Laboratory-Scale Bismuth Phosphate ExtractionProcess Simulation To Track Fate of ^{99}Tc

R. Jeff Serne[1], Mike J. Lindberg[1], and Tom E. Jones[2];

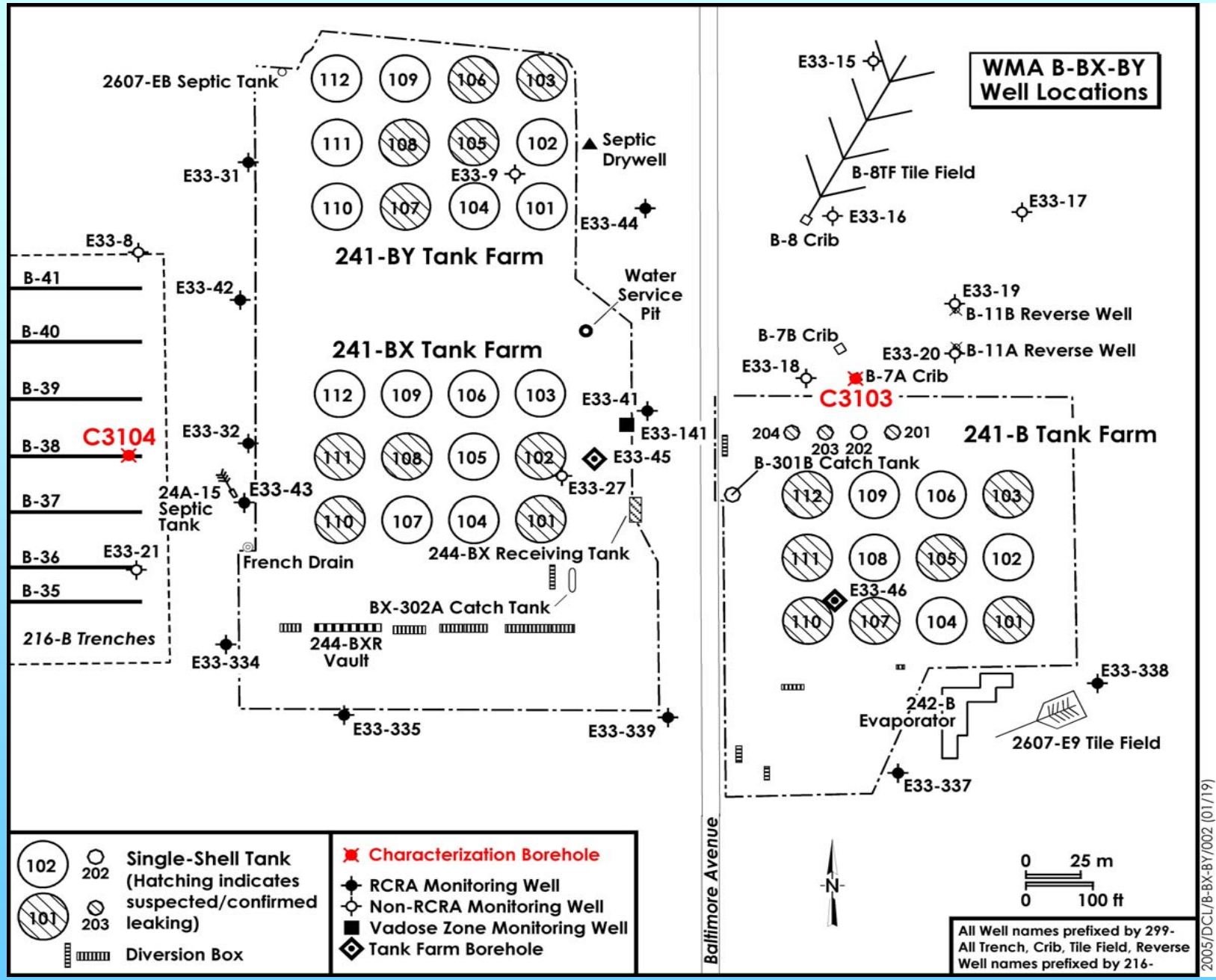
[1]Pacific Northwest National Laboratory, Richland WA, 99354
[2]Fluor Federal Services, Richland, WA, 99352

