americium," in *The Chemistry of the Actinide Elements*, J. J. Katz, G. T. Seaborg, and L. R. Morss, Eds., Chapman and Hill, New York, New York.

Weaver, B., and R. R. Shoun, 1971, "Basicities of Trivalent Actinides and Lanthanides and Solubilities of their Hydroxides," in *Proceedings of the 9th Rare Earth Research Conference*, Oct. 10-14, 1971, Blacksburg, Virginia, USAEC Report CONF-711001 (Vol. 1), p 232.

Table A-2. Best-Basis Solubility Estimates for Am-241 and Am-243.

Hanford Defined Waste Model Waste Type[1]	Fraction Insoluble Americium
Process High Activity Waste	
$BiPO_4$ process[2]	0.98
Other processes[3]	0.98
Cladding Waste	
Aluminum[4]	0.98
Zircaloy[5]	0.98
Miscellaneous Wastes	
Solid Wastes Ferrocyanide solids[6] Other solids[7]	 0.0 0.98
Complexed waste[8]	0.0
Other liquid wastes[9]	0.98

Notes:

[1] After addition of NaOH

[2] Includes HDW Model (Rev 4) Waste Types: MW1, MW2, 1C1, 1C2, 2C1, 2C2, 224, and UR

[3] Includes HDW Model (Rev 4) Waste Types: R1, R2, P1, P2, P2', Th1, Th2, P3, PL1, PL2, and Z

[4] Includes HDW Model (Rev 4) Waste Types: CWR1, CWR2, CWP1, and CWP2

[5] Includes HDW Model (Rev 4) Waste Types: CWZr1 and CWZr2

[6] Includes HDW Model (Rev 4) Waste Types: PFeCN1, PFeCN2, TFeCN, and 1CFeCN

[7] Includes HDW Model (Rev 4) Waste Types: DE, CEM, and AR

[8] Includes HDW Model (Rev 4) Waste Types: HS and SRR

[9] Includes HDW Model (Rev 4) Waste Types: OWW1, OWW2, OWW3, NIT, BL, CSR, DW, N, PASF, and B

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A3.0 ANTIMONY

A3.1 MASS NUMBER, HALF-LIFE, AND INVENTORY

Isotope Mass Number	Half Life
125	2.77 y

Antimony-125 is a relatively short-lived product of the fission of U-235. As of January 1, 1994 it is estimated that the Hanford Site tanks contained 208,000 Ci or about 200 g of Sb-125. Now (September 1998) these tanks contain less than 100 g of Sb-125. The assumption made in this report is that all of the Sb-125 is present in one or more DSTs and that only a negligible amount of Sb-125 is present in the SSTs. This assumption is based upon the fact that the last wastes containing Sb-125 were added to the SSTs in 1971; thus Sb-125 present in 1971 has decayed through approximately 9 half-lives to a negligible amount. Wastes derived from reprocessing stored N Reactor fuel in the period 1983-1988 were routed directly to one or more DSTs; these wastes contained the Sb-125 now present in the DSTs.

A3.2 EXPECTED BEHAVIOR DURING FUEL DISSOLUTION

The behavior of massive antimony metal exposed to boiling, concentrated nitric acid is not known. But, Sb-125 dispersed on an atomic scale in irradiated uranium metal, presumably went into aqueous solution.

A3.3 PREDICTED OXIDATION STATES

A3.3.1 In Nitric Acid

Heslop and Jones (1976) state that antimony is predominantly a trivalent element. Antimony, thus, tends to form three electron-pair bonds roughly at right angles. Heslop and Jones go on to state that antimony may use all five of its valence electrons in bonding, d-hybridization, yielding various sets of bonds. The overriding important point noted by Heslop and Jones is, "In solution the only ion which occurs is Sb^{+3}, moreover it is hydrated." Thus, in nitric acid dissolver solutions Sb-125 was present as a trivalent cation.

A3.3.2 In Alkaline Media

Antimony-125 in the trivalent oxidation state in acidic waste solutions undoubtedly remained in the same oxidation state when sodium hydroxide was added to the waste solutions. There were no conditions which would have promoted oxidation to the pentavalent state.

A3.4 CHEMISTRY IN ALKALINE MEDIA

The chemistry of Sb-125 in alkaline Hanford tank waste is essentially the chemistry of an amphoteric substance. That is, tervalent antimony in acid media likely precipitated, initially, as a hydrated oxide, but, in the presence of excess hydroxide, redissolved as a stable antimonate,$[Sb(OH)_6]^{-3}$, ion. However, some Sb-125 in the form of an antimonate ion was surely occluded in the large mass of hydroxide and hydrated oxide solids which were present in many wastes, especially in neutralized process HAW and zircaloy cladding waste. Over time, as the hydrated solids dried, any Sb-125 was incorporated into one or more crystalline lattices.

A3.5 BEST-BASIS SOLUBILITY ESTIMATES

A3.5.1 From Chemistry Considerations

Antimony chemistry teaches that most of the Sb-125 reported as a soluble species to the DSTs and likely a smaller fraction reported to the salt cake in the SSTs. Chemistry considerations indicate that some, likely small, amount of Sb-125 reported to the sludge phases in the SSTs as a result of occlusion phenomena. Antimony chemistry by itself, however, sheds no light upon how much Sb-125 might have been trapped by hydrated oxide precipitates.

A3.5.2 *From Analytical Considerations*

The available data for Sb-125 is very sparse. The most useful datum is recorded for sludge in DST 241-AZ-101; this tank received neutralized PUREX process HAW in the 1983-1988 time frame. The analytical data for DST 241-AZ-101 show that some 15% of the total Sb-125 thought to be in the tank is in the sludge phase. The amount of Sb-125 in the supernatant in Tank 241-AZ-101 was not determined in that set of analyses. DST 241-AZ-102 also received neutralized PUREX process HAW in the 1983-1988 period; there are no analytical data for Sb-125 in DST 241-AZ-102.

Also, in the 1983-1988 time frame, DSTS 241-AW-103 and AW-105 received neutralized Zirflex process cladding waste. There are no data for Sb-125 in DST

241-AW-103. The sludge in DST 241-AW-105 is reported to contain Sb-125 (at least of January 1, 1994), but insufficient analytical information is available to estimate the percent of the total Sb-125 in the tank which reported to the solid sludge phase.

Beyond the very limited data for Sb-125 in DSTs 241-AW-105 and 241-AZ-101, there are almost no other analytical data for Sb-125, certainly no meaningful or useful data.

A3.5.3 Tabulated Best-Basis Solubility Estimates

Table A-3 lists best-basis estimates of the fraction of Sb-125 which precipitated when various kinds of waste were added to or generated in the SSTs. The estimate that 15% of the Sb-125 in neutralized process HAW and zircaloy cladding waste derives both from chemistry and, especially, analytical considerations. Based upon the single available analytical datum and known antimony chemistry, it is estimated that 15% of the Sb-125 inventory in neutralized process HAW and neutralized zircaloy cladding waste reported to the solids. In the absence of significant solids to occlude Sb-125, it is estimated that all the antimony remained soluble. This situation was assumed characteristic of complexed waste, aluminum cladding waste, and various miscellaneous liquid wastes added to the SSTs. Of course, it is recognized that many wastes added to the SSTs did not contain Sb-125. But, for those that did, the data in Table A-3 apply. Note that for the DE, CEM and AR waste types, because of their solids definition, have fraction precipitated solids (fraction insoluble) values near unity. This also applies to nearly all other radionuclides.

A3.6 REFERENCES

Heslop, R. B., and K. Jones, 1976, *Inorganic Chemistry: A Guide to Advanced Study*, Elsevier Scientific Publishing Co., New York, New York, p. 451.

Table A-3. Best-Basis Solubility Estimates for Sb-125.

Hanford Defined Waste Model Waste Type[1]	Fraction Insoluble Sb-125
Process High Activity Waste	
$BiPO_4$ process[2]	0.15
Other processes[3]	0.15
Cladding Wastes	
Aluminum[4]	0.0
Zircaloy[5]	0.15
Miscellaneous Wastes	
Solid Wastes	
Ferrocyanide solids[6]	0.0
Other solids[7]	0.98
Complexed wastes[8]	0.0
Other liquid wastes[9]	0.0

Notes:

[1] After addition of NaOH
[2] Includes HDW Model (Rev 4) Waste Types: MW1, MW2, 1C1, 1C2, 2C1, 2C2, 224, and UR
[3] Includes HDW Model (Rev 4) Waste Types: R1, R2, P1, P2, P2', Th1, Th2, PL1, PL2, P3, and Z
[4] Includes HDW Model (Rev 4) Waste Types: CWR1, CWR2,CWP1, and CWP2.
[5] Includes HDW Model (Rev 4) Waste Types: CWZr1 and CWZr2
[6] Includes HDW Model (Rev 4) Waste Types: PFeCN1, PFeCN2, TFeCN, 1CFeCN
[7] Includes HDW Model (Rev 4) Waste Types: DE, CEM, and AR
[8] Includes HDW Model (Rev 4) Waste Types: HS and SRR
[9] Includes HDW Model (Rev 4) Waste Types: OWW1, OWW2, OWW3, NIT, BL, CSR, DW, N, PASF, and B

A4.0 BARIUM

A4.1 PRODUCTION AND HALF-LIFE

Isotope Mass Number	Half Life
137m	2.6 min

Barium-137m results from beta decay of Cs-137. Because of its very short half life, 2.6 min, compared to that of its parent Cs-137, 30.17 y, Ba-137m is always in radioactive equilibrium with Cs-137.

A4.2 EXPECTED BEHAVIOR DURING FUEL DISSOLUTION

The key to understanding the behavior of Ba-137m during fuel dissolution and subsequent fuel reprocessing and waste management operations is to remember that Ba-137m is always in equilibrium with Cs-137. As noted in a subsequent section (Section A7.0) fission product Cs-137 is considered to have been completely solubilized during nitric acid dissolution of irradiated uranium metal fuel. Because barium is a very electropositive element, Ba-137m was also likely solubilized in the fuel dissolution step. However, even if none of the initial Ba-137m dissolved, an equivalent amount would have been quickly established in the various waste matrices by beta decay of dissolved Cs-137.

A4.3 PREDICTED OXIDATION STATE

Only the divalent state of barium is known in alkaline solution. Therefore, Ba-137m was present as Ba(II) in both initial nitric acid dissolver solution and in the alkaline waste after addition of sodium hydroxide to acidic processing wastes.

A4.4 CHEMISTRY IN ALKALINE MEDIA

The chemistry of Ba-137m in alkaline process wastes is dominated by its short half-life (2.6 min) and its close parent-daughter relation with Cs-137. Thus, any of the initially present Ba-137m which may have precipitated, e.g., as $BaSO_4$, when sodium hydroxide was added to acidic process wastes quickly disappeared because of the very short half-life of Ba-137m.

As noted in Section A7.0, approximately 10% of the Cs-137 introduced into the SSTs is predicted to have precipitated as an insoluble form and remain in the SSTs in the sludge phase. The Cs-Ba-137 equilibrium was, of course, quickly established in those SSTs which contained Cs-137. Thus, those SST sludges which now contain Cs-137 also contain the equilibrium inventory of Ba-137m.

The exact chemical form of Ba-137m in SST sludges is not known. Such form may vary from tank to tank. Certainly, because of its short half-life, Ba-137m only exists in SST sludge which contain Cs-137. As noted elsewhere in this report, Cs-137 in sludge is believed to be present as an insoluble aluminosilicate or as cesium nickel ferrocyanide or as Cs-137 simply originally occluded in precipitates of iron, nickel, and other metals, and it probable that the Ba-137m parallels this distribution.

A4.5 BEST BASIS SOLUBILITY ESTIMATES

A4.5.1 From Chemistry Considerations

Radiochemistry tells us that Ba-137m is distributed in and between SST and DST wastes exactly like Cs-137. Such behavior is a natural consequence of (a) the short half life of Ba-137m and (b) the relatively long half life of Cs-137 and (c) Ba-137m is a decay product of Cs-137.

A4.5.2 From Analytical Considerations

Available analytical data for SST and DST wastes are completely in accord with conclusions drawn from radiochemistry expectations.

A4.5.3 Tabulated Best-Basis Solubility Estimates

Table A-4 lists best-basis estimates of the fraction of Ba-137m precipitated when various types of waste were neutralized with sodium hydroxide and added to the SSTs. These estimates parallel exactly those for Cs-137 and follow from the previous discussion Sections A4.5.1 and A4.5.2.

Table A-4. Best-Basis Solubility Estimates for Ba-137m.

Hanford Defined Waste Model Waste Types[1]	Fraction Insoluble Ba-137m
Process High Activity Waste	
$BiPO_4$ process[2]	0.10
Other processes[3]	0.10
Cladding Waste	
Aluminum[4]	0.0
Zircaloy[5]	0.30
Miscellaneous Wastes	
Solid Wastes	
Ferrocyanide solids[6]	0.98
Other solids[7]	0.0
Complexed waste[8]	0.0
Other liquid waste[9]	0.0

Notes:

[1] After addition of NaOH
[2] Includes HDW Model (Rev 4) Waste Types: MW1, MW2, 1C1, 1C2, 2C1, 2C2, 224, and UR
[3] Includes HDW Model (Rev 4) Waste Types: R1, R2, P1, P2, P2', Th1, Th2, PL1, PL2, and P3
[4] Includes HDW Model (Rev 4) Waste Types: CWR1, CWR2, CWP1, and CWP2
[5] Includes HDW Model (Rev 4) Waste Types: CWZr1 and CWZr2
[6] Includes HDW Model (Rev 4) Waste Types: PFeCN1, PFeCN2, TFeCN, and 1CFeCN
[7] Includes HDW Model (Rev 4) Waste Types:DE, CEM, and AR
[8] Includes HDW Model (Rev 4) Waste Types: HS and SRR
[9] Includes HDW Model (Rev 4) Waste Types: OWW1, OWW2, OWW3, NIT, BL, CSR, N, PASF, and B

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A5.0 CADMIUM

A5.1 MASS NUMBER AND HALF-LIFE

Isotope Mass Number	Half Life
113m	14 y

Cadmium-113m resulted from neutron activation of Cd-112, an impurity in aluminum used to clad uranium fuel. Some Cd-113m was also produced as a product of the fission of U-235.

A5.2 EXPECTED BEHAVIOR DURING FUEL DISSOLUTION

Cadmium is a nontransition electropositive metal. Thus, atoms of Cd-113m in either irradiated cladding or irradiated uranium metal fuel were readily solubilized during fuel decladding and dissolution operations.

A5.3 PREDICTED OXIDATION STATE

There have been unconfirmed (James and Stoner 1963) reports of Cd(I) in melts. But, there is no evidence for Cd(I) in aqueous solution. Indeed, there is no evidence for any cadmium oxidation state in aqueous solution higher than II. This latter observation follows from the fact that the third ionization potential for cadmium is very high, and the energy of solvation or lattice formation is not sufficient to make Cd(III) chemically stable. Thus, the valence of Cd-113m in aqueous solutions resulting from fuel decladding and dissolution operations was Cd(II).

A5.4 CHEMISTRY IN ALKALINE MEDIA

Cadmium hydroxide precipitates when base is added to an aqueous solution containing Cd(II). The solubility product of $Cd(OH)_2$ is about 1.0E-14 (Cotton and Wilkenson 1966). Unlike the similar compound $Zn(OH)_2$, $Cd(OH)_2$ does not dissolve in excess base since cadmiate ions are of negligible stability.

Cadmium(II) forms strong complexes with many organic reagents, EDTA, HEDTA, citric acid, etc., but in the absence of such ligands, the chemistry of Cd(II) in alkaline media is the simple and straightforward precipitation of $Cd(OH)_2$. As noted for many other radionuclides, coprecipitation of large amounts of Fe(III) and Ni(II) acted to agglomerate and scavenge small amounts of $Cd(OH)_2$.

A5.5 BEST-BASIS SOLUBILITY ESTIMATES

A5.5.1 From Chemistry Considerations

Known cadmium chemistry strongly indicates that any Cd-113m in various alkaline waste streams added to the SSTs precipitated almost completely as $Cd(OH)_2$. Agglomeration and removal of precipitated Cd-113m was no doubt aided by co-precipitation of large amounts of hydrated iron and nickel oxides.

A5.2 FROM ANALYTICAL CONSIDERATIONS

There is not a single analytical datum for Cd-113m in any SST or DST waste. It has not been designated as an analyte of concern in the past, and results for it are not obtained as a benefit of performing other analyses.

A5.3 TABULATED BEST-BASIS SOLUBILITY ESTIMATES

Table A-5 provides best-basis estimates of the fraction of Cd-113m precipitated in the various types of neutralized waste added to the SSTs. In the absence of any analytical data for Cd-113m, these estimates derive solely from consideration of the known chemistry of cadmium. Not all the miscellaneous wastes added to the SSTs contained Cd-113m. But, for those that did, the best-basis solubility estimates in Table A-5 apply.

A5.6 REFERENCES

Cotton, F. A., and G. Wilkinson, 1966, *Advanced Inorganic Chemistry*, Interscience Pub, New York, New York.

James, W. L., and G. E. Stoner, 1963, J. Amer. Chem. Soc., 85, 1354.

Table A-5. Best-Basis Solubility Estimates for Cd-113m.

Hanford Defined Waste Model Waste Type[1]	Fraction Cd-113m Precipitated
Process High-Activity Waste	
$BiPO_4$ process[2]	0.98
Other processes[3]	0.98
Cladding Wastes	
Aluminum[4]	0.0
Zircaloy[5]	0.98
Miscellaneous Wastes	
Solid Wastes Ferrocyanide solids[6] Other solids[7]	 0.0 0.98
Complexed Wastes[8]	0.0
Other Liquid Wastes[9]	0.0

Notes:

[1] After addition of NaOH

[2] Includes HDW Model (Rev 4) Waste Types : MW1, MW2, 1C1, 1C2, 2C1, 2C2, 224, and UR

[3] Includes HDW Model (Rev 4) Waste Types: R1, R2, P1, P2, P2', Th1, Th2, PL1, PL2, and P3

[4] Includes HDW Model (Rev 4) Waste Types: CWR1, CWR2, CWP1, and CWP2

[5] Includes HDW Model (Rev 4) Waste Types: CWZr1 and CWZr2

[6] Includes HDW Model (Rev 4) Waste Types: PFeCN1, PFeCN2, TFeCN and 1CFeCN

[7] Includes HDW Model (Rev 4) Waste Types: DE, CEM, and AR

[8] Includes HDW Model (Rev 4) Waste Types: HS and SRR

[9] Includes HDW Model (Rev 4) Waste Types: OWW1, OWW2, OWW3, and NIT, BL, CSR, DW, N, PASF, and B

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A6.0 CARBON

A6.1 MASS NUMBER AND HALF LIFE

Isotope Mass Number	Half Life
14	5,730 y

Carbon-14 is an activation product produced by neutron irradiation of N-14, a common impurity in uranium metal, according to the reaction:

N-14 (n, p) C-14.

Because of considerable uncertainty in the amount of N-14 in various batches of uranium metal over 40 years of plutonium production, there is great uncertainty in the total amount of C-14 ever produced at Hanford. Also, as noted in Section 3.1, some C-14 was lost as CO_2, to the environment during dissolution of the irradiated uranium metal, therefore, the total amount of C-14 in the 177 Hanford tanks is uncertain. These uncertainties do not, however, prevent estimating the fraction of C-14 that precipitated when neutralized wastes containing C-14 were added to the SSTs.

A6.2 EXPECTED BEHAVIOR DURING FUEL DISSOLUTION

Much of the C-14 in irradiated fuel evolved as CO_2 gas when the fuel was dissolved in nitric acid. Pruett (1990) states, "Greater than 95% of the C-14 in irradiated fuel is evolved from the dissolver solution as CO_2." Other knowledgeable scientists/engineers suggest that perhaps only 80% of the available C-14 volatilized during fuel dissolution operations. In any case, the presence of C-14 in some tank wastes, as determined by analyses, indicates that not all the C-14 volatilized.

A6.3 PREDICTED OXIDATION STATE

A6.3.1 In Nitric Acid

There is no definitive knowledge of the species or oxidation state of C-14 present in nitric acid dissolver solutions. One attractive hypothesis, suggested by several authorities, is that residual C-14 was present as some unknown aqueous-soluble organic compound, perhaps oxalic acid or other carboxylic acid, somewhat stable to oxidation in boiling nitric acid dissolver solution. This hypothesis does not seem at all that untenable. Certainly, the chemical literature does not suggest any inorganic carbon compound that might have been present in such solutions.

A6.3.2 In Alkaline Media

Some people have assumed that C-14 in alkaline Hanford wastes is present as carbonate ion. There is no experimental evidence to either confirm or refute this assumption. It also seems fairly certain that if C-14 were present in nitric acid dissolver solution as some aqueous-soluble organic compound, this organic species would have persisted when sodium hydroxide was added to the acidic waste.

A6.4 CHEMISTRY IN ALKALINE MEDIA

From the available information, little is known with any certainty about the chemistry of C-14 in Hanford tank waste. If C-14 was present in wastes added to the SSTs as either carbonate ion or as an aqueous-soluble organic compound or both, then the major fraction of C-14 would have remained in the supernatant phase in the SSTs. Only minor amounts of C-14 would have been occluded by the massive amounts of hydroxide or hydrated oxide solids which precipitated from most alkaline wastes added to the SSTs. If it was present as amorphous particulate, then the C-14 reported to the sludge.

A6.5 BEST-BASIS SOLUBILITY ESTIMATES

A6.5.1 From Chemistry Considerations

As stated in Section A6.4, the chemistry of C-14 in Hanford SSTs is not known and can only be speculated on. Such speculation leads to the finding that little, if any, C-14 reported to the sludge phase in the SSTs.

A6.5.2 From Analytical Considerations

Fragmentary analytical data for C-14 are available for waste solids in DSTs 241-AZ-101 and AZ-102. Both of these tanks currently contain PUREX process sludge from neutralization of process HAW generated in the 1983-1988 time frame. The calculated amount of C-14 added to DST 241-AZ-101 is 334 Ci (as of January 1, 1994); of this amount only 0.433 Ci

(0.13%) was found by analysis to be in the sludge phase. Similarly, for DST 241-AZ-102, of 178 Ci (as of January 1, 1994) C-14 calculated to have been added to the tank, 0.83 Ci (0.47%) was found, by analysis, to be in the sludge solids. No C-14 analytical data were obtained for the alkaline PUREX process supernatant originally present in these two DSTs.

DST 241-AW-105 contains neutralized zircaloy cladding waste generated in the period 1983-1988 from PUREX plant operation. The sludge in this tank was found, by sampling and analysis, to contain 2.3 Ci of C-14. No analytical data for C-14 in the supernatant in this tank were obtained.

A6.5.3 Tabulated Best-Basis Solubility Estimates

Table A-6 lists best-basis estimates of the fraction of C-14 precipitated when various alkaline wastes were added to the SSTs. These estimates are derive primarily from chemistry considerations presented and discussed in Section A6.4. The C-14 present in alkaline wastes are not believed to exist in any form that would have precipitated. However, there is very little evidence that describes the behavior of C-14 present. Furthermore the data available is suspect because of biases in the analytical method. It is believed that C-14, which reported to tank sludges, did so as the result of occlusion by hydroxide and hydrated oxides. Because of its very voluminous nature, hydrated zirconium oxides which precipitated from neutralized zircaloy cladding waste are believed to have occluded more C-14 than did other types of hydroxide and hydrated oxide solids.

A6.6 REFERENCES

Pruett, D. J., 1990, "Extraction Chemistry of Fission Products," in *Science and Technology of Tributyl Phosphate*, Vol III, W. W. Schulz, L. L. Burger, and J. D. Navratil, Eds, CRC Press, Boca Raton, Florida.

Table A-6. Best-Basis Solubility Estimates for C-14.

Hanford Defined Waste Model Waste Type[1]	Fraction C-14 Precipitated
Process High-Activity Waste	
$BiPO_4$ Process[2]	0.05
Other processes[3]	0.05
Cladding Wastes	
Aluminum[4]	0.0
Zircaloy[5]	0.50
Miscellaneous Wastes	
Solid Wastes Ferrocyanide solids[6] Other solids[7]	 0.0 0.98
Complexed waste[8]	0.0
Other liquid wastes[9]	0.0

Notes:

[1] After addition of NaOH
[2] Includes HDW Model (Rev 4) Waste Types: MW1, MW2, 1C1, 1C2, 2C1, 224, and UR
[3] Includes HDW Model (Rev 4) Waste Types: R1, R2, P1, P2, P2', P3, Th1, Th2, PL1, PL2,and Z
[4] Includes HDW Model (Rev 4) Waste Types: CWR1, CWR2, CWP1, and CWP2
[5] Includes HDW Model (Rev 4) Waste Types: CWZr1 and CWZr2
[6] Includes HDW Model (Rev 4) Waste Types: PFeCN1, PFeCN2, TFeCN, and 1CFeCN
[7] Includes HDW Model (Rev 4) Waste Types: DE, CEM, and AR
[8] Includes HDW Model (Rev 4) Waste Types: HS and SRR
[9] Includes HDW Model (Rev 4) Waste Types: OWW1, OWW2, OWW3, NIT, BL, CSR, DW, N, PASF and B

A7.0 CESIUM

A7.1 MASS NUMBERS AND HALF-LIVES

Isotope Mass Number	Half Life
134	2.1 y
137	30 y

Both Cs-134 and Cs-137 are principal products of the fission of U-235.

A7.2 EXPECTED BEHAVIOR DURING FUEL DISSOLUTION

As principal fission products, atoms of both Cs-134 and Cs-137 were very likely uniformly dispersed throughout the irradiated uranium fuel. Cesium nitrate is extremely soluble in nitric acid solution. Therefore, all the Cs-134 and Cs-137 in the irradiated fuel were solubilized in the fuel dissolution process.

A7.3 PREDICTED OXIDATION STATES

A7.3.1 In Nitric Acid

Cesium, being an alkali metal element, exists only as the monovalent positive ion in acid solution.

A7.3.2 In Alkaline Waste

Cesium existed as the +1 cation in the alkaline solution resulting when acidic process raffinates were neutralized with sodium hydroxide. Indeed, under all conditions existing in the Hanford waste tanks, cesium was always in oxidation state I.

A7.4 CHEMISTRY IN ALKALINE MEDIA

The normal expectation for an alkali metal cation in alkaline media such as neutralized reprocessing wastes is that the alkali metal cation, e. g., Cs(I), is completely soluble. This was precisely the behavior of Cs-134 and Cs-137 provided either that (a) specific separation steps were not executed to precipitate radioactive cesium, or (b) reagents and conditions were not present to precipitate cesium as an insoluble mineral, e.g., cancrinite.

Deliberate precipitation of Cs-137 and Cs-134 occurred in the period from 1954 to 1957. Nickel ferrocyanide, an excellent co-precipitant for cesium, was used to scavenge Cesium both in the Metal Recovery Plant and in tank farms containing bismuth phosphate and Metal Recovery Plant raffinates. The resulting nickel ferrocyanide solids containing Cs-137 and Cs-134 were eventually allowed to settle in 20 different SSTs. Recent studies have shown that $Cs_2NiFe(CN)_6$ decomposed by both radiolytic and hydrolytic mechanisms under conditions that very likely existed in the Hanford tanks. It has been suggested that these pathways would have led to a reduction in the overall hexacyanoiron(III) concentration in the sludges (Lilga et al. 1995). However, cesium nickel hexacyanoiron(III) salts are far less soluble in aqueous NaOH; thus, their decomposition might be slower than their sodium analog. Thus, there is good reason to believe that the 20-some SSTs which received nickel ferrocyanide solids may still contain insoluble Cs-137 and Cs-134 (Bryan et al. 1995).

Even in some SSTs which do not and never did contain insoluble cesium nickel hexacyanoiron(III) salts, a fraction of the Cs-137 and Cs-134 is present as an insoluble species in the sludge (Lumetta et al. 1998). To account for this latter observation, it is reasonably postulated that cesium is present in one or more insoluble aluminosilicate minerals. Two likely candidate minerals are cancrinite and pollucite. However, it is not possible to predict in which SSTs cesium may have precipitated in a mineral form and in which such mineralization did not occur.

It must also be noted that at least some radiocesium could have been and likely was simply occluded by the voluminous hydrated iron oxide precipitates which formed in practically all process wastes. The ability of hydrated iron oxide to occlude (co-precipitate) and/or adsorb many cations is well known.

Finally, the recently reported results of Lumetta et al. should be carefully noted. Lumetta and his colleagues at the Pacific Northwest National Laboratory studied effects of simple water and NaOH washing on removal of both radionuclides and nonradioactive components from 29 different Hanford SST sludges. Two significant observations with respect to radiocesium emerged from this work. Firstly, all the sludges sampled or received contained various amounts of Cs-137 (Cs-134 was not analyzed for). And, except in only seven cases (sludges from tanks 241- B-201, U-110, C-103, C-106, T-104, T-111, and TY-104), simple NaOH washing solubilized essentially all the radiocesium. Solubilization of cesium would be consistent if cesium were originally retained either as a hexacyanoiron(III) species, an aluminosilicate mineral, or an occluded species, or, for that matter, all three retention mechanisms.

A7.5 BEST-BASIS SOLUBILITY ESTIMATES

A7.5.1 From Chemistry Considerations

It is clear from the discussion provided in Section A7.4 that available knowledge of the chemistry of radiocesium in alkaline Hanford tank wastes cannot provide definitive estimates of the general distribution of Cs-134 and Cs-137 between tank solution and solid phases. Cesium is extremely soluble, and is thus broadly distributed among the tank wastes. However, it is affected by both process history (scavenging and reprocessing efforts) and in-tank chemistry (occlusion and mineralization). Therefore, generally applicable split factors are relatively poor at predicting Cesium behavior. In isolated cases, e.g., solid ferrocyanide compounds, radiocesium precipitated nearly quantitatively. In other cases, e.g., some neutralized aluminum cladding wastes, most of the radiocesium may have remained mostly in the supernatant phase. But, in most cases, it seems very likely that radiocesium split between solid and liquid phases with the split dependent upon the nature and properties of the solid phase(s) present.

A7.5.2 From Analytical Considerations

A7.5.2.1 General Sludge/Salt Cake/Liquid Radiocesium Data. Scattered analytical data for a myriad of samples of tank sludges, salt cakes, and supernatants do little more than show radiocesium is present in all samples. These scattered data are far from sufficient to claim with any certainty the fraction of radiocesium precipitated from any particular type of waste.

Typical of the radiocesium data available are those for sludge and supernatant in DST 241-AY-102 and for sludges in 51 other tanks. The former analytical data show that 23% of the total Cs-137 in the tank is in the supernatant. The relation, if any, of the sludge to the liquid in this tank is completely unknown. Lumetta et al. (1998) found, as mentioned earlier, that of some different Hanford tank sludges examined every one contained some Cs-137.

A7.5.2.2 Process High-Activity Wastes.

PUREX Process HAW. .Analytical data for neutralized PUREX process HAW in Tank 241-AZ-101 indicate that, of the total Cs-137 believed added to the tank, 75% is in the supernatant and 3.8% in the sludge. Similar data for neutralized PUREX process HAW in Tank 241-AZ-102 show 78% of the Cs-137 is in the supernatant and 5% in the sludge. The poor Cs-137 material balance reflects uncertainty concerning the amount of Cs-137 calculated to have been in the solids heel left in the tank prior to addition of neutralized PUREX process HAW and thus in the total amount of Cs-137 added to each tank.

There are no analytical data from which to estimate the distribution of radiocesium between solid and liquid phases for other types of process HAW.

Cladding Wastes. Analytical data for neutralized zircaloy cladding waste in DST 241-AW-103 indicate only about 9% of the Cs-137 in the tank was in the supernatant phase. Similar data for neutralized zircaloy cladding waste in Tank 241-AW-105 show that only 2.4% of the total Cs-137 in the tank was in the supernatant phase.

There are no analytical data from which to judge the split of radiocesium between liquid and solid phases in neutralized aluminum cladding waste.

A7.5.2.3 Material Balance Considerations. Unlike other radionuclides in Hanford tank wastes, Sr-90 and Cs-137 have been extensively partitioned. For example, in the 1960's and 1970's large amounts of Cs-137 in tank waste were recovered, purified, and converted to solid CsCl for double encapsulation and storage in water basins. Other quantities of Cs-137 were loaded onto inorganic sorbents for transport to the Oak Ridge National Laboratory while other amounts of Cs-137 were discarded as solid waste.

A comprehensive evaluation and analysis of the total amount of Cs-137 ever generated at the Hanford site and its subsequent disposition is provided in Kupfer et al. (1998). This evaluation took into account all known information concerning amounts of Cs-137 in irradiated fuel not processed at Hanford; quantities of Cs-137 converted to solid CsCl and encapsulated; Cs-137 sorbed onto solid inorganic exchangers and shipped to the Oak Ridge National Laboratory; Cs-137 sent to cribs at the Hanford site; and Cs-137 disposed of a solid waste. The important result of this material balance evaluation was that, as of January 1, 1994, only 40 MCi Cs-137 were still present in the Hanford site tanks. Of this total, 10.9 MCi of Cs-137 were estimated to be in the SSTs and 29.2 MCi of Cs-137 were estimated to be in the DSTs. This latter value of 29.2 MCi compares very favorably with the value of 27.0 MCi of Cs-137 (as of January 1, 1994) calculated by summing all the analytically determined quantities of Cs-137 in each of the 28 DSTs. Analytical data do not exist for Cs-137 in all the SSTs, so it is not possible to compare the value of 10.9 MCi estimated from material balance considerations with an analytically-determined value.

A7.5.3 Tabulated Best-Basis Solubility Estimates

Table A-7 provides best-basis estimates of the fraction of Cs-134 and Cs-137 which precipitated from various neutralized wastes added to the SSTs. It is extremely difficult to justify the solubility estimates listed in Table A-7. For example, the very limited data for Cs-137 in existing neutralized PUREX process HAW in Tanks 241-AZ-101 and AZ-102 provide a basis for estimating that perhaps 10% of the radiocesium in all different types of HAW precipitated when such wastes were made alkaline. Similarly, analytical data for Cs-137 in existing zircaloy cladding removal waste in DSTs 241-AW-103 and AW-105 provide the basis for estimating that perhaps 30% of the Cs-137 in such wastes precipitated.

It is assumed from known cesium chemistry that the small amount of radiocesium in aluminum cladding waste did not precipitate when additional sodium hydroxide was added to such waste. Likewise, it is assumed that any radiocesium which may have been present in other liquid wastes did not precipitate when sodium hydroxide was added to these miscellaneous waste. But, solid wastes, e.g. metal ferrocyanide precipitates, diatomaceous earth, etc., are assumed to have nearly completely precipitated any radiocesium which may have been present.

What cannot be emphasized enough is that solubility data in Table A-7 may not be really of much value for predicting either a current tank-by-tank or global SST inventory of Cs-134 and Cs-137. Such predictions are extremely complicated by historical recovery operations which removed radiocesium from some tanks, converted some of it to solid form, and returned some of the inventory to tanks different than the ones it first resided in. We already know, from analytical data, for DSTs the amount of Cs-137 in each DST as well as the total inventory in all 28 DSTs. We also know from previous material balance calculations that, globally, the 149 SSTs contain 11 to 13 MCi of Cs-137 distributed, presumably, mainly in sludge solids with a small fraction also present in the salt cakes in various tanks. Data of Lumetta et al. indicate that washing sludge solids with dilute sodium hydroxide solutions will solubilize almost all the Cs-137 in sludge solids. Also, there is no reason to not believe that any radiocesium in salt cakes will not be easily solubilized when such salt cakes are sluiced and retrieved. Given all this latter information, it may not be necessary to have precise knowledge of the amount of Cs-137 in any particular SST.

A7.6 REFERENCES

Bryan, S. A., K. H. Pool, S. L. Bryan, S. V. Forbes, F. V. Hoopes, B. D. Lerner, G. M. Mong, P. T. Nguyen, G. F. Schiefelbein, R. L. Sell, and L. M. P. Thomas, 1995, *Ferrocyanide Safety Program Cyanide Speciation Studies Final Report*, PNL-10696, Pacific Northwest Laboratory, Richland, Washington.

Kupfer, M. J., A. L. Boldt, B. A. Higley, K. M. Hodgson, L. W. Shelton, B.C. Simpson, R. A. Watrous, M. D. LeClair, G. L. Borsheim, R. T. Winward, R. M. Orme, N. G. Colton, S. L. Lambert, D. E. Place, and W. W. Schulz, 1998, *Standard Inventories of Chemicals and Radionuclides in Hanford Site Tanks*, HNF-SD-WM-TI-740, Rev. 0B, Lockheed Martin Hanford Corporation, Richland, Washington.

Lilga, M. A., E. V. Alderson, R. T. Hallam, M. O. Hogan, T. L. Hobler, G. L. Jones, D. J. Kowalski, M. R. Lumetta, G. F. Schiefelbein, and M. R. Telander, 1995, *Ferrocyanide Safety Project Management Hexacyano(II) Aging Studies FY 1995 Annual Report*, PNL-10713, Pacific Northwest Laboratory, Richland, Washington.

Lumetta, G. J., B. M. Rapko, J. Liu and D. J. Temer, 1998, "Enhanced Sludge Washing for Pretreating Hanford Tank Sludges," in *Science and Technology For Disposal of Radioactive Tank Wastes*, W. W. Schulz and N. J. Lombardo, Eds, Plenum Press Pub., New York, New York.

Table A-7. Best-Basis Solubility Estimates for Radiocesium.

Hanford Defined Waste Model Waste Type[1]	Fraction of Insoluble Radiocesium[2]
Process High-Activity Waste	
$BiPO_4$ process[3]	0.10
Other processes[4]	0.10
Cladding Wastes	
Aluminum[5]	0.0
Zircaloy[6]	0.30
Miscellaneous Wastes	
Solid wastes Ferrocyanide wastes[7] Other solids[8]	 0.98 0.98
Complexed wastes[9]	0.0
Other liquid wastes[10]	0.0

Notes:

[1] After addition of NaOH
[2] Includes all cesium isotopes
[3] Includes HDW Model (Rev 4) Waste Types: MW1, MW2, 1C1, 1C2, 2C1, 2C2, 224, and UR
[4] Includes HDW Model (Rev 4) Waste Types: R1, R2, P1, P2, P2', P3, Th1, Th2, PL1, PL2 and Z
[5] Includes HDW Model (Rev 4) Waste Types: CWR1, CWR2, CWP1, and CWP2
[6] Includes HDW Model (Rev 4) Waste Types: CWZr1 and CWZr2
[7] Includes HDW Model (Rev 4) Waste Types: PFeCN1, PFeN2, TFeCN, and 1CFeCN
[8] Includes HDW Model (Rev 4) Waste Types: DE, CEM, and AR
[9] Includes HDW Model (Rev 4) Waste Types: HS and SRR
[10] Includes HDW Model (Rev 4) Waste Types: OWW1, OWW2, OWW3, NIT, BL, CSR, DW, N, PASF, and B

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A8.0 COBALT

A8.1 MASS NUMBER AND HALF LIFE

Isotope Mass Number	Half Life
60	5.27 y

Cobalt-60 was produced as an activation product of stable Co-59, i.e., Co-59 (n, gamma) Co-60. Co-59 was a common impurity in uranium metal fuel and in both zircaloy and aluminum fuel cladding.

A8.2 EXPECTED BEHAVIOR DURING FUEL DECLADDING AND DISSOLUTION

According to Cotton and Wilkinson (1966), "Cobalt is relatively unreactive, although it dissolves slowly in dilute mineral acids." Since Co-60 was dispersed on an atomic scale in both irradiated fuel and cladding, it passed into solution during decladding and dissolution operations.

A8.3 PREDICTED OXIDATION STATES

A8.3.1 In Nitric Acid

Dissolution of cobalt in dilute acids is known (Cotton and Wilkinson 1966) to give the pink aquo ion $[Co(H_20)_6]^{+2}$. Cobalt is also known to exist in the trivalent oxidation state in aqueous solutions. Co(III) is nitric acid solutions is stabilized by the formation of the $[Co(NO_2)_6]^{+3}$ ion, the so-called "cobaltinitrite" ion in older chemical literature (Noyes and Bray 1948). Conditions during fuel dissolution, e.g., elevated temperature, strong oxidizing power, excess nitric acid, etc., were favorable for conversion of part, perhaps a large fraction, of the Co-60 to the $[Co(NO_2)_6]^{+3}$ species. The stability of the $[Co(NO_2)_6]^{+3}$ ion to reduction is well known. Overall, the expectation is that the nitric acid feed solution to any of the separations processes contained both $[Co(H_2O)_6]^{+2}$ and $[Co(NO_2)]^{+3}$; the relative amount of each species is unknown and may have varied from batch to batch of acid dissolver solution.

A8.3.2 In Alkaline Media

The species Co(II) and $[Co(NO_2)_6]^{+3}$ are believed to have persisted when sodium hydroxide was added to waste solutions before they were added to the SSTs.

A8.4 CHEMISTRY IN ALKALINE MEDIA

Cobalt(II) forms an insoluble hydroxide. The large volume of other precipitates, e.g., hydrated oxides of iron and hydroxides of nickel and rare earths acted to scavenge small amounts of $Co(OH)_2$. The solubility product of $Co(OH)_2$ is reported (Cotton and Wilkinson 1966) to be 2.5E-16. Given this value, it appears likely that essentially all Co-60 in the divalent state precipitated in the sludge phase.

The hexanitrito complex of Co(III), $[Co(NO_2)_6]^{+3}$, is quite stable in both acidic and alkaline media. Thus, it is believed that any Co-60 which was present as the hexanitrito complex remained soluble and, eventually, reported either to a salt cake or to the DSTs.

A8.5 BEST-BASIS SOLUBILITY ESTIMATES

A8.5.1 From Chemistry Considerations

Cobalt chemistry in neutralized wastes, insofar as is known, indicates that Co-60 in the divalent state reported to the sludge phase while any Co(III) remained soluble. What chemistry cannot tell us, however, is what fraction of the Co-60 in the wastes added to the tanks was present as Co(II) and how much was present as Co(III).

A8.5.2 From Analytical Considerations

Fortunately, there are some relevant analytical data which shed some light on the distribution of Co-60 in actual wastes between the divalent and trivalent oxidation states. For example, Co-60 in DST 241-AW-105, which contains solids precipitated from zircaloy cladding waste, is almost all (99.9%) in the sludge phase. This behavior is consistent, for a waste which contained all divalent Co-60. Nitrite was not an important component of the NH_4F-NH_4NO_3 solvent in the Zirflex process used to dissolve zircaloy cladding.

On the other hand, the sludge in Tank 241-AZ-101 contains only 77% of the Co-60 calculated to have been added to the tank. Neutralized PUREX process HAW was added to DST 241-AZ-101 in the period 1983-1988. Nitrite was very much a component of the acid solution used to prepare PUREX process feed. Thus, conditions were favorable during fuel dissolution for oxidizing some Co-60 to the trivalent state and stabilizing in this oxidation state by forming the hexanitrito complex.