Work **funded by CH2M-HILL Hanford Group**

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

Objective of Study

- ^{99}Tc is a major risk driver at Hanford
  - Relatively high fission abundance (~25,100 curies generated)
  - 687 curies of ^{99}Tc disposed/leaked to subsurface
  - High mobility in subsurface sediments ($K_d \approx 0$ mL/g)
  - Long half live –213,000 y
- Large discrepancy in ^{99}Tc concentration found in sediment below B-38 trench and estimate for waste stream [BiPO4 1st Cycle] disposed
- Review of historical literature on waste streams suggested an error in interpretation


WMA B-BX-BY
Well Locations
2607-EB Septic Tank
241-BY Tank Farm
241-BX Tank Farm
241-B Tank Farm
Septic
Drywell
Water
Service
Pit
E33-8
E33-31
E33-9
E33-44
E33-42
E33-41
E33-141
E33-45
E33-32
E33-43
E33-27
E33-21
E33-334
E33-335
E33-339
E33-15
E33-16
E33-17
E33-19
E33-20
E33-18
E33-46
E33-338
E33-337
B-8 Crib
B-8TF Tile Field
B-7B Crib
B-7A Crib
B-11B Reverse Well
B-11A Reverse Well
C3103
C3104
B-41
B-40
B-39
B-38
B-37
B-36
B-35
216-B Trenches
24A-15
Septic
Tank
French Drain
244-BX Receiving Tank
BX-302A Catch Tank
244-BXR
Vault
B-301B Catch Tank
242-B
Evaporator
2607-E9 Tile Field
Baltimore Avenue
Single-Shell Tank
(Hatching indicates
suspected/confirmed
leaking)
Diversion Box
Characterization Borehole
RCRA Monitoring Well
Non-RCRA Monitoring Well
Vadose Zone Monitoring Well
Tank Farm Borehole
All Well names prefixed by 299-
All Trench, Crib, Tile Field, Reverse
Well names prefixed by 216-
0 25 m
0 100 ft
2005/DCL/B-BX-BY/002 (01/19)

Bismuth Phosphate Process
(1944 - 1956)

Pu Separation from Irradiated Fuel

$U(VI) + Pu(VI) + \text{fission products} + NaNO_2 \rightarrow Pu(IV) + U(VI) + \text{fission products}$

$Pu(IV) + U(VI) + \text{fission products} + H_3PO_4 + Bi(III) \rightarrow$ $Pu(IV)\text{-}BiPO_4$ + "metal waste" (contained all U + *~90% of fission products*)

Reference: Anderson (1990) "A History of 200 Area Single-Shell Tank Farms", WHC-MR-0132

Bismuth Phosphate Process (Continued)

First Recycle

$\underline{Pu(IV)\text{-}BiPO_4} + HNO_3 + Cr_2O_7^{=} + Zr^{+4} + Bi^{+3} + PO_4^{-3} \rightarrow$
$Pu(VI) + \underline{Zr(IV)\text{-}BiPO_4}$

$Pu(VI)$ + fission products + $NaNO_2$ + H_3PO_4 + $Bi(III) \rightarrow$
$\underline{Pu(IV)\text{-}BiPO_4}$ + "first cycle" waste (containing ~10% of fission products)

First cycle waste went to B-38 trench (and many others)

Irradiate Fuel (Metal Storage Solution) Simulant (per liter):

Reagents	g	Wt %
H_2O	709.58	54.3
HNO_3 70%	14.87	1.14
H_2SO_4 96%	79.63	6.10
UNH solid	498.71	38.2
Se	2.76E-04	2.12E-05
Rb	1.91E-03	1.46E-04
Sr	5.64E-03	4.32E-04
Y	2.91E-03	2.23E-04
Zr	1.92E-02	1.47E-03
Mo	1.47E-02	1.13E-03
Pd	1.66E-03	1.27E-04
I	1.70E-04	1.30E-05
Cs	1.29E-02	9.91E-04
Ba	6.25E-03	4.79E-04
La	5.97E-03	4.57E-04
Ce	1.61E-02	1.23E-03
Pr	2.00E-02	1.53E-03
Eu	2.41E-03	1.85E-04
Np	5.10E-04	3.91E-05
Tc	4.16E-03	3.19E-04
Ru	8.90E-03	6.81E-04
Total	1305.91	1.00E+02