A8.5.3 Tabulated Best-Basis Solubility Estimates

Table A-8 lists best-basis estimates of the fraction of Co-60 which precipitated when various alkaline wastes were added to the SSTs. Both known cobalt chemistry and the limited analytical data for Co-60 inventories in actual waste were utilized in making the listed best-basis estimates. Thus, for those process HAW solutions where some of the Co-60 was deemed likely to be in the stable $[Co(NO_2)_6]^{+3}$ complex only 90% of the cobalt was estimated to have precipitated. For other wastes in which the presence of $[Co(NO_2)_6]^{+3}$ was considered unlikely, 98% of the Co-60 was assumed to have precipitated as cobalt hydroxide and reported to the sludge phase. Of course, it is well recognized that not all miscellaneous wastes added to the SSTs contained Co-60. But for those that did, the solubility estimates listed in Table A-8 apply.

A8.6 REFERENCES

Cotton, F. A., and G. Wilkinson, 1966, *Advanced Inorganic Chemistry*, Interscience Publishers, Inc., New York, New York.

Noyes, A. A., and W. C. Bray, 1948, *A System of Qualitative Analysis for the Rare Elements*, The MacMillan Co., New York, New York.

Table A-8. Best-Basis Solubility Estimates for Co-60.

Hanford Defined Waste Model Waste Type[1]	Fraction Co-60 Precipitated
Process High-Activity Waste	
$BiPO_4$ process[2]	0.90
Other processes[3]	0.90
Cladding Wastes	
Aluminum[4]	0.0
Zircaloy[5]	0.98
Miscellaneous Wastes	
Solid Wastes	
Ferrocyanide solids[6]	0.0
Other solids[7]	0.98
Complexed wastes[8]	0.0
Other liquid wastes[9]	0.0

Notes:

[1] After addition of NaOH
[2] Includes HDW Model (Rev 4) Waste Types: MW1, MW2, 1C1, 1C2, 2C1, 2C2, 224, and UR
[3] Includes HDW Model (Rev 4) Waste Types: R1, R2, P1, P2, P2', Th1, Th2, P3, PL1,PL2, and Z
[4] Includes HDW Model (Rev 4) Waste Types: CWR1, CWR2, CWP1, and CWP2
[5] Includes HDW Model (Rev 4) Waste Types: CWZr1 and CWZr2
[6] Includes HDW Model (Rev 4) Waste Types: PFeCN1, PFeCN2, TFeCN, and 1CFeCN
[7] Includes HDW Model (Rev 4) Waste Types: DE, CEM, and AR
[8] Includes HDW Model (Rev 4) Waste Types: HS and SRR
[9] Includes HDW Model (Rev 4) Waste Types: OWW1, OWW2, OWW3, NIT, BL, CSR, DW, N, PASF, and B

A9.0 CURIUM

A9.1 MASS NUMBERS AND HALF-LIVES

Isotope Mass Number	Half Life
242	162.9 d
243	28.5 y
244	18.1 y

Curium isotopes of interest result from efficient nuclear processes (Eller and Penneman 1986). For example, Cm-244 results from multiple n, gamma reactions starting with Pu-239. Curium-243 results from neutron irradiation of Am-241 according to the following reaction sequence:

Am-241(n, gamma)------> Am-242------> Cm-242(n,gamma)Cm-243

And, Cm-242 is a beta decay daughter of Am-242; Cm-242 also results from an alpha, n reaction on Pu-239.

A9.2 EXPECTED BEHAVIOR DURING FUEL DISSOLUTION

Curium is the chemical analogue of americium. Curium nitrate is very soluble in aqueous solution. Thus, all the curium isotopes in the irradiated fuel passed easily into solution when the fuel was dissolved in nitric acid.

A9.3 PREDICTED OXIDATION STATES

A9.3.1 In Nitric Acid

As noted earlier in the discussion on americium isotopes, the trivalent oxidation state of the actinide elements becomes increasingly stable with increasing atomic number. Indeed, it is very, very difficult, if not impossible, to either oxidize or reduce Cm(III) in aqueous solution. Certainly, therefore, curium was present as Cm(III) in nitric acid solutions resulting from fuel dissolution.

A9.3.2 In Alkaline Media

Curium also remained as Cm(III) when sodium hydroxide was added to aqueous wastes added to the underground SSTs.

A9.4 CHEMISTRY IN ALKALINE MEDIA

Curium, like its neighboring element (americium), forms a very insoluble hydroxide in alkaline media. Insoluble fluoride and phosphate compounds can also be precipitated in alkaline media. Therefore, curium isotopes in acidic process HAW solution precipitated almost completely (95-100%) when sodium hydroxide was added to such acidic wastes. As noted earlier, hydrated iron oxide and nonradioactive lanthanide precipitates which also formed when acidic wastes were made alkaline acted to agglomerate and co-precipitate curium solids.

A9.5 BEST-BASIS SOLUBILITY ESTIMATES

A9.5.1 From Chemistry Considerations

Evaluation of the curium chemistry described in Section A9.4 demonstrates that curium isotopes in alkaline media, especially in the presence of hydrated iron oxide and nonradioactive lanthanum and zirconium solids, and in the absence of strong organic complexing agents, precipitated nearly completely from neutralized process HAW and zircaloy cladding waste. Thus, chemistry considerations show that 99-100% of Cm-242, Cm-243, and Cm-244 introduced into the SSTs precipitated as an insoluble material in the sludge phase.

A9.5.2 From Analytical Considerations

The analytical data base for curium in Hanford tank solutions and solids is not considered sufficient to make suitable estimates of the solubility of curium in such phases.

A9.5.3 Tabulated Best-Basis Solubility Estimates

Table A-9 provides best-basis solubility (fraction precipitated) estimates for Cm-242, Cm-243, and Cm-244 in various neutralized wastes added to the SSTs. Because of the almost identical chemistry of americium and curium, the estimates listed in Table A-9 correspond exactly to those provided for americium isotopes.

A9.6 REFERENCES

Eller, P. G. and R. Penneman, 1986, "Curium," in *The Chemistry of the Actinide Elements*, Vol 2, J. J. Katz, G. T. Seaborg, and L. R. Morss, Eds, Chapman and Hall, New York, New York.

Table A-9. Best-Basis Solubility Estimates for Curium Isotopes.

Hanford Defined Waste Model Waste Type[1]	**Fraction Insoluble Curium**
Process High Activity Waste	
$BiPO_4$ process[2]	0.98
Other processes[3]	0.98
Cladding Waste	
Aluminum[4]	0.98
Zircaloy[5]	0.98
Miscellaneous Wastes	
Solid Wastes	
Ferrocyanide solids[6]	0.0
Other solids[7]	0.98
Complexed waste[8]	0.0
Other liquid wastes[9]	0.98

Notes:

[1] After addition of NaOH

[2] Includes HDW Model (Rev 4) Waste Types: MW1, MW2, 1C1, 1C2, 2C1, 2C2, 224, and UR

[3] Includes HDW Model (Rev 4) Waste Types: R1, R2, P1, P2, P2', Th1, Th2, P3, PL1, PL2, and Z

[4] Includes HDW Model (Rev 4) Waste Types: CWR1, CWR2, CWP1, and CWP2

[5] Includes HDW Model (Rev 4) Waste Types: CWZr1 and CWZr2

[6] Includes HDW Model (Rev 4) Waste Types: PFeCN1, PFeCN2, TFeCN and 1CFeCN

[7] Includes HDW Model (Rev 4) Waste Types: DE, CEM, and AR

[8] Includes HDW Model (Rev 4) Waste Types: HS and SRR

[9] Includes HDW Model (Rev 4) Waste Types: OWW1, OWW2, OWW3, NIT, BL, CSR, DW, N, PASF, and B

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A10.0 EUROPIUM

A10.1 MASS NUMBERS AND HALF LIVES

Isotope Mass Number	Half Life
152	13.6 y
154	8.62 y
155	4.97 y

All the listed europium isotopes of interest are products of the fission of U-235.

A10.2 EXPECTED BEHAVIOR DURING FUEL DISSOLUTION

Atoms of europium, because they were the products of fission of U-235, were dispersed throughout the irradiated fuel. Europium(III) nitrate is quite soluble in nitric acid solutions. Therefore, all the fission product europium was solubilized during the fuel dissolution operations.

A10.3 PREDICTED OXIDATION STATE

A10.3.1 In Nitric Acid

Europium is a member of the lanthanides, those elements with atomic numbers 58 through 72 inclusive. A distinguishing characteristic of the lanthanides is the stability of the tripositive oxidation state in aqueous solutions.

A10.3.2 In Alkaline Media

Europium is expected to persist in oxidation state III in alkaline wastes added to the SSTs. Certain reducing agents will reduce Eu(III) to Eu(II). However, no such reducing agents were present in any of the alkaline wastes of relevance.

A10.4 Chemistry in Alkaline Media

Europium(III) forms a very insoluble hydroxide; the fluoride and phosphate compounds of europium are also insoluble in aqueous solutions. Large concentrations of hydroxide ion, relative to the small concentrations of Eu-152, Eu-154, and Eu-155, were present in all neutralized process HAW. Many process wastes also contained appreciable amounts of phosphate or fluoride ion or both. Thus, there are excellent chemical reasons for believing that fission product europium in process HAW precipitated almost completely when such wastes were made alkaline.

Two other points are of importance with respect to precipitation of europium isotopes in neutralized process HAW. Appreciable amounts of nonradioactive lanthanide element isotopes were produced during irradiation of uranium fuel along with various radioactive isotopes. Also, in some cases lanthanum was deliberately added during fuel reprocessing. The nonradioactive lanthanide isotopes precipitated as hydroxides (and possibly in part as fluorides or phosphates) when the process HAW-type wastes were neutralized with NaOH. These precipitates, because of their volume and chemical similarity, acted as scavengers for precipitated radioactive rare earth isotopes.

In the 1960s and 1970s, some PUREX process sludges were sluiced and treated with nitric acid as a first step in removing most of the inventory of Sr-90. Such acid treatment also solubilized a fraction of the europium inventory. Europium isotopes were not coextracted with Sr-90 and remained in the aqueous raffinate. The latter raffinate, after addition of NaOH, was later concentrated to produce so-called Complexed Concentrate which is now stored in the DSTs.

A10.5 BEST-BASIS SOLUBILITY ESTIMATES

A10.5.1 From Chemistry Considerations

Evaluation of the europium chemistry detailed in Section A10.4 demonstrates that Eu-152, Eu-154, and Eu-155 in alkaline media, especially in the presence of hydrated iron oxide and nonradioactive lanthanide hydroxides, precipitated nearly quantitatively. Thus, chemistry considerations show that, in the absence of strong aqueous-soluble organic complexants, 75-100% of Eu-152, Eu-154, and Eu-155 in SST wastes, as generated, were in an insoluble form in the sludge phase.

A10.5.2 From Analytical Considerations

Only fragmentary analyses for europium isotopes in SST and DST solid and liquid phases exist. For example, the solids (sludge from neutralized zircaloy cladding waste) in Tank 241-AW-105 are reported to contain both Eu-154 and Eu-155; but, the europium content of the supernatant in this tank was apparently not analyzed. Similarly, analyses of sludges in DSTs 241-AZ-101 and 241-AZ-102 show the presence of europium isotopes, but there are no analyses for europium isotopes in the supernatant in either tank. Also, several of the SST sludges used by Lumetta et al. in sludge washing experiments contained varying amounts of radioactive europium isotopes. There are simply not sufficient europium analytical data to allow quantitative statements concerning the partition of europium between solid and liquid phases when various neutralized wastes were added to the SSTs.

A10.5.3 Tabulated Best-Basis Solubility Estimates

Table A-10 provides best-basis estimates of the fraction of europium isotopes which precipitated when various alkaline wastes were added to the SSTs. Europium is a lanthanide element. Thus, the solubility estimates provided in Table A-10 correspond exactly to those given for Sm-151 and Y-90.

Table A-10. Best-Basis Solubility Estimates for Europium Isotopes.

Hanford Defined Waste Model Waste Type[1]	Fraction Europium Precipitated[2]
Process High-Activity Waste	
$BiPO_4$ process[3]	0.75
Other processes[4]	0.75
Cladding Wastes	
Aluminum[5]	0.0
Zircaloy[6]	0.90
Miscellaneous Wastes	
Solid wastes	
Ferrocyanide solids[7]	0.0
Other solids[8]	0.98
Complexed waste[9]	0.0
Other liquid wastes[10]	0.0

Notes:

[1] After addition of NaOH

[2] For Eu-152, Eu-154, and Eu-155

[3] Includes HDW Model (Rev 4) Waste Types: MW1, MW2, 1C1, 1C2, 2C1, 2C2, 224, and UR

[4] Includes HDW Model (Rev 4) Waste Types: R1, R2, P1, P2, P2', Th1, Th2, P3, PL1, PL2, and Z

[5] Includes HDW Model (Rev 4) Waste Types: CWR1, CW2, CWP1, and CWP2

[6] Includes HDW Model (Rev 4) Waste Types: CWZr1 and CWZr2

[7] Includes HDW Model (Rev 4) Waste Types: PFeCN1, PFeCN2, TFeCN, and 1CFeCN

[8] Includes HDW Model (Rev 4) Waste Types: DE, CEM, and AR

[9] Includes HDW Model (Rev 4) Waste Types: HS and SRR

[10] Includes HDW Model (Rev 4) Waste Types: OWW1, OWW2, OWW3, NIT, BL, CSR, DW, N, PASF, and B

A11.0 HYDROGEN

A11.1 MASS NUMBER AND HALF LIFE

Isotope Mass Number	Half Life
3	12.3 y

The hydrogen isotope of mass number 3, tritium, is one of the products of the fission of U-235 and is an important nuclear weapons component. Other nuclear reactions, not found under tank conditions, are used to produce tritium.

A11.2 EXPECTED BEHAVIOR DURING FUEL DISSOLUTION

Nitric acid attack of the irradiated uranium metal released the H-3 atoms which were dispersed throughout the metal. Nitric acid did not oxidize hydrogen ions to hydrogen gas. Rather, the hydrogen atoms in the irradiated metal passed into solution as simple hydrogen ions.

A11.3 PREDICTED OXIDATION STATES

A11.3.1 In Nitric Acid

In the nitric acid dissolver solution obtained from the fuel dissolution step H-3 existed as hydrated hydrogen ions. Other possibilities, e.g., hydride ion, molecular hydrogen, etc., are not chemically reasonable.

A11.3.2 In Alkaline Media

There is no chemical reason that the oxidation state of H-3 in alkaline wastes was other than I.

A11.4 CHEMISTRY IN ALKALINE MEDIA

Agnew et al., in Rev. 4 of the Hanford Defined Waste (HDW) model (Agnew et al. 1997), report states that H-3 in wastes added to the SSTs became part of the water in such wastes and subsequently tracked with the fate of the water. There is no reason to discredit this view. Naturally, no chemical reactions occurred to precipitate H-3. Of course, water containing both H-1 and H-3 is part of the interstitial liquor held in the interstices of sludges and salt cakes. Such water is considered in the HDW Report and also here as part of the sludge or salt cake composition.

And, finally, evaporation of millions of gallons of dilute alkaline supernatant yielded condensates containing some H-3. Most of these condensates were disposed of to the soil underlying the Hanford site.

A11.5 BEST-BASIS SOLUBILITY ESTIMATES

A11.5.1 From Chemistry Considerations

Known tritium chemistry indicates that H-3 in Hanford tank wastes tracks as does water in such tanks. That is, H-3 is diluted with all the H-1 in the millions of gallons of water used in fuel reprocessing and waste management activities through the years.

A11.5.2 From Analytical Considerations

As expected, small amounts of H-3 have been detected in various Hanford site tank wastes. These scattered analytical data do not quarrel with the belief that H-3 in such wastes is part of the water that is present.

A11.5.3 Tabulated Best-Basis Solubility Estimates

Table A-11 lists best-basis estimates of the fraction of H-3 that precipitated when various alkaline wastes were introduced into the SSTs. In every case, it is believed that none of the H-3 precipitated. This conclusion is in agreement with the fraction precipitated data reported by Agnew et al. in Rev. 4 of the HDW Model report. There are no chemical behavior or direct analytical data to refute this assumption.

A11.6 REFERENCES

Agnew, S. F., J. Boyer, R. A. Corbin, T. B. Duran, J. R. Fitzpatrick, K. A. Jurgensen, T. P. Ortiz, and B. L. Young, 1997, *Hanford Tank Chemical and Radionuclide Inventories: HDW Model Rev. 4*, LA-UR-96-3860, Los Alamos National Laboratory, Los Alamos, New Mexico.

Table A-11. Best-Basis Solubility Estimates for H-3.

Hanford Defined Waste Model Waste Types[1]	Fraction H-3 Precipitated
Process High-Activity Waste	
$BiPO_4$ process[2]	0.0
Other processes[3]	0.0
Cladding Wastes	
Aluminum[4]	0.0
Zircaloy[5]	0.0
Miscellaneous Wastes	
Solid Wastes	
Ferrocyanide solids[6]	0.0
Other solids[7]	0.0
Complexed wastes[8]	0.0
Other liquid wastes[9]	0.0

Notes:

[1] After addition of NaOH

[2] Includes HDW Model (Rev 4) Waste Types: MW1, MW2, 1C1, 1C2, 2C1, 2C2, 224, and UR

[3] Includes HDW Model (Rev 4) Waste Types: R1, R2, P1, P2, P2', Th1, Th2, P3, PL1, PL2, and Z

[4] Includes HDW Model (Rev 4) Waste Types: CWR1, CWR2, CWP1, and CWP3

[5] Includes HDW Model (Rev 4) Waste Types: CWZr1 and CWZr2

[6] Includes HDW Model (Rev 4) Waste Types: PFeCN1, PFeCN2, TFeCN and 1CFeCN

[7] Includes HDW Model (Rev 4) Waste Types: DE, CEM, and AR

[8] Includes HDW Model (Rev 4) Waste Types: HS and SRR

[9] Includes HDW Model (Rev 4) Waste Types: OWW1, OWW1, OWW3, NIT, BL, CSR, DW, N, PASF, and B

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A12.0 IODINE

A12.1 MASS NUMBER AND HALF LIFE

Isotope Mass Number	Half Life
129	1.56E+07 y

Long-lived I-129 is a product of the fission of U-235 along with the much shorter lived I-131. As noted in Section 3.1.1, there is some uncertainty about the total inventory of I-129 in the Hanford tanks.

A12.2 EXPECTED BEHAVIOR DURING FUEL DISSOLUTION

According to Pruett (1990), "The major solid form of iodine in reactor fuel is CsI. In the gaseous phase, iodine can be found as CsI,Cs_2I_2, ZrI_2, ZrI_3, and ZrI_4, depending on the conditions. These iodides are all readily dissolved and oxidized to elemental iodine in hot nitric acid-NO_x dissolver solutions." All authorities agree iodine in irradiated fuel volatilized to some degree during fuel dissolution operations at the Hanford Site. Some authorities suggest that as much as 99% of the iodine present in the irradiated uranium fuel volatilized.

A12.3 PREDICTED OXIDATION STATES

A12.3.1 In Nitric Acid

Sparse analytical data, indicate that at least some I-129 is present in some tank wastes. Thus, not all the I-129 volatilized from solution during fuel dissolution operations. Residual radioiodine in the nitric acid dissolver solution likely existed in several oxidation states. There are no known data to establish what the oxidation state(s) of I-129 were in the nitric acid dissolver solution. Reasonable candidates, however, are -1 (as iodide ion) and +5 (as iodate ion, IO_3^{-1}). Very possibly, residual I-129 could have been present in both the -I and V oxidation states. It is considered very unlikely that any significant fraction of the residual I-129 was present as a periodate ion in nitric acid dissolver solutions.

There is also a good chance that process HAW from the REDOX and PUREX solvent extraction processes contained some amount of I-129 as an organic iodide. From time to time, numerous separations experts have claimed such a possibility is very real.

A12.3.2 In Alkaline Media

Although analytical data show I-129 is present in some Hanford tank alkaline liquid and solid wastes, these data do not describe the species or oxidation states of the I-129. As for nitric acid wastes, reasonable candidates in alkaline media are -I and V.

A12.4 Chemistry in Alkaline Media

Exactly what chemistry I-129 exhibited in wastes in SSTs is not known. It seems certain, however, that any I-129 present as an organic iodide likely did not precipitate. It is also doubtful that any insoluble iodates were formed. Thus, I(V), if present, is believed to have remained mainly soluble.

The fate of any I-129 which was present as iodide ion in the alkaline wastes added to the SSTs is uncertain. Some of the iodide ion may have reacted with fission product Ag-110m in process HAW-type wastes to form a very insoluble iodide. It is also possible, of course, that other metal ions in some wastes added to the SSTs formed insoluble iodides with I-129.

No matter what chemical species of I-129 were present in wastes added to the SSTs, all were occluded to some extent by the hydroxide and hydrated oxide precipitates present along with I-129.

A12.5 BEST-BASIS SOLUBILITY ESTIMATES

A12.5.1 From Chemistry Considerations

As is evident from the discussion in Section A12.4, little, is known about the chemistry of iodine in the alkaline wastes introduced into the SSTs. All known iodine chemistry can do for us is to tell us that I-129 can be present in the SST wastes in several oxidation states and that it is likely to have been distributed between solid and liquid phases. The fraction of I-129 which reported to various phases in the SSTs cannot be deciphered from our present knowledge of iodine chemistry in the SSTs.

A12.5.2 From Analytical Considerations

Reliable analytical data for I-129 in Hanford tank wastes are sparse. Some data are available which show PUREX process sludge in Tank 241-AZ-101 contains I-129. These data indicate that the sludge contains 7.14 Ci of I-129 while other data indicate that only 2.79 Ci of I-129 were ever added to Tank 241-AZ-101. (This large discrepancy likely reflects not only analytical difficulties but the uncertainty associated with the total inventory of residual I-129 which was not volatilized during fuel dissolution and which supposedly was routed to the underground tanks.) The I-129 content of the supernatant in Tank 241-AZ-101 was not determined. Available I-129 analytical data do not help establish the distribution of I-129 between solid and liquid phases in the SSTs.

A12.5.3 Tabulated Best-Basis Solubility Estimates

It should be noted that so-called silver reactors were used to sorb both I-131 and I-129 from the separations plants dissolver off-gas. In some cases, spent reactors were flushed with aqueous solutions. The spent flushes containing at least some radioactive iodine were neutralized with NaOH and routed to one or more SSTs. Often water was used to rinse the spent silver reactors. But on at least on one early occasion, a sodium thiosulfate solution was used as the flush media. Neither the volume of spent sodium thiosulfate solution nor the amount of I-129 present in such solution is known. Also, neither the form or ultimate fate of I-129 in sodium thiosulfate solutions added to one or more SSTs is known.

Table A-12 lists best-basis estimates of the fraction of I-129 that precipitated when various alkaline wastes were added to the SSTs. In the absence of any definitive chemistry or analytical considerations, it is estimated that 50% of any I-129 present in both neutralized process HAW and cladding wastes precipitated. It certainly recognized that the "50% soluble-50% insoluble" is an initial guess. Hopefully, additional analytical data will be available sometime in the future to provide more reliable estimates of the I-129 fraction which precipitated from neutralized process HAW and cladding wastes added to the SSTs.

The estimates for the fraction of I-129 in the many miscellaneous wastes added to the SSTs take into account the fact that very few of these wastes contained I-129. For example, Complexed Waste and ferrocyanide solids are not believed to have contained any insoluble I-129.

A12.6 REFERENCES

Pruett, D. J., 1990, "Extraction Chemistry of Fission Products," in *Science and Technology of Tributyl Phosphate*, Vol III., W. W. Schulz, L. L. Burger, and J. D. Navratil, Eds., CRC Press, Boca Raton, Florida.

Table A-12. Best-Basis Solubility Estimates for I-129.

Hanford Defined Waste Model Waste Type[1]	Fraction I-129 Precipitated
Process High-Activity Waste	
$BiPO_4$ process[2]	0.50
Other processes[3]	0.50
Cladding Wastes	
Aluminum[4]	0.50
Zircaloy[5]	0.50
Miscellaneous Wastes	
Solid wastes	
Ferrocyanide solids[6]	0.0
Other solids[7]	0.98
Complexed waste[8]	0.0
Other liquid wastes[9]	0.0

Notes:

[1] After addition of NaOH
[2] Includes HDW Model (Rev 4) Waste Types: MW1, MW2, 1C1, 1C2, 2C1, 2C2, 224, and UR
[3] Includes HDW Model (Rev 4) Waste Types: R1, R2, P1, P2, P2', Th1, Th2, P3, PL1, PL2, and Z
[4] Includes HDW Model (Rev 4) Waste Types: CWR1, CWR2, CWP1, and CWP3
[5] Includes HDW Model (Rev 4) Waste Types: CWZr1 and CWZr2
[6] Includes HDW Model (Rev 4) Waste Types: PFeCn1, PFeCn2, TFeCN, and 1CFeCN
[7] Includes HDW Model (Rev 4) Waste Types: DE, CEM, and AR
[8] Includes HDW Model (Rev 4) Waste Types: HS and SRR
[9] Includes HDW Model (Rev 4) Waste Types: OWW1, OWW2, OWW3, NIT, BL, CSR, DW, N, PASF, and B

A13.0 NEPTUNIUM

A13.1 MASS NUMBER AND HALF LIFE

Isotope Mass Number	Half Life
237	2.14E+06 y

In uranium-fueled nuclear reactors, Np-237 is produced by the following reactions (Schulz and Benedict 1972):

U-238(n, 2n)U-237------>Np-237

U-235(n, gamma)U-236(n,gamma)U-237------>Np-237

A13.2 EXPECTED BEHAVIOR DURING FUEL DISSOLUTION

Neptunium in any of its three principal oxidation states in aqueous solution, namely, +4, +5, and +6, forms very soluble nitrates. Neptunium metal is also vigorously attacked by boiling nitric acid. Therefore, Np-237 atoms in irradiated uranium metal were readily solubilized when the uranium was exposed to hot nitric acid.

A13.3 PREDICTED OXIDATION STATES

A13.3.1 In Nitric Acid

As indicated, Np-237 in aqueous nitric acid medium can exist simultaneously in the +4, +5, and +6 oxidation states. Np(V) is the stable oxidation state in dilute nitric acid where nitrate complexing shifts oxidation-reduction potentials. From about 1965, Np-237 was routinely recovered at the Hanford site by suitable modifications of the REDOX and PUREX solvent extractions processes. For this purpose, Np(V) was oxidized to extractable Np(VI) by nitrite ion. Also, purification and concentration of the recovered Np-237 involved the conversion of neptunium to the anionic nitrate complex of Np(IV), namely $[Np(NO_3)_6]^{-2}$ sorption onto anion exchange resins.

Thus, at various times in the history of the Hanford site, acidic wastes prior to neutralization with NaOH, likely contained Np-237 in one or, possibly, two of the oxidation states +4, +5, and +6.

A13.3.2 In Alkaline Media

It is believed that simple addition of NaOH to various process wastes prior to their addition to the SSTs did not change the oxidation state of Np-237 present in such wastes.

A13.4 CHEMISTRY IN ALKALINE MEDIA

Keller (1971) notes that the precipitate obtained by the addition of a base to a Np(IV) solution is a hydrous oxide, NpO_2 (aq), with varying amounts of adsorbed water rather than a distinct compound such as $Np(OH)_4$. Keller also states that Np(V) hydroxide, NpO_2OH, is a gelatinous material only sparingly soluble in water.

Neptunium(VI) in alkaline solution appears to be easily reduced to Np(IV). Thus, it is considered likely that any Np(VI) in neutralized process wastes added to the SSTs was reduced to Np(IV) by radiolytically-generated nitrite ions.

Removal of Np(IV) and Np(V) hydroxide particles from alkaline waste solutions added to the SSTs was undoubtedly aided by the scavenging action of hydrated iron oxide and other solids present in many of the waste solutions, particularly those containing relatively large concentrations of neptunium. As noted elsewhere in this report, hydrated iron oxide, in particular, is well-known for its large surface area and its propensity for scavenging +3 and +4 actinides from alkaline waste solutions. Hydroxides of nickel, zirconium, and rare earth elements also helped remove precipitates of neptunium from solution.

A13.5 BEST-BASIS SOLUBILITY ESTIMATES

A13.5.1 From Chemistry Considerations

Known neptunium chemistry provides good insight into the most likely fate of Np-237 in alkaline wastes introduced into the SSTs. All Np(VI) in the waste is likely reduced to Np(V). And, Np-237 present either as Np(IV) or as Np(V) formed an insoluble hydroxide. And, most importantly, hydrated iron oxide and other solids scavenged or co-precipitated both Np(IV) and Np(V). The conclusion reached is that a large percentage, over 98%, of the Np-237 added to the SSTs precipitated and was incorporated into sludge phases in these tanks.

A13.5.2 From Analytical Considerations

Np-237 is not one of the analytes typically measured in Hanford tank waste samples. It is not surprising, therefore, few Np-237 analytical data are available.

Some of the most relevant available Np-237 analytical data are for the wastes in Tanks 241-AW-103, 241-AZ-101, and 241-AZ-102. The first of these tanks contains the solids that precipitated when neutralized zircaloy cladding waste was added to the tank. The AZ tanks both contain the sludge phase resulting from addition of neutralized PUREX HAW to the tanks. Wastes added to all three of these tanks were generated in the period 1983-1988.

The analytical data for Tank 241-AW-103 show that the solid phase contains only a small amount of Np-237 as is expected for a cladding waste. The concentration of Np-237, if any, in the supernatant phase of the decladding waste was not determined.

The analytical data for Tank 241-AZ-101 indicate a total of 19.6 Ci of Np-237 was added to the tank of which 12.6 Ci (64%) are present in the sludge; unfortunately, the concentration of Np-237 in the supernatant liquid was not measured. For Tank 241-AZ-102 analyses show the sludge to contain 60.1 Ci of Np-237; the Np-237 content of the supernatant liquor is again not known. But, the calculated amount of Np-237 added to Tank 241-AZ-102 is only 49.2 Ci.

The available data, including those from sludges from various SSTs show that some Np-237 precipitated with the sludge solids. The fraction precipitated is addressed in Section A13.5.3.

A13.5.3 Tabulated Best-Basis Solubility Estimates

Listed in Table A-13 are best-basis estimates of the fraction of Np-237 which precipitated when various neutralized wastes were added to the SSTs. Of course, process HAW and spent decladding solutions contained the majority of the Np-237 added to any and all SSTs. It is tempting to believe that, just as for the other actinides, e.g., americium and plutonium, as much as 98% of the Np-237 in alkaline liquid wastes introduced into the SSTs was incorporated into the sludge solids in the tanks. But, unlike americium and plutonium, neptunium exhibits a +5 state which may have been somewhat soluble in the alkaline supernatant. For this reason, it is believed that only about 85% of the Np-237 inventory is in the SST sludges.

Also, as indicated in Table A-13, it is believed that Np-237 did not precipitate from neutralized waste streams which did not contain large amounts of solids such as aluminum cladding waste, complexed waste, and all other miscellaneous liquid wastes. Also, for the most part, these latter wastes did not contain significant amounts of Np-237.

A13.6 REFERENCES

Keller, C., 1971, *The Chemistry of the Transuranium Elements*, Verlag Chemie, Weinheim, Germany.

Schulz, W. W., and G. E. Benedict, 1972, *Neptunium-237: Production and Recovery*, U.S. Atomic Energy Commission, Oak Ridge, Tennessee.

Table A-13. Best-Basis Solubility Estimates for Np-237.

Hanford Defined Waste Model Waste Types[1]	Fraction Np-237 Precipitated
Process High-Activity Waste	
$BiPO_4$ process[2]	0.85
Other processes[3]	0.85
Cladding Wastes	
Aluminum[4]	0.0
Zircaloy[5]	0.85
Miscellaneous Wastes	
Solid wastes	
Ferrocyanide solids[6]	0.0
Other solids[7]	0.98
Complexed waste[8]	0.0
Other liquid wastes[9]	0.0

Notes:

[1] After addition of NaOH
[2] Includes HDW Model (Rev 4) Waste Types: MW1, MW2, 1C1, 1C2, 2C1, 2C2, 224, and UR
[3] Includes HDW Model (Rev 4) Waste Types: R1, R2, P1, P2, P2', Th1, Th2, P3, PL1, PL2, and Z
[4] Includes HDW Model (Rev 4) Waste Types: CWR1, CWR2, CWP1, and CWP2
[5] Includes HDW Model (Rev 4) Waste Types: CWZr1 and CWZr2
[6] Includes HDW Model (Rev 4) Waste Types: PFeCN1, PFeCN2, TFeCN and 1CFeCN
[7] Includes HDW Model (Rev 4) Waste Types: DE, CEM, and AR
[8] Includes HDW Model (Rev 4) Waste Types: HS and SRR
[9] Includes HDW Model (Rev 4) Waste Types: OWW1, OWW2, OWW3, NIT, BL, CSR, DW, N, PASF, and B

A14.0 NICKEL

A14.1 MASS NUMBERS AND HALF LIVES

Isotope Mass Number	Half Life
59	8.0E+04 y
63	92 y

Nickel-59 and Ni-63 are activation products produced, respectively, by neutron capture by naturally occurring Ni-58 and Ni-62. Nickel was a common impurity in both the uranium fuel irradiated in Hanford Site reactors and, especially, in the aluminum and zirconium alloys used to clad the uranium metal.

A14.2 EXPECTED BEHAVIOR DURING FUEL DECLADDING AND DISSOLUTION

Nickel(II) nitrate is quite soluble in aqueous solutions. Thus, any Ni-59 and Ni-63 in the irradiated fuel passed into solution when the irradiated fuel was dissolved in nitric acid. Any Ni-59 and Ni-63 in irradiated zircaloy cladding is believed to have been solubilized when such cladding was dissolved in NH_4F-NH_4NO_3 solutions. Atoms of nickel isotopes, both inert and radioactive, in irradiated aluminum cladding are believed to have been converted to Ni(II) ion when the cladding was dissolved in NaOH-$NaNO_3$ solution.

A14.3 PREDICTED OXIDATION STATE

A14.3.1 In Nitric Acid

In aqueous solution the divalent ion, Ni(II), is highly soluble. Thus, acidic nitrate solutions produced by dissolution of irradiated fuel and by subsequent plutonium/uranium recovery operations contained divalent Ni-59 and Ni-63. Nickel isotopes in decladding wastes would have been present as Ni(II).

A14.3.2 In Alkaline Media

Nickel(II) in acidic process HAW and in decladding wastes remained as Ni(II) when NaOH was added to the wastes. Nickel in other alkaline wastes is believed to have been present as Ni(II).

A14.4 CHEMISTRY IN ALKALINE MEDIA

Before discussing the chemistry of Ni-59 and Ni-63 in neutralized wastes, it is important to note that these radioactive isotopes, in many wastes routed to the SSTs, were typically diluted with a large amount of nonradioactive nickel isotopes. Nonradioactive nickel isotopes were introduced into the SSTs as the result of corrosion of the stainless steel equipment used in fuel decladding, fuel dissolution, and reprocessing operations (Kupfer et al. 1998).

According to Cotton and Wilkenson (1966), "The hydroxide, $Ni(OH)_2$ may be precipitated from aqueous solutions of Ni(II) salts on addition of alkali metal hydroxides as a voluminous green gel which becomes crystalline upon standing. It is readily soluble in acid and also in aqueous ammonia owing to the formation of ammine complexes. The crystalline substance is a definite hydroxide which, like the other hydroxides of divalent metals of the first transition series, has the $Mg(OH)_2$ structure. $Ni(OH)_2$ has little or no amphoteric tendency, and no nickelate(II) species of any kind have been reported."

Small amounts of radioactive nickel hydroxide were intimately mixed with large amounts of the hydroxides of nonradioactive nickel isotopes. The relatively huge amount of the latter hydroxides acted to agglomerate the hydroxides of Ni-59 and Ni-63. In many cases, large amounts of Fe(III) in waste solutions also precipitated when NaOH was added to the wastes. Copious amounts of hydrated iron oxide also acted to scavenge Ni-59 and Ni-63.

A14.5 BEST-BASIS SOLUBILITY ESTIMATES

A14.5.1 From Chemistry Considerations

Known nickel chemistry clearly indicates that 98 to 100% of both Ni-59 and Ni-63 precipitated when most wastes containing these radionuclides were neutralized by addition of NaOH. Only in the cases where waste solutions contained large concentrations of strong organic complexing agents, e.g, EDTA or HEDTA, did Ni(II) remain in solution and not precipitate under alkaline conditions.

A14.5.2 From Analytical Considerations

Nickel containing a mixture of radioactive and nonradioactive isotopes is a universal constituent of all SST sludges which have been sampled and analyzed to date. Solids in DSTs 241-AZ-101 and AZ-102, which contain neutralized PUREX process HAW, contain kilogram amounts of nickel as do solids in DSTs 241-AW-103 and AW-105 which contain neutralized zircaloy cladding waste. Unfortunately, for these DSTs, there are no nickel analyses for supernatants; thus, it is not possible to determine the distribution of nickel between solid and liquid phases.

A14.5.3 Tabulated Best-Basis Solubility Estimates

Table A-14 summarizes current best-basis estimates of the fraction of Ni-59 and Ni-63 that precipitated when various classes of neutralized wastes were introduced into the SSTs. These estimates derive primarily from considerations of the chemistry of nickel in alkaline media. But, they are not at all inconsistent with fragmentary analytical data which tend to show the presence of a large amount of nickel in sludges and very little in salt cake and supernatants. The reader is reminded that not all miscellaneous wastes added to the SSTs, by any means, contained nickel. But, for those miscellaneous wastes where nickel was present, the best-basis solubility estimates listed in Table A-14 apply.

A14.6 REFERENCES

Cotton, F. A., and G. Wilkinson, 1966, *Advanced Inorganic Chemistry*, 2nd Ed. Interscience Pub. Co., New York, New York.

Kupfer, M. J., A. L. Boldt, B. A. Higley, K. M. Hodgson, L. W. Shelton, B.C. Simpson, R. A. Watrous, M. D. LeClair, G. L. Borsheim, R. T. Winward, R. M. Orme, N. G. Colton, S. L. Lambert, D. E. Place, and W. W. Schulz, 1998, *Standard Inventories of Chemicals and Radionuclides in Hanford Site Tanks*, HNF-SD-WM-TI-740, Rev. 0B, Lockheed Martin Hanford Corporation, Richland, Washington.

Table A-14. Best-Basis Solubility Estimates for Nickel Isotopes.

Hanford Defined Waste Model Waste Types[1]	Fraction Nickel Precipitated[2]
Process High-Activity Waste	
$BiPO_4$ process[3]	0.98
Other processes[4]	0.98
Cladding Wastes	
Aluminum[5]	0.98
Zircaloy[6]	0.98
Miscellaneous Wastes	
Solid wastes	
Ferrocyanide wastes[7]	0.0
Other solids[8]	0.98
Complexed waste[9]	0.0
Other liquid wastes[10]	0.98

Notes:

[1] After addition of NaOH
[2] For all nickel isotopes including Ni-59 and Ni-63
[3] Includes HDW Model (Rev 4) Waste Types: MW1, MW2, 1C1, 1C2, 2C1, 2C2, 224, and UR
[4] Includes HDW Model (Rev 4) Waste Types: R1, R2, P1, P2, P2', Th1, Th2, P3, PL1, PL2, and Z
[5] Includes HDW Model (Rev 4) Waste Types: CWR1, CWR2, CWP1, and CWP2
[6] Includes HDW Model (Rev 4) Waste Types: CWZr1 and CWZr2
[7] Includes HDW Model (Rev 4) Waste Types: PFeCN1, PFeCN2, TFeCN, and 1CFeCN
[8] Includes HDW Model (Rev 4) Waste Types: DE, CEM, and AR
[9] Includes HDW Model (Rev 4) Waste Types: HS and SRR
[10] Includes HDW Model (Rev 4) Waste Types: OWW1, OWW2, OWW3, NIT, BL, CSR, DW, N, PASF, and B

A15.0 NIOBIUM

A15.1 MASS NUMBER AND HALF LIFE

Isotope Mass Number	Half Life
93m	3.6 y

Niobium-93m results from beta decay of Zr-93. The latter radioisotope has a half life of about a million years; Zr-93 is both a product of the fission of U-235 and an activation product, e.g., Zr-92(n,gamma)Zr-93.

A15.2 EXPECTED BEHAVIOR DURING FUEL DECLADDING AND DISSOLUTION

Any Nb-93m formed by beta decay of Zr-93 in irradiated zircaloy cladding readily dissolved in the NH_4F-NH_4NO_3 solution used to dissolve the cladding. Fluoride solutions are known to solubilize niobium. Niobium metal, in the absence of fluoride ion, is insoluble in nitric acid. But, only very, very small amounts of Nb-93m were formed in irradiated uranium metal as the result of beta decay of Zr-93. Also, some fluoride ion carried over to the nitric acid dissolution step in the form of a heel of spent zircaloy decladding waste. Thus, it appears very likely that Nb-93m present in irradiated uranium metal passed into aqueous solution as a soluble species when the uranium metal was dissolved in nitric acid.

A15.3 PREDICTED OXIDATION STATE

A15.3.1 In Nitric Acid

Niobium is in group 5B of the periodic table along with tantalum. The characteristic oxidation state of group 5B elements in aqueous solutions is the pentavalent one. As already noted, because of the carry over of a heel of zircaloy decladding solution to the nitric acid dissolution step, Nb-93m in the acid dissolver solution was likely present as a fluoride complex of Nb(V).

A15.3.2 In Zircaloy Decladding Solution

A solution containing large concentrations of NH_4F and NH_4NO_3 was used to chemically remove zircaloy cladding. The large concentration of fluoride ion in the decladding solution helped to solubilize any Nb-93m present from beta decay of the activation product Zr-93. Because of this, niobium went into aqueous solution as some Nb(V)species.

A15.4 CHEMISTRY IN ALKALINE MEDIA

Just as for Pa(V) discussed in Section A17.0, Nb(V) shows a strong tendence to hydrolyze in the absence of complexing agents. Also, just as for Pa(V), the least hydrolyzed cation is very likely $NbOOH^{+2}$.

Cotton and Wilkinson (1966) note that niobium has virtually no cationic chemistry but forms numerous anionic species. Niobium forms polymeric oxo anions in aqueous solutions. For example, there is evidence that the species $[H_2Nb_6O_{19}]^{-6}$, $[HNb_6O_{19}]^{-7}$, and $[Nb_6O_{19}]^{-8}$ exist (Neumann 1964).

Cotton and Wilkinson also note that Nb(V) does not form simple salts such as sulfates, nitrates, etc. The Russian scientist Nabivanets (1964) states that in nitric acid solution Nb(V) can exist as cationic, neutral, and anionic species hydrolyzed, polymeric, and colloidal forms in equilibrium, depending upon conditions.