Initial Bismuth Phosphate Precipitation (IBPP):

To simulate the precipitation step, we scaled down the production process (1120 gal) to 60 mL batches of Metal Storage solution; then

1) Add Metal Solution with fission products to a 125 mL glass serum bottle.
2) Heat solution to 85^0 C.
3) Add 25% Sodium Nitrite Solution at a rate of 0.1 mL/min. Takes 22 min.
4) Digest for 1 hour.
5) Add 24% Bismuth Nitrate/19% Nitric Acid Solution
6) Wait 15 minutes.
7) Add 73.5 % Phosphoric/1.2 % Nitric Acid Solution at a rate of 0.05 mL/ min. Takes 161 minutes.
8) Digest for 2 hours.
9) Cool to at 50^0 C.

Centrifugation,Washing (C&W) and Dissolution

- Centrifuged BiPO4 slurry
- Liquids were separated
- Solids triple rinsed with deionized water
- Solids dissolved in nitric acid
- Combine nitric acid and rinse water
- Fission products in the acid digestate & water rinsate represent maximum present in the 1st cycle waste.

Fig 1: Initiation of process (Metal Storage Solution with Tc-99 dissolved)

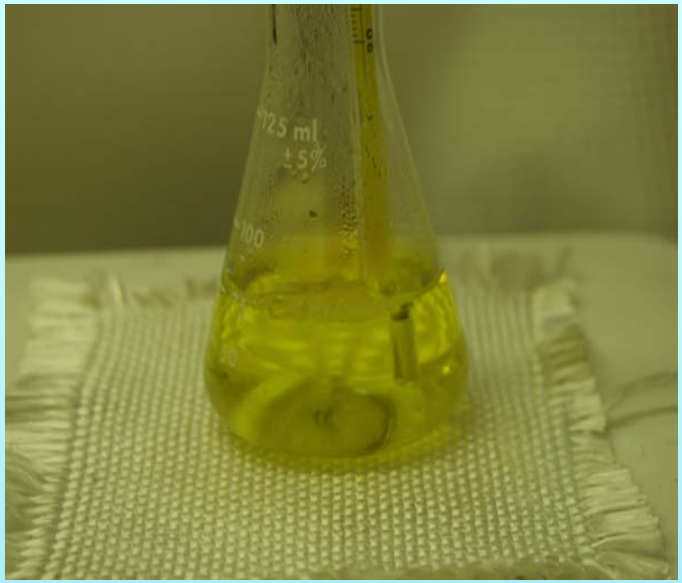


Fig 2: Addition of Sodium Nitrite

Fig 3: Completion of Phosphoric Acid Addition

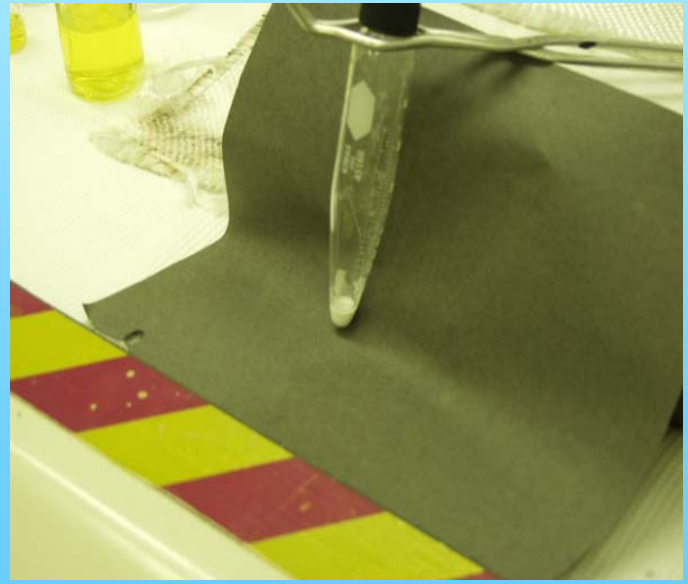


Fig 4: Bismuth Phosphate (Product) Solid after rinsing

Laboratory Simulation

- 4 simulations performed
- Starting dissolved Irradiated Fuel, Metal waste liquid, and dissolved BiPO4 solids analyzed
- Complete mass balance start to end
- ^{99}Tc by ICP-MS and ^{95m}Tc tracer by γ-counting (GEA)