An important observation concerning the chemistry of niobium in alkaline media is that polyanions are readily degraded to the hydrous pentoxide, Nb_2O_5. The hydrous pentoxide precipitates as a white gelatinous solid and redissolves in hydrofluoric acid.

Thus, it seems very likely that Nb-93m precipitated as $Nb_2O_5 \cdot H_20$ when sodium hydroxide was added to acid or neutral solutions containing niobium. Agglomeration and removal of the niobium precipitates from alkaline supernatant was also greatly facilitated by the co-precipitation of large amounts of iron and nickel. Because of their large surface area, these latter precipitates undoubtedly acted to efficiently scavenge $Nb_2O_5 \cdot nH_20$ from solution.

A15.5 BEST-BASIS SOLUBILITY ESTIMATES

A15.5.1 From Chemistry Considerations

Known niobium chemistry leaves little doubt that any Nb-93m in various neutralized waste streams added to the SSTs precipitated almost completely as some sort of hydrous oxide.

Agglomeration and removal of precipitated Nb-93m from solution was no doubt facilitated by co-precipitation of copious amounts of hydrated nickel and iron oxides.

A15.5.2 From Analytical Considerations

There is not a single analytical datum for Nb-93m in any SST or DST waste.

A15.5.3 Tabulated Best-Basis Solubility Estimates

Table A-15 provides best-basis estimates of the fraction of Nb-93m that precipitated in the various types of neutralized waste added to the SSTs. In the absence of any analytical data whatsoever for Nb-93m, these estimates derive solely from consideration of the known chemistry of niobium. As noted previously, not all miscellaneous wastes added to SSTs contained Nb-93m. But, for those that did, the best-basis solubility estimates in Table A-15 apply.

A15.6 REFERENCES

Cotton, F. A., and. G. Wilkinson, 1966, *Advanced Inorganic Chemistry*, Interscience Pub., New York, New York.

Nabivanets, B. I., 1964, Russ. J. Inorg. Chem, 9, 590.

Neumann, G., 1964, Acta. Chem. Scand., 18, 278.

Table A-15. Best-Basis Solubility Estimates for Nb-93m.

Hanford Defined Waste Model Waste Types[1]	Fraction Nb-93m Precipitated
Process High-Activity Waste	
$BiPO_4$ process[2]	0.98
Other processes[3]	0.98
Cladding Wastes	
Aluminum[4]	0.98
Zircaloy[5]	0.98
Miscellaneous Wastes	
Solid wastes	
Ferrocyanide solids[6]	0.0
Other solids[7]	0.98
Complexed waste[8]	0.0
Other liquid wastes[9]	0.98

Notes:

[1] After addition of NaOH
[2] Includes HDW Model (Rev 4) Waste Types: MW1, MW2, 1C1, 1C2, 2C1, 2C2, 224, and UR
[3] Includes HDW Model (Rev 4) Waste Types: R1, R2, P1, P2, P2', Th1, Th2, P3, PL1, PL2,and Z
[4] Includes HDW Model (Rev 4) Waste Types: CWR1, CWR2, CWP1, and CWP2
[5] Includes HDW Model (Rev 4) Waste Types: CWZr1 and CWZr2
[6] Includes HDW Model (Rev 4) Waste Types: PFeCN1, PFeCN2, TFeCN and 1CFeCN
[7] Includes HDW Model (Rev 4) Waste Types: DE, CEM, and AR
[8] Includes HDW Model (Rev 4) Waste Types: HS and SRR
[9] Includes HDW Model (Rev 4) Waste Types: OWW1, OWW2, OWW3, NIT, BL, CSR, DW, N, PASF, and B

A16.0 PLUTONIUM

A16.1 MASS NUMBERS AND HALF LIVES

Isotope Mass Number	Half Life
238	87.7 y
239	2.41E+04 y
240	6.56E+03 y
241	14.4 y
242	3.75E+05 y

Plutonium-239 atoms were produced as the result of the capture of neutrons by U-238 atoms to produce U-239 atoms which then decayed to long-lived Pu-239 by emission of a beta particle. Plutonium-240, -242, and -242 resulted from neutron capture by Pu-239 atoms. And, Pu-238 resulted from the nuclear reaction: Np-237(n, gamma)Pu-238.

A16.2 EXPECTED BEHAVIOR DURING FUEL DISSOLUTION

Many years of plant-scale experience at both the DOE Hanford and Savannah River Sites testify that plutonium atoms in irradiated uranium metal readily dissolve in the nitric acid solution used to dissolve the uranium metal.

A16.3 PREDICTED OXIDATION STATES

A16.3.1 In Nitric Acid

Depending upon conditions, e.g., plutonium concentration, acidity, etc., plutonium can exist in the +3, +4, +5, and +6 oxidation states. Indeed, under certain conditions, all four oxidation states can exist simultaneously.

Abundant experimental evidence exists, to show that +4 plutonium resulted when the irradiated uranium metal was dissolved in nitric acid. Depending on the particular reprocessing scheme used, plutonium was extracted either as Pu(IV) or Pu(VI) (dichromate oxidation). In all the reprocessing schemes used at the Hanford site, Pu(IV) and Pu(VI), if present, were routinely reduced to Pu(III) to separate plutonium from uranium and/or various fission products. Subsequently, Pu(III) was oxidized to Pu(IV) either as part of continuing plant-scale purification efforts or during thermal concentration of the acidic high level waste. Thus, final concentrated HAW prior to addition of NaOH contained plutonium as Pu(IV).

A16.3.2 In Alkaline Media

Addition of NaOH to HAW containing Pu(IV) did not change the oxidation state of the plutonium. There were no oxidants or reductants in such alkaline media to either oxidize Pu(IV) to Pu(V) or Pu(VI) or reduce Pu(IV) to Pu(III).

A16.4 CHEMISTRY IN ALKALINE MEDIA

The chemical literature (Weigel et al. 1986) indicates that Pu(IV) and Pu(III) form very insoluble hydroxides in alkaline solution. Thus, the normal expectation is that all plutonium in acidic HAW was quantitatively precipitated when NaOH was added to HAW.

Complicating this simple expectation is the well known tendency of Pu(IV) to form neutral and anionic complexes with many inorganic ligands which were present in neutralized HAW. For example, in some neutralized waste solutions, a fraction of the plutonium may have persisted as soluble complexes of carbonate or phosphate ions. In any event, the possibility that at least some of the plutonium in some neutralized HAW solutions was in a soluble form cannot be discounted.

Finally, it is noted that just as for many other radionuclides, e.g., Am-241, Cm-242, etc., freshly precipitated hydrated iron oxide in neutralized HAW had a great affinity for plutonium isotopes. Such affinity was probably represented by adsorption rather than by isomorphous replacement. In any event, precipitation of hydrated iron oxide tended to scavenge plutonium hydroxide particles and generally decrease the amount of soluble plutonium.

A16.5 BEST-BASIS SOLUBILITY ESTIMATES

A16.5.1 From Chemistry Considerations

Careful evaluation and consideration of known plutonium chemistry in alkaline media leads to the conclusion that, in the absence of strong aqueous-soluble organic complexing agents, from 90 to 95% of the plutonium introduced into the SSTs precipitated and was incorporated into the solid sludge phase. The remaining plutonium likely remained in the supernatant as a soluble complex ion.

A16.5.2 From Analytical Considerations

Relevant analytical data for plutonium isotopes in neutralized PUREX process zircaloy cladding waste and in HAW were presented and discussed earlier (Section 3.3). These data, with appropriate qualifications, clearly support the conclusion drawn in Section A16.5.1 to the effect that at least 95-98% of the plutonium in SST alkaline process wastes precipitated as an insoluble form in the sludge phase.

There are no analytical data from which to ascertain the behavior of plutonium which may have been present in miscellaneous liquid and solid wastes added to the SSTs. In the absence of such data, the assumption made here is that, except for aqueous wastes containing high concentrations of aqueous-soluble organic complexing agents, plutonium which might have been present in these miscellaneous waste precipitated essentially completely. Plutonium in neutralized wastes resulting from Sr-90 solvent extraction operations in B plant is assumed to have been strongly complexed and completely soluble. These latter waste solutions were eventually concentrated and routed to the DSTs.

A16.5.3 Tabulated Best-Basis Solubility Estimates

Table A-16 provides best-basis estimates of the fraction of plutonium isotopes which precipitated when various neutralized wastes were added to the SSTs. Even though listed analytical data indicate greater than 99.9% of the plutonium in process HAW and decladding waste solutions precipitated when these solutions were neutralized with NaOH, the best-basis solubility estimate is set at 97% insoluble. This lower conservative value allows for some errors in the analytical data and also acknowledges that plutonium is present in various salts and in some DST wastes.

A16.6 REFERENCES

Weigel, F., J. J. Katz, and G. T. Seaborg, 1986, "Plutonium," in *The Chemistry of the Actinide Elements*, 2nd Ed, J. J. Katz, G. T. Seaborg, and L. R. Morss, Eds., Chapman and Hall, New York, New York.

Table A-16. Best-Basis Solubility Estimates for Plutonium Isotopes.

Hanford Defined Waste Model Waste Type[1]	Fraction of Plutonium Precipitated[2]
Process High-Activity Waste	
$BiPO_4$ process[3]	0.97
Other processes[4]	0.97
Cladding Wastes	
Aluminum[5]	0.97
Zircaloy[6]	0.97
Miscellaneous Wastes	
Solid wastes	
Ferrocyanide solids[7]	0.0
Other solids[8]	0.98
Complexed waste[9]	0.0
Other liquid wastes[10]	0.98

Notes:

[1] After addition of NaOH

[2] For all plutonium isotopes

[3] Includes HDW Model (Rev 4) Waste Types: MW1, MW2, 1C1, 1C2, 2C1, 2C2, 224, and UR

[4] Includes HDW Model (Rev 4) Waste Types: R1, R2, P1, P2, P2', Th1, Th2, P3, PL1, PL2, and Z

[5] Includes HDW Model (Rev 4) Waste Types: CWR1, CWR2, CWP1, and CWP2

[6] Includes HDW Model (Rev 4) Waste Types: CWZr1 and CWZr2

[7] Includes HDW Model (Rev 4) Waste Types: PFeCN1, PFeCN2, TFeCN, and 1CFeCN

[8] Includes HDW Model (Rev 4) Waste Types: DE, CEM, and AR

[9] Includes HDW Model (Rev 4) Waste Types: HS and SRR

[10] Includes HDW Model (Rev 4) Waste Types: OWW1, OWW2, OWW3, NIT, BL, CSR, DW, N, PASF, and B

A17.0 PROTACTINIUM

A17.1 MASS NUMBER AND HALF LIFE

Isotope Mass Number	Half Life
231	3.25E+04 y

Protactinium-231 occurs naturally as one of the decay products of U-235, i.e.,

U-235------>Th-231------>Pa-231.

A17.2 EXPECTED BEHAVIOR DURING FUEL DISSOLUTION

Because uranium metal fuel irradiated at the Hanford site, even when enriched, contained only a small amount of U-235, only a very, very small amount of Pa-231 was ever introduced into the Hanford SSTs. Known protactinium chemistry (Kirby 1959) indicates that Pa(V) is not soluble in nitric acid; but, considering that the amount of Pa-231 in all irradiated fuel was exceedingly small, it is likely that the solubility of Pa-231 in any batch of nitric acid dissolver solution was not exceeded.

A17.3 PREDICTED OXIDATION STATE

A17.3.1 In Nitric Acid

Protactinium is a member of Group 5B of the periodic table; Group 5B also includes niobium and tantalum. On this basis, the expected and predicted oxidation state of protactinium in nitric acid solutions is +5. According to Kirby (1959), "...freshly prepared solutions in which [Pa(V)] <E-05 and $[HNO_3] > 1$ M are fairly stable. Such systems contain monomeric nitratohydroxide complexes of the form $[Pa(OH)_n(NO_3)_m]^{+5-n-m}$ where $n > 2$ and $m < 4$." Certainly, there is nothing known about the chemistry and the origin of nitric acid dissolver solutions to suggest soluble Pa-231 would not have been present in the pentavalent state.

A17.3.2 In Alkaline Media

If soluble Pa(V) were indeed present in acidic process solutions,then very likely protactinium remained in the pentavalent oxidation state when NaOH was added to such solutions. Reagents and/or conditions which might have taken Pa(V) to a different oxidation state were not present in alkaline Hanford tank wastes.

A17.4 CHEMISTRY IN ALKALINE MEDIA

Protactinium(V) shows a strong tendency to hydrolyze in the absence of complexing agents. The least hydrolyzed cation may be $PaOOH^{+2}$. At $[H] < 1M$, $PaO(OH_2)^{+1}$ begins to form and becomes predominant at pH of approximately 3. Further hydrolysis to insoluble species readily occurs at high higher pHs.

It should be noted that anionic complexes of Pa(V) are well established, e.g., fluoro, oxalato, and sulfato, etc. Such complexes may have been present in some of the process HAW solutions added to the SSTs. These anionic complexes resist hydrolysis more effectively than $PaOOH^{+2}$ or $PaO(OH_2)^{+1}$. Although Pa-231 may have been present in some neutralized wastes as an anionic species, it is believed that the Pa-231 precipitated as an insoluble hydrolysis product under the conditions used to neutralize wastes added to the SSTs.

A17.5 BEST-BASIS SOLUBILITY ESTIMATES

A17.5.1 From Chemistry Considerations

Known protactinium chemistry strongly indicates that any Pa-231 in various alkaline wastes added to the SSTs precipitated essentially as a hydrolyzed form, e.g., $PaO_2 \cdot nH_20_2O$. Agglomeration and removal of precipitated Pa-231 from solution was certainly facilitated by co-precipitation of hydrated oxides of iron and nickel and hydroxides of rare earth elements.

A17.5.2 From Analytical Considerations

There are no data for Pa-231 in any SST or DST waste.

A17.5.3 Tabulated Best-Basis Solubility Estimates

Table A-17 lists best-basis estimates of the fraction of Pa-231 that precipitated when various types of waste were neutralized with sodium hydroxide and added to the SSTs. In the absence of analytical data, the solubility estimates shown in Table A-17 derive entirely from considerations of the known chemistry of protactinium. Very few of the miscellaneous wastes added to the SSTs contained Pa-231; however, for those that did the solubility estimates listed in Table A-17 apply.

A17.6 REFERENCES

Kirby, H. W., 1959, *The Radiochemistry of Protactinium*, NAS-NS-3016, National Academy of Sciences, National Research Council, Washington, D.C.

Table A-17. Best-Basis Solubility Estimates for Pa-231.

Hanford Defined Waste Model Waste Types[1]	Fraction Pa-231 Precipitated
Process High-Activity Waste	
$BiPO_4$ process[2]	0.98
Other processes[3]	0.98
Cladding Wastes	
Aluminum[4]	0.98
Zircaloy[5]	0.98
Miscellaneous Wastes	
Solid wastes Ferrocyanide solid[6] Other solids[7]	 0.0 0.98
Complexed waste[8]	0.98
Other liquid wastes[9]	0.98

Notes:

[1] After addition of NaOH

[2] Includes HDW Model (Rev 4) Waste Types: MW1, MW2, 1C1, !C2, 2C1, 2C2, 224, and UR

[3] Includes HDW Model (Rev 4) Waste Types: R1, R2, P1, P2, P2', Th1, Th2, P3, PL1, PL2 and Z

[4] Includes HDW Model (Rev 4) Waste Types: CWR1, CWR2, CWP1, and CWP2

[5] Includes HDW Model (Rev 4) Waste Types: CWZr1 and CWZr2

[6] Includes HDW Model (Rev 4) Waste Types: PFeCN1, PFeCN2, TFeCN and 1CFeCN

[7] Includes HDW Model (Rev 4) Waste Types: DE, CEM, and AR

[8] Includes HDW Model (Rev 4) Waste Types: HS and SRR

[9] Includes HDW Model (Rev 4) Waste Types: OWW1, OWW2, OWW3, NIT, BL, CSR, DW, N, PASF, and B

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A18.0 RADIUM

A18.1 MASS NUMBERS AND HALF LIVES

Isotope Mass Number	Half Life
226	1.6E+03 y
228	6.69 y

Both Ra-226 and Ra-228 are decay products of uranium isotopes. Ra-226 results from radioactive decay of U-238; the complete decay scheme for decay of U-238 to stable Pb-206 is given in Friedlander, Kennedy, and Miller(1955). Ra-228 is the primary product from the alpha decay of Th-232.

A18.2 EXPECTED BEHAVIOR DURING FUEL DISSOLUTION

Radium is a member of the same group, IIa, of the periodic table as strontium and barium. The electropositive nature of these elements increase with increasing atomic number. All the Group IIa elements form nitrate salts that are quite soluble in aqueous solution. Hence, both Ra-226 and Ra-228 passed into solution when the irradiated uranium metal was dissolved in hot nitric acid.

A18.3 PREDICTED OXIDATION STATE

A18.3.1 In Nitric Acid

The characteristic oxidation state of members of Group IIa in aqueous media is +2. Therefore, Ra-226 and Ra-228 in nitric acid process solutions were present as Ra(II).

A18.3.2 In Alkaline Media

Radium ion in neutralized waste solutions added to the SSTs was present in the +2 oxidation state. Addition of NaOH would not have changed this.

A18.4 CHEMISTRY IN ALKALINE WASTE SOLUTIONS

According to Cotton and Wilkinson (1955), Ra(II), just like Ba(II) in the same group of the periodic table, forms a very insoluble sulfate. Conversely, $Ra^{+2}(aq)$ is not hydrolyzed and, in alkaline solution, forms a hydroxide of moderate solubility.

On the basis of this chemistry, it seems likely that Ra-226 and Ra-228 in separation process HAW solutions precipitated as insoluble sulfates. All these process HAW solutions contained appreciable concentrations of sulfate ions as the result of extensive use in the separations processes of ferrous sulfamate to reduce Pu(IV) to Pu(III).

Also, because of their very small concentration and the relatively high solubility of $Ra(OH)_2$, Ra-226 and Ra-228 in neutralized waste solutions which did not contain any or only very low concentrations of sulfate ion likely remained as soluble Ra(II) in the alkaline supernatant. These latter waste solutions included spent aluminum decladding solution and miscellaneous liquid wastes. Spent zircaloy decladding solutions also did not contain sulfate ion. But, it is believed that the massive amounts of $ZrO_2 \cdot nH_2O$ which precipitated when these decladding solutions were neutralized carried down with them the small amounts of Ra-226 and Ra-228 which were probably present.

Finally, any Ra-226 and Ra-228 in complexed wastes remained as soluble species as the result of strong complexing by organic compounds present.

A18.5 BEST-BASIS SOLUBILITY ESTIMATES

A18.5.1 From Chemistry Considerations

Almost all the Ra-226 and Ra-228 in neutralized process HAW is believed to have precipitated as an insoluble sulfate. Ra-226 and Ra-228 in neutralized spent Zirflex process wastes is also believed to have been carried down with the massive precipitate of $ZrO_2 \cdot nH_20$. Radium in all other alkaline liquid wastes added to SSTs is believed to have remained in a soluble form.

A18.5.2 From Analytical Considerations

There are no analytical data for either Ra-226 or Ra-228 in any SST or DST waste.

A18.5.3 Tabulated Best-Basis Solubility Estimates

Table A-18 lists best-basis estimates of the fraction of Ra-226 and Ra-228 that precipitated when various alkaline waste streams were introduced into the SSTs. In the absence of any analytical data, the estimates shown are based upon the radium chemistry considerations discussed in Section A18.4.

Table A-18. Best-Basis Solubility Estimates for Ra-226 and Ra-228.

Hanford Defined Waste Model Waste Types[1]	Fraction Radium Precipitated
Process High-Activity Waste	
$BiPO_4$ process[2]	0.90
Other processes[3]	0.90
Cladding Wastes	
Aluminum[4]	0.0
Zircaloy[5]	0.90
Miscellaneous Wastes	
Solid wastes	
Ferrocyanide solids[6]	0.0
Other solids[7]	0.98
Complexed wastes[8]	0.0
Other liquid wastes[9]	0.0

Notes:

[1] After addition of NaOH

[2] Includes HDW Model (Rev 4) Waste Types: MW1, MW2, 1C1, 1C2, 2C1, 2C2, 224, and UR

[3] Includes HDW Model (Rev 4) Waste Types: R1, R2, P1, P2, P2', Th1, Th2, P3, PL1, PL2, and Z

[4] Includes HDW Model (Rev 4) Waste Types: CWR1, CWR2, CWP1, and CWP2

[5] Includes HDW Model (Rev 4) Waste Types: CWZr1 and CWZr2

[6] Includes HDW Model (Rev 4) Waste Types: PFeCN1,PFeCN2, TFeCN, and 1CFeCN

[7] Includes HDW Model (Rev 4) Waste Types: DE, CEM, and AR

[8] Includes HDW Model (Rev 4) Waste Types: HS and SRR

[9] Includes HDW Model (Rev 4) Waste Types: OWW1, OWW2, OWW3, NIT, BL, CSR, DW, N, PASF, and B

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A19.0 RUTHENIUM

A19.1 MASS NUMBER AND HALF LIFE

Isotope Mass Number	Half Life
106	1.0 y

Ruthenium-106 is a product of the fission of U-235. Because of its very short half life (ca. 1 y), the inventory of Ru-106 in Hanford waste tanks is rapidly decreasing. For example, of 1.04E+05 Ci estimated to be present in the tanks on January 1, 1994, only about 1.3E+04 Ci remains as of the date (September 1998) of this report. And, in another three years or so, when large scale disposal of some of the DST wastes may begin, the Ru-106 inventory will have decreased to a very small amount indeed.

It should also be noted that the only significant inventory of Ru-106 in the Hanford Site resides in one or more DSTs. This inventory derives from wastes generated in the period 1983-1988 that were added directly to some DSTs. No wastes containing Ru-106 have been added to any of the SSTs for over 10 years.

A19.2 EXPECTED BEHAVIOR DURING FUEL DISSOLUTION

Massive ruthenium metal, one of the noble metals, is quite resistant to attack by nitric acid. Also, ruthenium and other platinum group metals in highly irradiated UO_2 fuel from commercial power reactors is converted during reactor irradiation to oxides which are very insoluble in nitric acid.

Neither of these conditions, however, applies to Ru-106 in uranium metal irradiated at the Hanford site. Ru-106 atoms were likely dispersed throughout all the uranium metal. Also, in a metallic fuel irradiated to low power levels, Ru-106 atoms were not converted to an insoluble oxide. Thus, Ru-106 in uranium metal irradiated at the Hanford site went into solution when the uranium was dissolved in nitric acid.

A19.3 PREDICTED OXIDATION STATE

A19.3.1 In Nitric Acid

Depending on conditions, ruthenium in aqueous solutions may exist in any of the oxidation states II, III, IV and VII. But, in nitric acid solutions, nitrosyl complexes, which contain the group RuNO, are a distinctive and highly important feature of ruthenium chemistry. Schulz, Metcalf, and Barney (1984) note that the RuNO group is remarkably resistant to either oxidation or reduction. Cotton and Wilkinson (1966) state, "Ruthenium solutions or compounds which have at any time been treated with nitric acid can be suspected of containing nitric oxide bound to the metal." Various aspects of the aqueous chemistry of ruthenium including the various species postulated to be present in nitric acid solution have been recently reviewed by Zeidan (1980).

Ruthenium(II) is stabilized in aqueous solution by forming complexes, particularly nitrosyl complexes. These include cationic, anionic, and neutral complexes. Such complexes are of particular importance to the radiochemistry of ruthenium since the exceptionally stable RuNO group is thought to exist in many radioactive waste solutions containing ruthenium.

Ru(III) forms numerous complex ions with fluoride ion, chloride ion, bromide ion, hyroxide ion, carboxylates, amines, and sulfite ion. No nitrosyl complexes of Ru(III) are known. Also, no cationic complexes of Ru(IV) are known. Finally, it should be noted that ruthenate ion, $(RuO_4)^{-2}$ is the only Ru(VI) complex ion of significance. It is not stable in neutral or acid solution but is stable in base.

A19.4 CHEMISTRY IN ALKALINE MEDIA

It is clear that the chemistry in alkaline solutions is quite complex because of the variety of oxidation states ruthenium might exhibit in such solutions.

It seems clear that Ru-106 in all liquid wastes, prior to addition of NaOH, was largely present as a nitrosyl species, most likely RuNO. But at least some of the Ru-106 in the original wastes was present as Ru(III) which does not form a nitrosyl species. It is also entirely possible that Ru(III) could have been converted to aqueous-soluble $(RuO_4)^{-2}$ ion.

Information presented in Schulz, Metcalf, and Barney (1984) shows that co-precipitation with hydrated iron oxide is frequently used to remove radioruthenium from aqueous solutions either for analytical or decontamination purposes. Ames, Fullerton, and Pearce (1964) and Barton et al. (1972) patented ferric hydroxide co-precipitation processes for removal of radioruthenium from nuclear waste solutions. Co-precipitation of Ru-106, Ru-97, and other ruthenium isotopes with Fe(III) hydroxide has also been studied by Kepak (1979) and by Music, Gessman, and Wolf (1979).

Finally, co-precipitation of ruthenium on various other metal hydroxides has been documented as follows: aluminum hydroxide (Strohol, Molnar, and Bacic, 1972); magnesium hydroxide (Novikov and Razankin 1972); and beryllium, zinc, lanthanum hydroxides (Strohol and Noethig-Hus 1974).

A19.5 BEST-BASIS SOLUBILITY ESTIMATES

A19.5.1 From Chemistry Considerations

Known, complex chemistry of ruthenium is not very helpful for estimating the fraction of Ru-106 that precipitated when various neutralized wastes were added to the SSTs. Ruthenium chemistry strongly indicates that some fraction of the Ru-106 in the alkaline waste was present as a $Ru(NO)^{+2}$ species and that this ruthenium species co-precipitated with iron, nickel, and rare earth hydroxides or hydrated oxides. But, known ruthenium chemistry also suggests that some fraction of the radioactive ruthenium did not precipitate and remained in the alkaline supernatant as one or more soluble ruthenium species.

A19.5.2 From Analytical Considerations

Considering the very short half life of Ru-106, there are no relevant data for this isotope in any SST. Indeed, the only reported analytical data for Ru-106 appear to be those for DST 241-AZ-101. These latter data indicate most, i.e., >99%, of the Ru-106 in acidic PUREX process HAW remained soluble when such waste was neutralized with NaOH. Lacking any other analytical data, it is assumed that Ru-106 in other neutralized process HAW and also in neutralized cladding waste remained soluble.

A19.5.3 Tabulated Best-Basis Solubility Estimates

Table A-19 lists best-basis estimates of the fraction of Ru-106 that precipitated when various alkaline wastes were added to the SSTs. These estimates rely heavily on analytical data for DST 241-AZ-101 that indicate little Ru-106 precipitated from neutralized PUREX process waste. There is nothing in known ruthenium chemistry which would seriously contradict the estimates shown in Table A-19. Finally, it is again recognized that many of the wastes added to the SSTs did not contain Ru-106. But, for those that did, the solubility estimates shown in Table A-19 apply.

A19.6 REFERENCES

Ames, L. L., Jr., D. R. Fullerton, and D. W. Pearce, 1964, *Process of Removing Ruthenium from Aqueous Solution*, U.S. Patent 3, 136,715.

Kepak, F., 1979, "Contribution to the Study of Sorption of Radionuclides on Hydrated Oxides," J. Radioanal. Chem., 51, 307.

Music, S., M. Gessner, and R. H. H. Wolf, 1979, "Sorption of Ruthenium-97 on Fe2O3, $Fe(OH)_2$, and $Fe(OH)_3$ Precipitates," Mikrochim Acta, 1, 95.

Novikov, A. I., and V. I. Ruzankin, 1972, "Coprecipitation of Fission Products with Magnesium Hydroxide. I. Coprecipitation of Cs, Sr, Y, Mo, Sb, Se, As, Nb, Zr, Ru, Zn, Cd, and Ce," Radiokhimya, 13, 134; Sov. Radiochem. (Engl. Transl.), 14, 521.

Schulz, W. W., S. G. Metcalf, and G. S. Barney, 1984, *Radiochemistry of Ruthenium*, NAS-NS-3029, Technical Information Center, U.S. Department of Energy, Oak Ridge, Tennessee.

Strohal, P., K. Molnar, and I. Bacic, 1972, "Preconcentration of Trace Elements By Aluminum Hydroxide," Mikrochim Acta, 5, 586.

Zeidan, Z., 1980, "Etude Bibliographique Des Differentes Especes Du Ruthenium En Solution Aqueuse," French Report CEA-R-5051, Centre d'Etudes Nucleaires de Fontenay-aux-Roses, Paris, France.

Table A-19. Best-Basis Solubility Estimates for Ru-106.

Hanford Defined Waste Model Waste Types[1]	Fraction of Ru-106 Precipitated
Process Wastes	
$BiPO_4$ process[2]	0.10
Other processes[3]	0.10
Cladding Wastes	
Aluminum[4]	0.0
Zircaloy[5]	0.10
Miscellaneous Wastes	
Solid Wastes	
Ferrocyanide solids[6]	0.0
Other solids[7]	0.98
Complexed wastes[8]	0.0
Other liquid waste[9]	0.0

Notes:

[1] After addition of NaOH

[2] Includes HDW Model (Rev 4) Waste Types: MW1, MW2, 1C1, 1C2, 2C1, 2C2, 224, and UR

[3] Includes HDW Model (Rev 4) Waste Types: R1, R2, P1, P2, P2', Th1, Th2, P3, PL1, PL2, and Z

[4] Includes HDW Model (Rev 4) Waste Types: CWR1, CWR2, CWP1, and CWP3

[5] Includes HDW Model (Rev 4) Waste Types: CWZr1 and CWZr2

[6] Includes HDW Model (Rev 4) Waste Types: PFeCN1, PFeCN2, TFeCN, and 1CFeCN

[7] Includes HDW Model (Rev 4) Waste Types: DE, CEM, AR

[8] Includes HDW Model (Rev 4) Waste Types: HS and SRR

[9] Includes HDW Model (Rev 4) Waste Types: OWW1, OWW2, OWW3, NIT, BL, CSR, DW, N, PASF, and B

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A20.0 SAMARIUM

A20.1 MASS NUMBER AND HALF LIFE

Isotope Mass Number	Half Life
151	9.01E+01 y

Samarium-151 is a product of the fission of U-235.

A20.2 EXPECTED BEHAVIOR DURING FUEL DISSOLUTION

Similar to the behavior of europium isotopes (cf. Section A10.0), the inventory of Sm-151 in irradiated uranium fuel was readily dissolved in nitric acid.

A20.3 PREDICTED OXIDATION STATE

A20.3.1 In Nitric Acid

Samarium, like fission product europium, is a lanthanide. In nitric acid solution, samarium exists as Sm(III).

A20.3.2 In Alkaline Media

Samarium(III) is not easily oxidized or reduced. Therefore, in alkaline waste solutions the chemistry of samarium was that of Sm(III).

A20.4 CHEMISTRY IN ALKALINE MEDIA

As a trivalent lanthanide, the behavior of Sm(III) paralleled that of Eu(III) and La(III). The chemistry expectation is that 95 to 99% of the Sm(III) reported to the sludge phase. Hydrous iron oxide, present in almost all neutralized HAW solutions, readily co-precipitated Sm(III). Also, as mentioned in the earlier text for radioactive europium isotopes, HAW-type solutions contained significant concentrations of nonradioactive lanthanides in addition to the radioactive isotopes. And, also as mentioned previously, some process HAW-type solutions contained deliberately-added lanthanum. All the nonradioactive lanthanide element isotopes precipitated as hydroxides, or, possibly phosphates and/or fluorides, when process HAW-type wastes were neutralized with NaOH. Precipitation of hydrated iron oxide and of nonradioactive lanthanides served to aggregate and scavenge precipitated radioactive rare earths.

In the 1960s and 1970s some PUREX process sludges were sluiced and treated with nitric acid as a first step in removing most of their inventory of Sr-90. Such acid treatment also solubilized a fraction of the Sm-151 inventory. Samarium-151 was not coextracted with Sr-90 and remained in the aqueous raffinate. The latter raffinate was later concentrated to produce Complexed Concentrate which is now stored in DSTs.

A20.5 BEST-BASIS SOLUBILITY ESTIMATES

A20.5.1 From Chemistry Considerations

Evaluation of the samarium chemistry described in Section A20.4 clearly demonstrates, that Sm-151 in alkaline media, especially in the presence of hydrated iron oxide and nonradioactive lanthanide hydroxides, precipitated nearly quantitatively. Thus, chemistry considerations show that, in the absence of strong aqueous-soluble complexants, 75 to 100% of the Sm-151 in SST wastes, was in an insoluble form in the sludge phase.

A20.5.2 From Analytical Considerations

The analytical data base for Sm-151 in Hanford tank solutions and solids is almost nonexistent. It is not sufficient to make reliable estimates of the partition of Sm-151 between phases when wastes were originally added to the SSTs.

A20.5.3 Tabulated Best-Basis Solubility Estimates

Table A-20 provides best-basis solubility estimates for Sm-151 in various waste types. Because of the similarity of the chemistry of Sm-151 to other lanthanides, Y-90, and to the trivalent actinides americium and curium, the estimates listed in Table A-20 correspond exactly to those provided in this report for other trivalent lanthanides.

Table A-20. Best-Basis Solubility Estimates for Sm-151.

Hanford Defined Waste Model Waste Types[1]	Fraction Sm-151 Precipitated
Process Wastes	
$BiPO_4$ processes[2]	0.75
Other processes[3]	0.75
Cladding Wastes	
Aluminum[4]	0.00
Zircaloy[5]	0.90
Miscellaneous Wastes	
Solid wastes	
Ferrocyanide solids[6]	0.0
Other solids[7]	0.98
Complexed wastes[8]	0.0
Other liquid wastes[9]	0.00

Notes:

[1] After addition of NaOH

[2] Includes HDW Model (Rev 4) Waste Types: MW1, MW2, 1C1,1C2, 2C1, 2C2, 224, and UR

[3] Includes HDW Model (Rev 4) Waste Types: R1, R2, P1, P2, P2', Th1, Th2, P3, PL1, PL2, and Z

[4] Includes HDW Model (Rev 4) Waste Types: CWR1, CWR2, CWP1, and CWP2

[5] Includes HDW Model (Rev 4) Waste Types: CWZr1 and CWZr2

[6] Includes HDW Model (Rev 4) Waste Types: PFeCN1, PFeCN2, TFeCN, and 1CFeCN

[7] Includes HDW Model (Rev 4) Waste Types: DE, CEM, and AR

[8] Includes HDW Model (Rev 4) Waste Types: HS and SRR

[9] Includes HDW Model (Rev 4) Waste Types: OWW1, OWW2, OWW3, NIT, BL, CSR, DW, N, PASF, and B

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A21.0 SELENIUM

A21.1 MASS NUMBER AND HALF LIFE

Isotope Mass Number	Half Life
79	8.05E+05 y

Selenium-79 is a product of the fission of U-235. The half life of 8.05E+05 y is newly calculated; the new value corrects a long-standing and well-recognized error in the previously reported value for the half life of Se-79.

A21.2 EXPECTED BEHAVIOR DURING FUEL DISSOLUTION

Heslop and Jones (1976) report that selenium is readily attacked by hot nitric acid solutions. Since Se-79 in the irradiated uranium metal was dispersed on an atomic scale, it was quite susceptible to dissolution in the nitric acid used to dissolve the irradiated uranium.

A21.3 PREDICTED OXIDATION STATE

A21.3.1 In Nitric Acid

Like other elements in Group VIa, selenium in aqueous solution and in solid compounds can exist in one of three principal oxidation states, namely, II, IV and VI. In nitric acid medium, selenium exists most likely as either a Se(IV) or a Se(VI) species. The latter species resembles sulfate ion formed by sulfur.

Heslop and Jones (1976) note that Se(VI) is a very strong oxidizing agent and thus is not especially stable in aqueous solution. (Indicative of its strong oxiding power, Se(VI) oxidizes $2C1^{-1}$ to $C1_2$.) Thus, in aqueous nitric acid solution the stable oxidation state of Se-79 was likely the tetravalent state. Heslop and Jones also note that Se(IV) is stable toward disproportination. Thus, it is likely that Se-79 in acidic process solutions was present as the $[SeO_3]^{-2}$ ion.

A21.3.2 In Alkaline Media

Neutralization, with sodium hydroxide, of various neutral and acidic process solutions did not either reduce or oxidize Se(IV). Thus, in these alkaline solutions and also in alkaline cladding waste Se-79 was, it is believed, present as the selenite ion.

A21.4 CHEMISTRY IN ALKALINE MEDIA

According to Cotton and Wilkinson (1966), "SeO_2 dissolves readily in water to give solutions which do contain selenous acid with the $OSe(OH)_2$ structure; Raman spectra show that it is negligibly dissociated in aqueous solution (Walrafen 1962), while in half and fully neutralized solutions the ions $[HSeO_3]^{-1}$ and $[SeO_3]^{-2}$ are formed, salts of which can be isolated." Thus, in alkaline solutions added to the SSTs the behavior of Se-79 was that of soluble selenite ion.

In the alkaline SST waste all the metals which might have formed insoluble selenite compounds precipitated as hydroxides or hydrated oxides. Alkali and alkaline earth cations which did not precipitate do not form insoluble selenite compounds.

Thus, Se-79, as the selenite ion, remained largely in the alkaline supernatant. A small amount, 5 to 15%, was occluded in the voluminous hydroxide and hydrated oxide precipitate of iron and other metals. The latter Se-79 remained in the sludge solids as they dehydrated and converted to crystalline materials.

A21.5 BEST-BASIS SOLUBILITY ESTIMATES

A21.5.1 From Chemistry Considerations

Known selenium chemistry indicates that Se-79 very likely divided between alkaline supernatants and solids when wastes containing this radionuclide were added to SSTs. This chemistry also indicates the larger (ca. 85 to 95%) fraction of the Se-79 reported to the supernatant.

A21.5.2 From Analytical Considerations

Only very fragmentary analytical data exist for Se-79 in Hanford wastes. For example, of 41.3 Ci of Se-79 calculated to have been added to Tank 241-AZ-101 only 1.3% was found in the sludge phase. Presumably, the remaining Se-79 reported to the supernatant, although analytical data to support this contention are not available. Also, for DST 241-AZ-102, the sludge in this tank is reported to contain <0.726 Ci of Se-79. Unfortunately, the Se-79 content of the supernatant in this DST was not determined. As far as is known, there are no other Se-79 analytical data.

A21.5.3 Tabulated Best-Basis Solubility Estimates

Table A-21 lists best-basis estimates of the fraction of Se-79 that precipitated when various alkaline wastes were introduced into the SSTs. In the absence of sufficient and relevant analytical data, the estimates shown in Table A-21 derive from the interpretation of selenium chemistry provided in Section A21.4. It is known, that Se-79 was not present in many of the wastes that were added to the SSTs. But, for those that did contain Se-79, the best-basis solubility estimates listed in Table A-21 apply.

A21.6 REFERENCES

Cotton, F. A., and G. Wilkinson, 1966, *Advanced Inorganic Chemistry*, Interscience Pub. Co., New York, New York.

Heslop, G. B., and H. Jones, 1976, *Inorganic Chemistry: A Guide to Advanced Study*, Elsevier Scientific Pub. Co., New York, New York.

Walrafen, G. E., 1962, J. Chem. Phys., 36, 90.

Table A-21. Best-Basis Solubility Estimates for Se-79.

Hanford Defined Waste Model Waste Types[1]	Fraction of Se-79 Precipitated
Process High-Activity Waste	
$BiPO_4$ process[2]	0.05
Other processes[3]	0.05
Cladding Wastes	
Aluminum[4]	0.00
Zircaloy[5]	0.05
Miscellaneous Wastes	
Solid wastes	
Ferrocyanide solids[6]	0.00
Other solids[7]	0.98
Complexed wastes[8]	0.00
Other liquid wastes[9]	0.00

Notes:

[1] After addition of NaOH
[2] Includes HDW Model (Rev 4) Waste Types: MW1, MW2, 1C1, 1C2, 2C1, 2C2, 224, and UR
[3] Includes HDW Model (Rev 4) Waste Types: R1, R2, P1, P2, P2', Th1, Th2, P3, PL1, PL2, and Z
[4] Includes HDW Model (Rev 4) Waste Types: CWR1, CWR2, CWP1, and CWP2
[5] Includes HDW Model (Rev 4) Waste Types: CWZr1 and CWZr2
[6] Includes HDW Model (Rev 4) Waste Types: PFeCN1, PFeCN2, TFeCN, and 1CFeCN
[7] Includes HDW Model (Rev 4) Waste Types: DE, CEM, and AR
[8] Includes HDW Model (Rev 4) Waste Types: HS and SRR
[9] Includes HDW Model (Rev 4) Waste Types: OWW1, OWW2, OWW3, NIT, BL, CSR, DW, N, PASF, and B

A22.0 STRONTIUM

A22.1 MASS NUMBER AND HALF LIFE

Isotope Mass Number	Half Life
90	29 y

Strontium-90 is a principal product of the fission of U-235.

A22.2 EXPECTED BEHAVIOR DURING FUEL DISSOLUTION

Strontium-90, being one of the principal products of the fission of U-235, was likely uniformly dispersed throughout the irradiated fuel. Strontium nitrate is very soluble in nitric acid solutions; hence, all the Sr-90 in the irradiated fuel was solubilized during the fuel dissolution operations.

A22.3 PREDICTED OXIDATION STATE

A22.3.1 In Nitric Acid

Strontium is a member of Group IIa of the periodic table. As expected, therefore, it exists exclusively as the divalent metal cation, Sr^{+2}, in nitric acid solutions.

A22.3.2 In Alkaline Media

Strontium in alkaline media existed solely in the divalent oxidation state. Some of the aqueous-soluble organic compounds in complexed wastes strongly complexed strontium but did not change its oxidation state. Thus, Sr-90 in complexed wastes still existed in the oxidation state II.

A22.4 CHEMISTRY IN ALKALINE MEDIA

In the absence of significant concentrations of aqueous-soluble organic compounds which can complex Sr(II), the chemistry of strontium in non-complexed tank waste is essentially that of insoluble compounds formed with carbonate, fluoride, and sulfate anions. Cotton and Wilkinson (1966) note that sulfates of strontium, barium, and radium are very insoluble and that strontium carbonate is rather insoluble. Cotton and Wilkinson also state, "The Ca-Ra hydroxides are all soluble in water, increasingly with increasing atomic number, $Ca(OH)_2$ ca. 2 g/L; $Ba(OH)_2$ ca. 60 g/L at ca. 20 °C." On the basis of this latter information, Sr-90 would likely have precipitated nearly quantitatively, possibly as a mixed carbonate, fluoride, and sulfate, when waste solutions containing it were neutralized.