Ave Results for 4 Simulations

	% To SST	% To Cribs/Trenches	% Material Unaccounted For
Tc-99 N=4 and Tc-95m N=2	Metals Waste	**Max in 1st Cycle Waste**	(+) mass missing
Tc-99 (ICP-MS)	97.8±4.42	1.07±1.17	1.34±3.75
Tc-95m (tracer)	97.4±3.77	<0.06±0.01	2.53±3.78

Conclusion:

•ICP-MS results show that less than 0.74 % of Tc-99 associates with the plutonium product that ultimately becomes 1st cycle waste .

• Using the gamma tracer Tc-95m (more precisely measured than stable isotopes), **< 0.1 %** of the Tc-95m precipitated with the plutonium-bismuth phosphate (end up in 1st cycle waste).

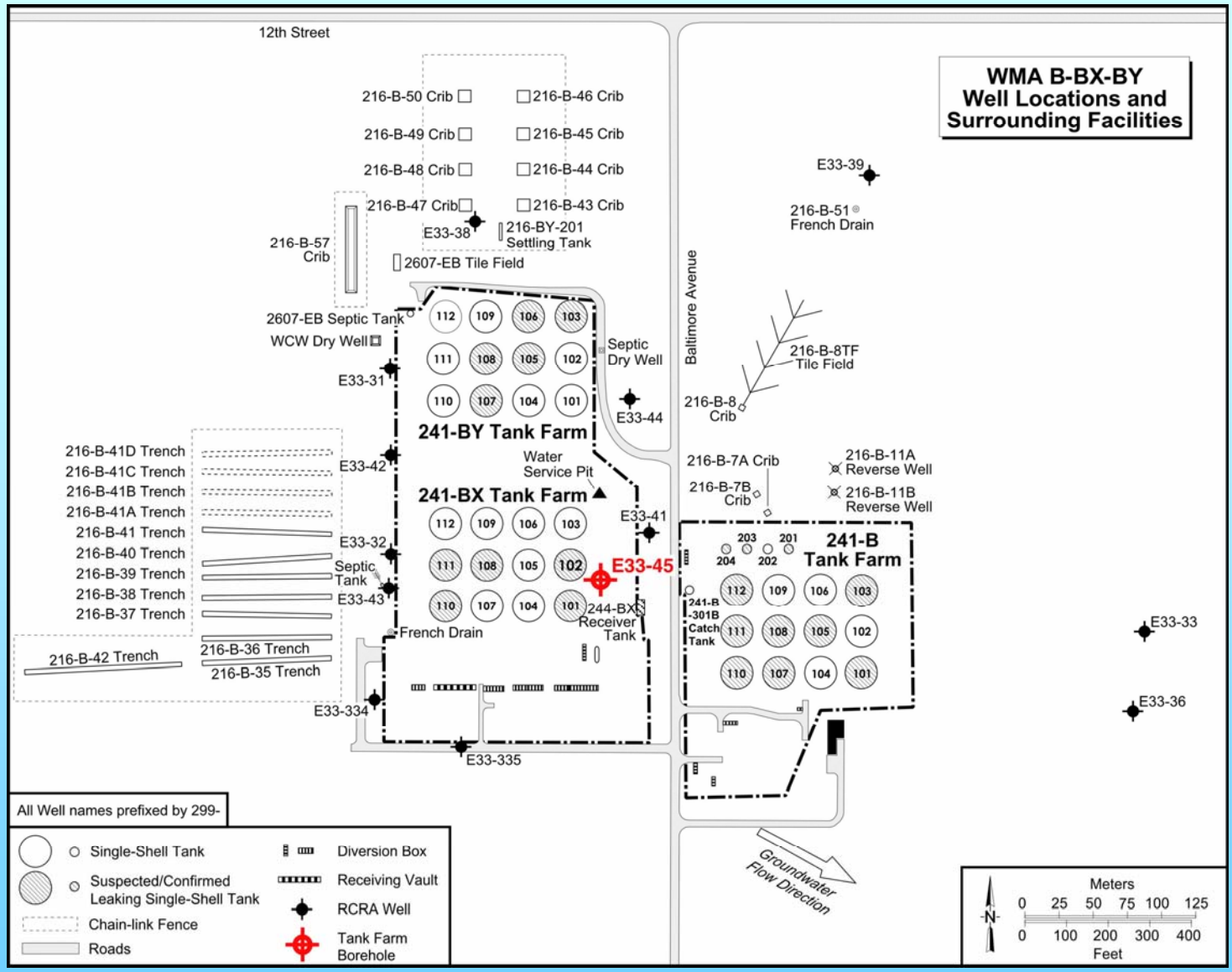
•Measurable quantities (~15 to 20%) of the beta emitting lanthanides, niobium, and zirconium do precipitate with the plutonium product; thus leading to the 10% (of gross beta) value used in past estimates