As already mentioned several times, large amounts of amorphous $Fe_2O_3 \cdot nH_2O$ precipitated when process wastes containing strontium and other radionuclides were neutralized prior to introduction into the SSTs. This iron precipitate, as noted in the discussion for actinide elements, has a great affinity for actinides, lanthanides, and strontium. The exact manner in which strontium is initially co-precipitated or scavenged by the hydrated oxide precipitate is not known. Eventually, however, an abundance of empirical evidence exists to demonstrate that strontium becomes strongly bound into the dehydrated iron oxide crystalline lattice. As such, strontium is not removed by simple water or NaOH leaching of the sludge. Indeed, plant-scale experience testifies to the fact that even strong nitric acid solutions are only partially effective in solubilizing strontium from aged iron oxides in Hanford sludges.

The net effect is that, in the absence of strong organic complexants, Sr-90 was essentially quantitatively precipitated in neutralized wastes sent to the SSTs. Data obtained by Lumetta et al. (1998) in the last few years show that water and NaOH washes do not remove appreciable Sr-90 from aged SST sludges

A22.5 BEST-BASIS SOLUBILITY ESTIMATES

A22.5.1 From Chemistry Considerations

Evaluation of the strontium chemistry described in Section A22.4 clearly demonstrates that Sr-90 in alkaline media, especially in the presence of hydrated iron oxide, precipitated quantitatively. Thus, chemistry considerations show that 85-100% of the Sr-90 in SSTs is present as an insoluble material.

A22.5.2 From Analytical Considerations

Relevant analytical data for Sr-90 in neutralized PUREX process Zircaloy cladding and HAW were presented and discussed earlier in Section 3.3. These data, with appropriate reservations concerning their limited sufficiency, support the conclusion drawn in Section A22.5.1 to the effect that 85-100% of the Sr-90 in neutralized process wastes precipitated as an insoluble form in the sludge phase.

There are no analytical data from which to ascertain the behavior of Sr-90 which may have been present in the miscellaneous liquid and solid wastes added to the SSTs. In absence of such data, the assumption made here is that, except for aqueous wastes containing high concentrations of soluble organic complexants, any Sr-90 in these miscellaneous wastes was completely precipitated. Small concentrations of Sr-90 in neutralized aqueous waste resulting from Sr-90 solvent extraction operations in B plant are assumed to have been strongly complexed and completely soluble.

A22.5.3 Tabulated Best-Basis Solubility Estimates

Table A-22 provides best-basis estimates of the fraction of Sr-90 that precipitated in various alkaline waste solutions added to the SSTs. Even though all analytical data indicate greater than 99.9% of the Sr-90 in process HAW and decladding solutions precipitated when NaOH was added to such solutions, the best-basis solubility estimate is set at 98%. This lower conservative value allows for some errors in the analytical data and also acknowledges that Sr-90 is present in various salt cakes and in some DST waste.

A22.6 REFERENCES

Cotton, F. A., and G. Wilkinson, 1966, *Advanced Inorganic Chemistry*, 2nd Ed. Interscience Pub. Co., New York, New York.

Lumetta, G. J., B. M. Rapko, J. Liu, and D. J. Temer, 1998, "Enhanced Sludge Washing for Pretreating Hanford Tank Sludges," in *Science and Technology for Disposal of Radioactive Tank Waste*, W. W. Schulz and N. J. Lombardo, Eds, Plenum Press Pub., New York, New York.

Table A-22. Best-Basis Solubility Estimates for Sr-90.

Hanford Defined Waste Model Waste Types[1]	Fraction of Sr-90 Precipitated
Process High-Activity Waste	
$BiPO_4$ process[2]	0.98
Other processes[3]	0.98
Cladding Wastes	
Aluminum[4]	0.98
Zircaloy[5]	0.98
Miscellaneous Wastes	
Solid wastes	
Ferrocyanide solids[6]	1.0
Other solids[7]	0.98
Complexed waste[8]	0.0
Other liquid wastes[9]	0.98

Notes:

[1] After addition of NaOH
[2] Includes HDW Model (Rev 4) Waste Types: MW1, MW2, 1C1, 1C2, 2C1, 2C2, 224, and UR
[3] Includes HDW Model (Rev 4) Waste Types: R1, R2, P1, P2,P2', Th1, Th2, P3, PL1, PL2, and Z
[4] Includes HDW Model (Rev 4) Waste Types: CWR1, CWR2, CWP1, and CWP2
[5] Includes HDW Model (Rev 4) Waste Types: CWZr1 and CWZr2
[6] Includes HDW Model (Rev 4) Waste Types: PFeCN1, PFeCN2, TFeCN, and 1CFeCN
[7] Includes HDW Model (Rev 4) Waste Types: DE, CEM, and AR
[8] Includes HDW Model (Rev 4) Waste Types: HS and SRR
[9] Includes HDW Model (Rev 4) Waste Types: OWW1, OWW2, OWW3, NIT, BL, CSR, DW, N, PASF, and B

A23.0 TECHNETIUM

A23.1 MASS NUMBER AND HALF LIFE

Isotope Mass Number	Half Life
99	2.1E+05 y

Technetium-99 is a product of the fission of U-235. There are no nonradioactive isotopes of technetium.

A23.2 BEHAVIOR DURING FUEL DISSOLUTION

As far as is known, Tc-99 atoms dissolve completely in the nitric acid solution used to dissolve the irradiated uranium metal. At high fissionable fuel burnup, noble metals are known to, at least in part, collect as an insoluble residue during nitric acid dissolution of highly irradiated UO_2. There is no evidence, whatsoever, for any precipitation of noble metals let alone technetium during dissolution of irradiated metal at the Hanford site.

A23.3 PREDICTED OXIDATION STATE

A23.3.1 In Nitric Acid

Technetium, like manganese, is known to exhibit a number of different oxidation states in aqueous solution. Oxidation state VII is particularly stable. Hence, in the acidic dissolver solution Tc-99 is believed to have existed as the pertechnetate ion,TcO_4^{-1}. Support for this contention is provided by Hanford PUREX plant-scale experience to the fact that 10-20% of the Tc-99 in the first extraction column feed coextracted with uranium. Tributyl phosphate is known to extract $HTcO_4$, similar to extraction of nitric acid.

A23.3.2 In Alkaline Media

In the absence of aminopolycarboxylic acids and their thermal and radiolytic degradation products, technetium in alkaline waste solutions is believed to exist as TcO_4^{-1} ion. In some DSTs containing aminopolycarboxylic acids and their degradation products, there is much evidence (Schroeder et al. 1998) to indicate only a fraction of the Tc-99 content is present as the pertechnetate ion. There is no evidence to suggest that Tc-99 in SSTs is present in other than the +7 oxidation state.

A23.4 CHEMISTRY IN ALKALINE MEDIA

The essential expectation is that Tc-99 would remain completely soluble as the TcO_4^{-1} ion when acidic process wastes were made alkaline. This expectation was not realized, however, when process wastes containing Fe(III) were neutralized. The behavior of voluminous precipitates of hydrated Fe(III) oxide in adsorbing and/or occluding many radionuclide cations has been mentioned earlier. Analytical evidence (Lumetta et al. 1998) indicate such precipitates also coprecipitate some Tc-99, probably by an occlusion rather than a sorption mechanism. It must be admitted, however, that the exact mechanism (or mechanisms) acting to retain a fraction of the Tc-99 in the sludge phase in SSTs is not known. In addition to simple occlusion of TcO_4^{-1} by the hydrated iron oxide precipitates it is conceivable that some reduction of TcO_4^{-1} to Tc(IV) occurred and the resulting Tc(IV) coprecipitated with iron and other metals. Lumetta et al., however, report that simple washing of SST sludges which contained Tc-99 with NaOH solutions removed essentially all the technetium. It is difficult to reconcile this latter observation with hypothetical reduction of TcO_4^{-1} to Tc(IV) and precipitation of the latter species.

No matter how it got there, the fact is that all or, at least, a great many SST sludges contain Tc-99. This fact must be taken into account when making best-basis estimates of Tc-99 solubility.

A23.5 BEST-BASIS SOLUBILITY ESTIMATES

A23.5.1 From Chemistry Considerations

As is evident from the review of technetium chemistry given in Section A23.4, known chemistry considerations do not provide an unequivocal estimate of the distribution of technetium between sludge (insoluble) and supernatant (soluble) phases as they originally formed in the SSTs. This consideration simply confirms that some of the Tc-99 precipitated and some stayed in solution.

A23.5.2 From Analytical Considerations

As for many other radionuclides, there is a lack of useful analytical data from which to judge how much Tc-99 reported to the sludge phase when various kinds of waste were made alkaline and introduced into the SSTs. Some reliable Tc-99 data are available for DSTs 241-AZ-101 and AZ-102; these two tanks, as noted earlier, contain neutralized PUREX process HAW solids and liquids. The Tc-99 data for DST 241-AZ-101 indicate that 32 to 53% of the technetium reported to the sludge phase and from 68 to 112% to the supernatant phase depending upon which value is chosen for the total inventory of Tc-99 in the tank. The technetium data for DST 241-AZ-102 indicate 36% of the technetium reported to the sludge and 58% to the supernatant.

Sludges in many other tanks are known from analytical data to contain Tc-99, e.g., solids in DSTs 241-AY-102, 241-AW-105, and 241-AW-103. But, the Tc-99 content of the supernatant liquid in these tanks was not analyzed for technetium. Lumetta et al. (1998) also noted that all the SST sludges examined in their studies contained at least some technetium. Lumetta et al. also reported that washing as-received sludge with NaOH solutions, in most cases, solubilized practically all the Tc-99.

A23.5.3 Tabulated Best-Basis Solubility Estimates

Table A-23 provides best-basis estimates of the fraction of Tc-99 that precipitated when various types of neutralized wastes were added to the SSTs. The estimate that one third of the Tc-99 in neutralized process HAW and zircaloy cladding waste precipitated is based upon:

a. Analytical data for recent neutralized PUREX HAW in Tanks 241-AZ-101 and AZ-102 which indicate about one third of the Tc-99 reported to the solid phase.

b. Analytical data for recent neutralized PUREX process zircaloy cladding waste which demonstrate the presence of what appears to be an appreciable amount of Tc-99 in the solid phase.

c. Analytical data for various SST sludges, all of which show that Tc-99 is present.

d. Analytical data for liquids in all 28 DSTs, all of which show that more than a trivial amount of Tc-99 is present.

The estimate that only 10% of the Tc-99 in aluminum cladding waste precipitated is pure conjecture. It is believed that the solids which may have precipitated when additional NaOH was added to spent aluminum cladding solution (NaOH-$NaNO_3$) did not carry significant amounts of Tc-99 down with them.

As far as the precipitation behavior of Tc-99 in the several miscellaneous wastes added to the SSTs, Tc-99, if present, is assumed to have been completely soluble in all the miscellaneous liquid wastes including those containing large concentrations of organic complexing agents. Conversely, Tc-99, if present at all, in miscellaneous solid wastes, e.g., diatomaceous earth, added to SSTs is assumed to have completely precipitated.

A23.6 REFERENCES

Lumetta, G. J., B. M. Rapko, J. Liu, and D. J. Temer, 1998, "Enhanced Sludge Washing for Pretreating Hanford Tank Sludges," in *Science and Technology for Disposal of Radioactive Tank Waste*, W. W. Schulz and N. J. Lombardo, Eds, Plenum Press Pub., New York, New York.

Schroeder, N. C., S. D. Radzinski, K. R.Ashley, A. P. Truong, and P. A. Szczepaniak, 1998, "Technetium Oxidation State Adjustment for Hanford Waste Processing," in *Science and Technology for Disposal of Radioactive Tank Wastes*, W. W. Schulz and N. J. Lombardo, Eds, Plenum Press Pub., New York, New York.

Table A-23. Best-Basis Solubility Estimates for Tc-99.

Hanford Defined Waste Model Waste Types[1]	Fraction Tc-99 Precipitated
Process High-Activity Waste	
$BiPO_4$ process[2]	0.33
Other processes[3]	0.33
Cladding Wastes	
Aluminum[4]	0.10
Zircaloy[5]	0.33
Miscellaneous Wastes	
Solid wastes	
Ferrocyanide solids[6]	0.0
Other solids[7]	0.98
Complexed wastes[8]	0.0
Other liquid wastes[9]	0.0

Notes:

[1] After addition of NaOH

[2] Includes HDW Model (Rev 4) Waste Types: MW1, MW2, 1C1, 1C2, 2C1, 2C2, 224, and UR

[3] Includes HDW Model (Rev 4) Waste Types: R1, R2, P1, P2, P2', Th1, Th2, P3, PL1, PL2, and Z

[4] Includes HDW Model (Rev 4) Waste Types: CWR1, CWR2, CWP1, and CWP2

[5] Include HDW Model (Rev 4) Waste Types: CWZr1 and C WZR2

[6] Includes HDW Model (Rev 4) Waste Types: PFeCN1, PFeCN2, TFeCN, and 1CFeCN

[7] Includes HDW Model (Rev 4) Waste Types: DE, CEM, and AR

[8] Includes HDW Model (Rev 4) Waste Types: HS and SRR

[9] Includes HDW Model (Rev 4) Waste Types: OWW1, OWW2, OWW3, NIT, BL, CSR, DW, N, PASF, and B

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A24.0 THORIUM

A24.1 MASS NUMBERS AND HALF LIVES

Isotope Mass Number	Half Life
229	7.3E+03 y
232	1.41E+10 y

Thorium-232 is the only naturally occurring isotope of thorium. Th-229 is a decay product of U-233. The latter isotope, is produced by neutron irradiation of Th-232.

A24.2 BEHAVIOR DURING FUEL DISSOLUTION

In the late 1960's and early 1970's, two thorium campaigns were conducted at the Hanford site. The objectives of these plant-scale campaigns were to isolate and purify a substantial quantity of U-233 for use in breeder reactor tests. To this end, in each campaign several hundreds of kg of irradiated thorium metal or thoria were dissolved in a HNO_3-HF-$A1(NO_3)_3$ solution. Dissolution proceeded smoothly to completion; presumably, all Th-232 and Th-229 were solubilized.

A24.3 PREDICTED OXIDATION STATE

A24.3.1 In Nitric Acid

Oxidation state IV is very characteristic of thorium and aqueous solutions and its compounds. There is no reason to believe that Th-232 and Th-229 solubilized in the headend dissolution process went into solution other than as Th(IV) ions.

A24.3.2 In Alkaline Media

Thorium(IV) ion is exceedingly resistant to either oxidation or reduction. Thus, Th(IV) in acid solutions remained as Th(IV) when such solutions were neutralized with NaOH.

A24.4 CHEMISTRY IN ALKALINE MEDIA

In alkaline solutions, in the absence of strong aqueous-soluble organic complexants, Th(IV) forms a very insoluble hydroxide. There is no reason to not believe that small concentrations of Th-232 and/or Th-229 in neutralized process HAW and cladding wastes did not precipitate almost completely. Of course, such process wastes contained fluoride ion added during the fuel dissolution step or used in the decladding step. Some of the thorium in the acidic HAW and in the Zirflex process decladding solution may have been complexed with fluoride to form neutral or anionic species. But, upon addition of NaOH to the acidic waste any fluoride complex was broken and thorium precipitated as the insoluble hydroxide.

A24.5 BEST-BASIS SOLUBILITY ESTIMATES

A24.5.1 From Chemistry Considerations

Evaluation of the thorium chemistry described in Section A24.4 clearly demonstrates that Th-232 and Th-229 in alkaline media precipitated quantitatively. Thus, chemistry considerations show that 99-100% of the thorium in SSTs, as generated, is in an insoluble form in the sludge phase.

A24.5.2 From Analytical Considerations

There are no analytical data for Th-232 or Th-229 in any SST or DST.

A24.5.3 Tabulated Best-Basis Solubility Estimates

Table A-24 provides best-basis estimates of the fraction of thorium isotopes which precipitated when various alkaline wastes were added to the SSTs. In the absence of any analytical data, these estimates are based solely upon thorium chemistry considerations.

Table A-24. Best-Basis Solubility Estimates for Thorium.

Hanford Defined Waste Model Waste Types[1]	Fraction Thorium Precipitated[2]
Process High-Activity Waste	
$BiPO_4$ process[3]	0.98
Other processes[4]	0.98
Cladding Wastes	
Aluminum[5]	0.98
Zircaloy[6]	0.98
Miscellaneous Wastes	
Solid wastes	
Ferrocyanide solids[7]	0.0
Other solids[8]	0.98
Complexed wastes[9]	0.0
Other liquid wastes[10]	0.98

Notes:

[1] After addition of NaOH
[2] Includes Th-232 and Th-229
[3] Includes HDW Model (Rev 4) Waste Types: MW1, MW2, 1C1, 1C2, 2C1, 2C2, 224, and UR
[4] Includes HDW Model (Rev 4) Waste Types: R1, R2, P1, P2, P2', Th1, Th2, P3, PL1, PL2, and Z
[5] Includes HDW Model (Rev 4) Waste Types: CWR1, CWR2, CWP1, and CWP2
[6] Includes HDW Model (Rev 4) Waste Types: CWZr1 and CWZr2
[7] Includes HDW Model (Rev 4) Waste Types: PFeCN1, PFeCN2, TFeCN, and 1CFeCN
[8] Includes HDW Model (Rev 4) Waste Types: DE, CEM, and AR
[9] Includes HDW Model (Rev 4) Waste Types: HS and SRR
[10] Includes HDW Model (Rev 4) Waste Types: OWW1, OWW2, OWW3, NIT, BL, CSR, DW, N, PASF, and B

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A25.0 TIN

A25.1 MASS NUMBER AND HALF LIFE

Isotope Mass Number	Half Life
126	2.50E+05 y

Tin-126 is a product of the fission of U-235.

A25.2 EXPECTED BEHAVIOR DURING FUEL DISSOLUTION

Massive tin metal is attacked by hot concentrated nitric acid to yield the beta form of $SnO_2 \cdot nH_20$. This material is quite inert (Cotton and Wilkinson 1966). Tin-26 was dispersed on an atomic scale in irradiated uranium metal. Under these conditions, it seems reasonable that most of the atoms of Sn-126 simply dissolved in the nitric acid solvent. However, consider that about 100 kg of Sn-126 were produced over the lifetime of the Hanford plutonium production mission. Given this rather large amount of tin, it seems prudent to believe that a fraction, perhaps as much as 25% of the Sn-126 in the irradiated uranium was indeed converted to inert and stable $SnO_2 \cdot nH_20$.

A25.3 PREDICTED OXIDATION STATE

A25.3.1 In Nitric Acid

Tin ordinarily occurs in acid solution in either oxidation state II or IV. Divalent tin is a very powerful reducing agent, often used as $SnCl_2$ in HCl solution. Even air will oxidize Sn(II) to Sn(IV); therefore, Sn(II) is not at all stable in nitric acid solutions and only Sn(IV) exists in such solutions.

A25.3.2 In Alkaline Media

Addition of NaOH to a nitric acid solution containing Sn(IV) did not affect the oxidation state of tin. Therefore, neutralized waste solutions added to the SSTs contained Sn(IV).

A25.4 CHEMISTRY IN ALKALINE MEDIA

Tin hydroxide is amphoteric. That is, in alkaline media Sn(IV) first precipitates as a hydroxide, i.e., $Sn(OH)_4$ (Noyes and Bray 1948). Then, in the presence of excess alkali hydroxide, as in the SSTs, the hydroxide redissolves to form a negatively charged soluble stannate ion, $[Sn(OH)_6]^{-2}$.

Of course, it is reasonable and realistic to believe that some stannate ion, perhaps as much as 10% of the total amount of Sn-126 present, was occluded in the large amount of hydroxides and hydrated oxides which precipitated when NaOH was added to process wastes. This occluded Sn-126 remained in the sludge phase and likely eventually converted to insoluble SnO_2.

A25.5 BEST-BASIS SOLUBILITY ESTIMATES

A25.5.1 From Chemistry Considerations

Known tin chemistry predicts as much as 25% of the inventory of Sn-126 may have precipitated as inert and insoluble $SnO_2 \cdot nH_20$ when irradiated uranium metal fuel was dissolved in nitric acid. Another 10% of the Sn-126 likely was occluded in the sludge phase when NaOH was added to most process wastes. Because of its very voluminous nature, the hydrated zirconium oxide precipitate which formed when NaOH was added to spent Zirflex process decladding waste may have carried down with it as much as 75% of any Sn-126 present in such wastes.

A25.5.2 From Analytical Considerations

No analytical data are apparently available for Sn-126 in any SST or DST waste.

A25.5.3 Tabulated Best-Basis Solubility Estimates

Table A-25 lists best-basis estimates of the fraction of Sn-126 that precipitated when various neutralized wastes were added to the SSTs. In the absence of any analytical data whatsoever, these estimates derive solely from considerations of known tin chemistry. Of course, not all the wastes added to the SSTs contained Sn-126. But, for those that did, the estimates in Table A-25 apply.

A25.6 REFERENCES

Cotton, F. A., and G. Wilkinson, 1966, *Advanced Inorganic Chemistry*, Interscience Pub. Co., New York, New York.

Noyes, A. A., and W. C. Bray, 1948, *A System of Qualitative Analysis for the Rare Elements*, MacMillan Co., New York, New York.

Table A-25. Best-Basis Solubility Estimates for Sn-126.