B-38 Trench Data-Revisited

- Nitrate was found at depth suggesting disposed waste still in vadose zone sediments—as expected
- Measured Nitrate-to-^{99}Tc ratio in sediment ~(3±2) x E+05 kg/Ci
- Using old estimate, ratio should be 717 kg /Ci
- Using new estimate of ^{99}Tc in 1st Cycle Waste the ratio ~ 5.30E+05 kg/Ci
- **Field Results makes sense now** that very little ^{99}Tc found in sediments below B-38 trench

Additional Activities

- Details on Fate of **Many Other** Fission Elements in both Metal Waste and 1st Cycle Available
- Studied the Metal Waste Solution Neutralization Process (for waste going to SSTs)
- Full report : PNNL-14120
- http://www.pnl.gov/main/publications/external/technical_reports/PNNL-14120.pdf


WMA B-BX-BY
Well Locations and
Surrounding Facilities
12th Street
216-B-50 Crib
216-B-46 Crib
216-B-49 Crib
216-B-45 Crib
216-B-48 Crib
216-B-44 Crib
216-B-47 Crib
216-B-43 Crib
E33-38
216-BY-201
Settling Tank
216-B-57
Crib
2607-EB Tile Field
2607-EB Septic Tank
WCW Dry Well
Septic
Dry Well
E33-31
E33-44
241-BY Tank Farm
Water
Service Pit
241-BX Tank Farm
E33-42
E33-41
E33-32
E33-45
Septic
Tank
E33-43
244-BX
Receiver
Tank
French Drain
216-B-41D Trench
216-B-41C Trench
216-B-41B Trench
216-B-41A Trench
216-B-41 Trench
216-B-40 Trench
216-B-39 Trench
216-B-38 Trench
216-B-37 Trench
216-B-42 Trench
216-B-36 Trench
216-B-35 Trench
E33-334
E33-335
E33-39
216-B-51
French Drain
Baltimore Avenue
216-B-8TF
Tile Field
216-B-8
Crib
216-B-7A Crib
216-B-7B
Crib
216-B-11A
Reverse Well
216-B-11B
Reverse Well
241-B
Tank Farm
241-B
-301B
Catch
Tank
E33-33
E33-36
Groundwater
Flow Direction
All Well names prefixed by 299-
Single-Shell Tank
Suspected/Confirmed
Leaking Single-Shell Tank
Chain-link Fence
Roads
Diversion Box
Receiving Vault
RCRA Well
Tank Farm
Borehole
N
Meters
0 25 50 75 100 125
0 100 200 300 400
Feet

Likely Dominant Speciation		% To SST	% To Cribs/Trenches	% Material Unaccounted For	Comments
		Metals Waste	Extraction Product	(+) mass missing	
TcO_4^-	Tc-99 (ICP-MS)	97.8±4.42	1.07±1.17	1.34±3.75	<1 % in $BiPO_4$ precipitate; quality very good; ICP-MS consistently >97 % in metals waste;very good agreement between two measurement methods
	(tracer)	97.4±3.77	<0.06±0.01	2.53±3.78	
I^-	I-125 (I-129) tracer	100	<0.65	-0.6	<1 % in $BiPO_4$ precipitate; quality very good; but only one data set
SeO_4^{2-}	Se (ICP-MS)	NA	NA	NA	ICP-MS not useable (poor sensitivity) radiocounting data suggests 11% in $BiPO_4$ precipitate
	tracer	88.6±5.3	10.6±0.10	0.87±5.2	
MoO_4^{2-} (?)	Mo (ICP-MS)	89.4±6.6	0.2±0.1	10.4±6.7	≤0.2 % in $BiPO_4$ precipitate; quality is good
RuO_4^{2-}(?)	Ru (ICP-MS)	97.4±0.6	0.04±0.03	2.6±0.6	≤1% in $BiPO_4$ precipitate; quality good; only one data set
SbO_4^{3-}	Sb (tracer)	99.3±3.6	1.3±0.01	"-0.63±3.6	1 % in $BiPO_4$ precipitate; Quality very good; only one data set
UO_2^{2+}	U-238 (ICP-MS)	96.87	0.02	3.11	
NpO_2^+	Np-237 (ICP-MS)	89.5±6.5	1.6±0.8	8.8±6.9	ICP-MS data is better: agreement between two measurement methods fair; < 5% in $BiPO_4$ precipitate
	(rad)	99.2	6.9	-6.9	
Cs^+	Cs (ICP-MS)	94.5±6.2	0.1±0.05	5.4±6.2	≤ 1 % in BiPO4 precipitate; quality very good; counting and ICP-MS agreement is excellent
	tracer	97.5±3.1	<1.3±0.03	1.6±2.5	
				(-) mass "created"	

Likely Dominant Speciation		% To SST	% To Cribs/Trenches	% Material Unaccounted For	Comments
		Metals Waste	Extraction Product	(+) mass missing	
Rb^{+}	Rb (ICP-MS)	92.0±12.2	0.3±0.3	7.7±12.3	≤0.5 % in $BiPO_4$ precipitate; quality very good
Sr^{2+}	Sr (ICP-MS)	89.6±7.5	1.2±0.3	9.3±7.7	< 2% in $BiPO_4$, Quality excellent; good agreement between radiocounting and ICP-MS
	tracer	93.6±4.7	<2.0±0.05	4.4±4.6	
Ba^{2+}	Ba (ICP-MS)	98.4±53.6	18.0±15.83	-16.4±59.5	Inconsistent ICP-MS results; most suggest loss of Ba from metal storage solution
Pd^{2+} (?)	Pd (ICP-MS)	96.4±50.2	15.6±23.9	"-12±45.6	Quality poor; all simulations suggest loss of Pd from metal storage solution
La^{3+}	La (ICP-MS)	88.1±6.8	7.4±2.1	4.5±7.1	~10% in $BiPO_4$ precipitate; all Lanthanides similar; Data Quality very good
Ce^{3+}	Ce (ICP-MS)	76.9±11.0	16.2±5.7	6.9±9.0	~ 15% in $BiPO_4$ precipitate; all Lanthanides similar; Data Quality very good
Pr^{3+}	Pr (ICP-MS)	75.2±12.4	19.2±6.9	5.7±9.6	~20% in $BiPO_4$ precipitate; all Lanthanides similar; Data Quality good
Eu^{3+}	Eu (ICP-MS)	84.4±8.5	14.1±3.1	1.5±8.7	15 to 20% in $BiPO_4$ precipitate; all Lanthanides similar; Data Quality good; adequate agreement between ICP-MS and radiocounting
	(tracer)	74.1	22.5	3.4	
Y^{3+}	Y (ICP-MS)	91.0±6.6	3.2±1.1	5.8±6.5	Quality very good; ~3% in $BiPO_4$ precipitate
Zr^{+4}	Zr (ICP-MS)	56.0±42.5	37.3±22.5	6.6±58.3	ICP-MS data inconsistent; two simulations suggest Zr precipitated in metals storage solution with time; significant amount in $BiPO_4$ precipitate
				(-) mass "created"	