Hanford Defined Waste Model Waste Types[1]	Fraction of Sn-126 Precipitated
Process High-Activity Waste	
$BiPO_4$ process[2]	0.35
Other processes[3]	0.35
Cladding Wastes	
Aluminum[4]	0.25
Zircaloy[5]	0.75
Miscellaneous Wastes	
Solid wastes	
Ferrocyanide solids[6]	0.0
Other solids[7]	0.98
Complexed wastes[8]	0.0
Other liquid wastes[9]	0.0

Notes:

[1] After addition of NaOH
[2] Includes HDW Model (Rev 4) Waste Types: MW1, MW2, 1C1, 1C2, 2C1, 2C2, 224, and UR
[3] Includes HDW Model (Rev 4) Waste Types: R1, R2, P1, P2, P2', Th1, Th2, P3, PL1, PL2, and Z
[4] Includes HDW Model (Rev 4) Waste Types: CWR1, CWR2, CWP1, and CWP2
[5] Includes HDW Model (Rev 4) Waste Types: CWZr1 and CWZr2
[6] Includes HDW Model (Rev 4) Waste Types: PFeCN1, PFeCN2, TFeCN, 1CFeCN
[7] Includes HDW Model (Rev 4) Waste Types: DE, CEM, and AR
[8] Includes HDW Model (Rev 4) Waste Types: HS and SRR
[9] Includes HDW Model (Rev 4) Waste Types: OWW1, OWW2, OWW3, NIT, BL, CSR, DW, N, PASF, and B

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A26.0 URANIUM

A26.1 MASS NUMBERS AND HALF LIVES

Isotope Mass Number	Half Life
232	74 y
233	1.62E+05 y
234	2.48E+05 y
235	7.13E+08 y
236	2.40E+07 y
238	4.51E+09 y

Of these isotopes, U-234, U-235, and U-238 are present in naturally-occurring uranium. Uranium-233 is produced by neutron irradiation of Th-232; such irradiation produces Th-233 which beta decays first to Pa-233 and then to U-233. Uranium-236 resulted from the nuclear reaction:

U-235(n, gamma)U-236

A26.2 EXPECTED BEHAVIOR DURING FUEL DISSOLUTION

Uranium metal, is readily attacked by nitric acid and completely dissolves. Dissolution of uranium metal in nitric acid was, of course, the principal headend step in all fuel processing operations performed at the Hanford site.

A26.3 PREDICTED OXIDATION STATE

A26.3.1 In Nitric Acid

Uranium metal dissolves in nitric acid to yield the oxocation UO_2^{+1}. Uranium (VI) can be reduced to U(IV) but such reduction did not occur under conditions used in the Hanford fuel reprocessing plants.

A26.3.2 In Alkaline Media

The uranyl ion, UO_2^{+1}, persisted when acidic process wastes were neutralized with NaOH. No reductants were present in the alkaline wastes to reduce U(VI) to U(IV).

A26.4 CHEMISTRY IN ALKALINE MEDIA

When process HAW was made alkaline by addition of NaOH some fraction, likely a large fraction, of the uranium in such wastes precipitated as the uranate $Na_2U_2O_7$. Several polyuranates are also known (Cotton and Wilkinson 1966.)

There are at least two excellent chemical reasons why some of the uranium may not have precipitated. Firstly, the uranyl ion is noted for forming very stable aqueous-soluble complexes with carbonate ion. In particular, the triscarbonato complex, $[UO_2(CO_3)_3]^{-4}$ ion, is noted for its stability. Carbonate ion was likely always present when acidic process liquors were neutralized with NaOH. Carbonate is an impurity in commercial NaOH. The triscarbonato ion reacts with hydroxide ion to form an insoluble uranate:

$$2\ Na_4UO_2(CO_3)_3 + 6\ NaOH = Na_2U_2O_7 + 6\ Na_2CO_3 + 3\ H_2O$$

Now, contrary to what may be commonly believed, Weigel (Katz, Seaborg, and Morss, 1986) states that sodium hydroxide does not completely precipitate uranium from carbonate solutions. Also, if a large excess of NaOH were not added to waste containing uranyl triscarbonato species, then surely not all the uranium would precipitate as the diuranate. This latter case is believed typical of what actually happened when process wastes were neutralized when the goal was only to reach a pH (ca. 10) where corrosion of the carbon steel tanks would be acceptably low.

Some uranium may also have remained soluble through formation of a peroxouranate rather than an uranate. According to Weigel (Katz, Seaborg, and Morss, 1986), peroxouranates are much more soluble than uranates or polyuranates. The peroxy free radical is a common product of the radiolysis of aqueous solutions.

A26.5 BEST-BASIS SOLUBILITY ESTIMATES

A26.5.1 From Chemistry Considerations

Likely over 50% of the uranium precipitated as a uranate or polyuranate and became part of the sludge phase in the SSTs. Possibly, retention of uranium in the insoluble sludge phase was aided by sorptive or occlusive properties of co-precipitated hydrated iron oxide. But, in addition to likely precipitation of the bulk of the uranium in the neutralized waste originally introduced into the SSTs, chemistry considerations also identify mechanisms whereby 15 to 25% of the uranium remained as a soluble species in the supernatant phase. Thus, chemistry considerations alone cannot provide an unchallenged answer to what is the best-basis estimate of the solubility of uranium in different types of SST sludge.

A26.5.2 From Analytical Considerations

Unfortunately, available analytical data for amounts of uranium in liquids and solids in various tanks do not provide a definitive answer to the split of uranium between supernatant and precipitate phases in various types of neutralized waste transactions. What appears to be the only available analytical data are briefly considered here.

A26.5.2.1 General Sludge-Salt Cake-Liquid Uranium Data. Scattered analytical data for a multitude of tank sludges, salt cakes, and liquids do little more than show uranium is present in all wastes. But, the available scattered data are insufficient to state with a high degree of certainty the fraction of uranium precipitated in any particular waste type.

As expected from known uranium chemistry, sludge phases contain a lot more uranium than do either salt cake or liquid phases. A case in point are analytical data for Tank 241-AY-102. These analyses show the sludge in this tank to contain 2,230 kg of uranium while the supernatant contains only 53 kg of uranium or 2% of the total. The relation, if any, of the sludge to the liquid phase in this DST is unknown.

A26.5.2.2 Process High-Activity Waste.

$BiPO_4$ Process. Of all the fuel reprocessing schemes used at the Hanford site, the $BiPO_4$ process was unique in that uranium was not recovered but routed to various high-activity waste streams. Concerning uranium behavior when these waste streams were made alkaline, Agnew et al. (1997) make two important references to information originally published (1951) in the $BiPO_4$ Process Technical Manual. One of these references stated that 75% of the uranium in the neutralized waste precipitated as a sludge while another claimed that, because of the very high, (>0.5 M) concentration of carbonate ion in the neutralized waste, uranium was soluble to the extent of as much as 0.11 M in the supernatant liquid. Agnew et al. (1997) calculates that if the 0.11M value were correct, only 35% of the uranium would have precipitated. Obviously, much more than 35% of the uranium routed to $BiPO_4$ process HAW was later recovered during operation of the Uranium Recovery process. Hence, at least for the purposes of this report, 75% of the uranium in $BiPO_4$ process HAW is assumed to have precipitated when such wastes were neutralized with NaOH.

REDOX/PUREX HAW Solutions. There are no analytical data which establish the amount of uranium which precipitated when NaOH was added to REDOX and PUREX process

HAW solutions. As noted elsewhere in this report, Tanks 241-AZ-101 and 241-AZ-102 contain what is believed to be essentially undiluted neutralized PUREX HAW from the most recent PUREX plant reprocessing campaign. Regrettably the supernatant from Tanks 241-AZ-101 and 241-AZ-102 was not analyzed for uranium.

Fortunately, Agnew et al. (1997) provide a very significant datum for the solubility of uranium in typical alkaline waste supernatants, namely 0.004 M. Agnew and Watkins (1994) arrived at this latter value from review of existing analytical data for 543 liquid waste samples. A solubility value of 0.004 M corresponds to precipitation of 98 to 99% of the uranium in neutralized REDOX and PUREX process HAW solutions. Neutralized REDOX and PUREX process HAW supernatants contained far less carbonate ion than did neutralized wastes from the $BiPO_4$ process; precipitation of 98-100% of the uranium in the former wastes is, therefore, not unexpected.

Cladding Wastes. There are no analytical data which establish the amount of uranium that precipitated when NaOH was added to wastes resulting from chemical dissolution of aluminum jackets. The assumption made here is that very little of the uranium in the fuel was solubilized during such decladding and that 98-100% of any solubilized uranium precipitated.

Tanks 241-AW-103 and AW-105 still contain solid wastes which formed when NaOH was added to zircaloy decladding wastes. Supernatant liquids resulting from the neutralization process were not analyzed for uranium; the solids still left in the tank, however, contain, according to analytical data, 10 to 20 kg of uranium..The assumption made here is that 98-100% of the soluble uranium in zircaloy decladding waste solutions precipitated when NaOH was added to such wastes.

A26.5.3 Tabulated Best-Basis Solubility Estimates

Table A-26 provides best-basis estimates of the fraction of uranium isotopes that precipitated from various waste solutions added to the SSTs after NaOH was added to such wastes. Solubility estimates for uranium in neutralized $BiPO_4$ process HAW are based upon information presented in the $BiPO_4$ Process Technical Manual and reflect the likely presence of considerable carbonate-complexed uranium in such wastes. REDOX and PUREX process HAW solutions as well as aluminum and zircaloy decladding solutions did not contain high concentrations of carbonate ion; thus, 98% of the uranium in such solutions, after addition of NaOH, is predicted to have precipitated. Very limited analytical data do not contradict the 98% value.

A26.6 REFERENCES

Agnew, S. F., and J. G. Watkins, 1994, *Estimation of Limiting Solubilities for Ionic Species in Hanford Waste Tank Supernates*, LAUR-94-3590, Los Alamos National Laboratory, Los Alamos, New Mexico.

Agnew, S. F., J. Boyer, R. A. Corbin, T. B. Duran, J. R. Fitzpatrick, K. A. Jurgensen, T. P. Ortiz, and B. L. Young, 1997, *Hanford Tank Chemical and Radionuclide Inventories: HDW Model Rev. 4*, LA-UR-96-3860, Los Alamos National Laboratory, Los Alamos, New Mexico.

Weigel, F., 1986, "Uranium," in *The Chemistry of the Actinide Elements*, 2nd Ed., Vol 1, J. J. Katz, G. T. Seaborg, and L. R. Morss, Eds., Chapman and Hall, New York, New York.

Table A-26. Best-Basis Solubility Estimates for Uranium.

Hanford Defined Waste Model Waste Types[1]	Fraction of Uranium Precipitated[2]
Process High-Activity Waste	
$BiPO_4$ process[3]	0.75
Other processes[4]	0.98
Cladding Wastes	
Aluminum[5]	0.98
Zircaloy[6]	0.98
Miscellaneous Wastes	
Solid wastes	
Ferrocyanide solids[7]	0.00
Other solids[8]	0.98
Complexed wastes[9]	0.00
Other liquid wastes[10]	0.98

Notes:

[1] After addition of NaOH
[2] Includes all uranium isotopes
[3] Includes HDW Model (Rev 4) Waste Types: MW1, MW2, 1C1, 1C2, 2C1, 2C2, 224, and UR
[4] Includes HDW Model (Rev 4) Waste Types: R1, R2, P1, P2, P2', Th1, Th2, P3, PL1, PL2, and Z
[5] Includes HDW Model (Rev 4) Waste Types: CWR1, CWR2, CWP1, and CWP2
[6] Includes HDW Model (Rev 4) Waste Types: CWZr1and CWZr2
[7] Includes HDW Model (Rev 4) Waste Types: PFeCN1, PFeCN2, TFeCN, and 1CFeCN
[8] Incudes HDW Model (Rev 4) Waste Types: DE, CEM, and AR
[9] Includes HDW Model (Rev 4) Waste Types: HSS and SRR
[10] Includes HDW Model (Rev 4) Waste Types: OWW1, OWW2, OWW3, NIT, BL, CSR,DW, N, PASF, and B

A27.0 YTTRIUM

A27.1 MASS NUMBER AND HALF LIFE

Isotope Mass Number	Half Life
90	0.0073 y

Yttrium-90 derives solely from the beta decay of its parent, Sr-90. Because of the difference in half-lives of Sr-90 and Y-90 they are in secular equilibrium. Hence, Y-90 tracked with Sr-90 throughout all the waste transactions involving the latter radionuclide.

A27.2 EXPECTED BEHAVIOR DURING FUEL DISSOLUTION

Yttrium-90 in irradiated fuel present as the time that the fuel was dissolved in nitric acid dissolved completely along with the Sr-90.

A27.3 PREDICTED OXIDATION STATE

A27.3.1 In Nitric Acid

The most stable oxidation state of yttrium in aqueous solution is the trivalent state. There is no reason to doubt that Y-90 in the nitric acid dissolver solution existed in any but oxidation state III.

A27.3.2 In Alkaline Media

There is no reason to doubt that Y-90 remained in the trivalent state when the acidic HAW solution were neutralized with NaOH. Sufficient energy and conditions were not present to either reduce or oxidize Y(III).

A27.4 CHEMISTRY IN ALKALINE MEDIA

The similarity of the chemistry of yttrium to that of the trivalent rare earths has been known for a very long time. Like the rare earths, Y(III) forms insoluble hydroxide, fluoride, and phosphate compounds. So, almost certainly, 75-100% of the Y-90 that was in secular equilibrium with Sr-90 precipitated as an insoluble compound when NaOH was added to acidic process HAW solutions (Yost, Russell, and Garner, 1947). As already noted, voluminous hydrated iron oxide and nonradioactive lanthanide hydroxide precipitates helped remove Y-90 from solution. Also additonal Y-90 by beta decay of Sr-90 in the sludge phase remained in the sludge phase.

A27.5 BEST-BASIS SOLUBILITY ESTIMATES

A27.5.1 From Chemistry Considerations

Evaluation of the yttrium chemistry described in Section A27.4 clearly demonstrates that Y-90 in secular equilibrium with Sr-90 in alkaline media precipitated completely, especially in the presence of hydrated iron oxides and nonradioactive lanthanum hydroxides and in the absence of strong organic complexants. Small amounts of Y-90, in secular equilibrium with any Sr-90 which did not precipitate in alkaline media, remained in solution. Thus, chemistry considerations show that 75-98% of the Y-90 introduced into the SSTs precipitated as an insoluble material in the sludge phase.

A27.5.2 From Analytical Considerations

The analytical data base for yttrium in Hanford tank solutions and solids is not sufficient to make reliable best-basis estimates of the solubility of Y-90 in such phases.

A27.5.3 Tabulated Best-Basis Solubility Estimates

Table A-27 provides best-basis estimates of the fraction of Y-90 that precipitated when various alkaline wastes were added to the SSTs. Because of the closeness of the chemistry of Y-90 to that of lanthanides, the estimates listed in Table A-27 correspond exactly to those provided for europium and samarium isotopes.

A27.6 REFERENCES

Yost, D. M., H. Russell, Jr., and C. S. Garner, 1947, *The Rare Earth Elements and Their Compounds*, John Wiley & Sons, New York, New York.

Table A-27. Best-Basis Solubility Estimates for Y-90.

Hanford Defined Waste Model Waste Types[1]	Fraction of Y-90 Precipitated
Process High-Activity Waste	
$BiPO_4$ process[2]	0.75
Other processes[3]	0.75
Cladding Wastes	
Aluminum[4]	0.00
Zircaloy[5]	0.90
Miscellaneous Wastes	
Solid wastes Ferrocyanide solids[6] Other solids[7]	 0.0 0.98
Complexed wastes[8]	0.0
Other liquid wastes[9]	0.0

Notes:
[1] After addition of NaOH
[2] Includes HDW Model (Rev 4) Waste Types: MW1, MW2, 1C1, 1C2, 2C1, 2C2, 224, and UR
[3] Includes HDW Model (Rev 4) Waste Types: R1, R2, P1, P2, P2', Th1, Th2, P3, PL1, PL2, and Z
[4] Includes HDW Model (Rev 4) Waste Types: CWR1, CWR2, CWP1, and CWP2
[5] Includes HDW Model (Rev 4) Waste Types: CWZr1 and CWZr2
[6] Includes HDW Model (Rev 4) Waste Types: PFeCN1, PFeCN2, TFeCN, and 1CFeCN
[7] Includes HDW Model (Rev 4) Waste Types: DE, CEM, and AR
[8] Includes HDW Model (Rev 4) Waste Types: HSS and SRR
[9] Includes HDW Model (Rev 4) Waste Types: OWW1, OWW2, OWW3, NIT, BL, DW, CSR, N, PASF, and B

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A28.0 ZIRCONIUM

A28.1 MASS NUMBER AND HALF-LIFE

Isotope Mass Number	Half Life
93	1.53E+06 y

Zirconium-93 is both a product of the fission of U-235 and an activation product, e.g., Zr-92(n, gamma)Zr-93. Zirconium-92 is a naturally-occurring isotope of zirconium present in zircaloy cladding.

A28.2 EXPECTED BEHAVIOR DURING FUEL DECLADDING AND DISSOLUTION

Any Zr-93 produced as an activation product surely readily dissolved in the NH_4F-NH_4NO_3 solution used to dissolve zircaloy cladding. Fluoride solutions are known to form soluble zirconium species.

Zirconium metal, in the absence of fluoride ion, is not attacked by nitric acid solutions. But, only very small amounts of Zr-93 were formed in irradiated uranium metal; atoms of Zr-93 probably dissolved in the acidic dissolvent. Also, some fluoride ion was carried over to the nitric acid dissolution step in the form of a heel of spent zircaloy decladding waste. Thus, it is highly probable that Zr-93 present in irradiated uranium metal passed into aqueous solution as a soluble species when the uranium was dissolved in nitric acid.

A28.3 PREDICTED OXIDATION STATE

A28.3.1 In Nitric Acid

The solution chemistry of zirconium is almost exclusively that of Zr^{+4}. Indeed, there are few authenticated compounds of zirconium where zirconium is not in the tetravalent state. Hence, Zr-93 in nitric acid process solutions surely was present as Zr(IV).

The Zirflex process used to chemically dissolve zircaloy cladding was based upon use of NH_4F to produce soluble $[ZrF_6]^{+2}$ ion. Surely, Zr-93 present in the irradiated zircaloy cladding also dissolved to yield the same complex ion. Observe, however, that the oxidation state of zirconium in the $[ZrF_6]^{+2}$ ion is IV.

A28.4 CHEMISTRY IN ALKALINE MEDIA

According to Clearfield (1964), addition of hydroxide to zirconium(IV) solutions causes the precipitation of white gelatinous $ZrO_2 \cdot nH_20$ where the water content is variable. Cotton and Wilkinson (1966) note that no true hydroxide, $Zr(OH)_4$, exists.

Zirconium(IV) forms strong complexes with many organic ligands, e.g., EDTA, HEDTA, etc. Most of the wastes added to the SSTs did not contain organic compounds which would have strongly complexed Zr(IV). Hence, it is considered extremely likely that Zr-93 in process HAW solutions precipitated almost completely when NaOH was added to such solutions prior to storage in SSTs. Co-precipitation of iron, nickel, and various other elements in many neutralized process HAW solutions also would have aided in removing precipitated Zr-93 from solution and incorporation of this radionuclide in the SST sludge phases. And, certainly in the case of neutralized Zirflex process waste, precipitation of massive amounts of stable zirconium would have greatly aided co-precipitation of Zr-93.

A28.5 BEST-BASIS SOLUBILITY ESTIMATES

A28.5.1 From Chemistry Considerations

Known zirconium chemistry strongly indicates that any Zr-93 in alkaline waste streams added to the SSTs precipitated completely as $ZrO_2 \cdot nH_20$. Agglomeration and removal of precipitated Zr-93 from solution was certainly facilitated by co-precipitation of hydrated oxides of iron, nickel, and, in certain cases, by stable zirconium.

A28.5.2 From Analytical Considerations

As far as is known, no analytical data for Zr-93 in any SST or DST waste exist.

A28.5.3 Tabulated Best-Basis Solubility Estimates

Table A-28 lists best-basis estimates of the fraction of Zr-93 that precipitated when various alkaline wastes were added to the SSTs. In the absence of any analytical data whatsoever, the estimates in Table A-28 derive solely from considerations of known zirconium chemistry.

A28.6 REFERENCES

Clearfield, A., 1964, Inorg. Chem., 3, 146.

Cotton, F. A., and G. Wilkinson, 1966, *Advanced Inorganic Chemistry*, 2nd Ed., Interscience Pub., New York, New York.

Table A-28. Best-Basis Solubility Estimates for Zr-93.

Hanford Defined Waste Model Waste Types[1]	**Fraction of Zr-93 Precipitated**
Process High-Activity Waste	
$BiPO_4$ process[2]	0.98
Other processes[3]	0.98
Cladding Wastes	
Aluminum[4]	0.98
Zircaloy[5]	0.98
Miscellaneous Wastes	
Solid wastes	
Ferrocyanide solids[6]	0.0
Other solids[7]	0.98
Complexed wastes[8]	0.0
Other liquid wastes[9]	0.98

Notes:

[1] After addition of NaOH

[2] Includes HDW Model (Rev 4) Waste Types: MW1, MW2, 1C!, 1C2, 2C1, 2C2, 224, and UR

[3] Includes HDW Model (Rev 4) Waste Types: R1, R2, P1, P2, P2', Th1, Th2, P3, PL1, PL2, and Z

[4] Includes HDW Model (Rev 4) Waste Types: CWR1, CWR2, CWP1, and CWP2

[5] Includes HDW Model (Rev 4) Waste Types: CWZR1 and CWZr2

[6] Includes HDW Model (Rev 4) Waste Types: PFeCN1, PFeCN2, TFeCN, 1CFeCN

[7] Includes HDW Model (Rev 4) Waste Types: DE, CEM, and AR

[8] Includes HDW Model (Rev 4) Waste Types: HSS and SRR

[9] Includes HDW Model (Rev 4) Waste Types: OWW1, OWW2, OWW3, NIT, BL, CSR, DW, N, PASF, and B

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