Plutonium and Americium Geochemistry at Hanford

ANDREW FELMY, WSU Research Professor, PNNL Laboratory Fellow (ret)
SUE CLARK, PNNL Battelle Fellow & WSU Regents Professor
MARK TRIPLETT, PNNL Senior Advisor

Presented to the Hanford Advisory Board, River and Plateau Committee, January 17, 2017
Richland, WA

PNNL-SA-123148
Outline

- Overview of Plutonium (Pu) and Americium (Am) contamination at Hanford
- Site specific examples
  - Groundwater
    - 216-B-5 Reverse Well
  - Soils and Sediments
    - 216-Z-1A Tile Field
    - 216-Z-12 Crib
    - 216-Z-9 Trench
- Recent advanced characterization efforts
Actinide Geochemistry is Complex

- Mobility in subsurface controlled by numerous hydrologic and geochemical processes.
- Hydrologic factors include dispersion, advection, and dilution.
- Geochemical processes include:
  - Oxidation/reduction reactions change valence state and alter chemical behavior.
  - Precipitation/dissolution likely most important in near-field environment with steep changes in pH or concentration.
  - Adsorption/desorption (tendency to bind with soil) is affected by many factors and likely controls contaminant retardation in far-field environments.
  - Complexation and colloid formation can also affect mobility.
- Radioactive decay (e.g., in-growth Am-241 from decay of Pu-241) can affect subsurface mobility.
Decades of environmental monitoring and characterization efforts have improved our understanding of plutonium geochemistry at Hanford

- **Groundwater:** Injection of a contaminated process stream into the groundwater aquifer via a well
  - 216-B-5 Reverse Well; alkaline (or neutral) bismuth phosphate waste

- **Soils & Sediments:** Release of contaminated process stream to subsurface area above the vadose zone
  - 216-B-5 Reverse Well; alkaline (or neutral) bismuth phosphate waste
  - 216-Z-1A Tile Field: acidic effluent from Pu Recovery Plan
  - 216-Z-12 Crib: alkaline, low-salt waste from conversion of Pu oxide to Pu tetrafluoride
  - 216-Z-9 Trench; acidic, high-salt, organic-rich effluent from the Recovery of Uranium and Plutonium by Extraction (RECUPLEX) process
Where are the Transuranics at Hanford?

The transuranics are predominately in the Central Plateau (200 Area)

Activities (Ci) of transuranic nuclides disposed at Hanford. Decayed to January 1, 2001.

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>100 Area</th>
<th>200 Area</th>
<th>300 Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pu-239</td>
<td>30</td>
<td>12,000</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(200Kg)</td>
<td></td>
</tr>
<tr>
<td>Am-241</td>
<td>-</td>
<td>29,000</td>
<td>&lt;1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(8.5Kg)</td>
<td></td>
</tr>
<tr>
<td>Np-237</td>
<td>-</td>
<td>50</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Pu-241</td>
<td>-</td>
<td>38,000</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.4kg)</td>
<td></td>
</tr>
</tbody>
</table>
216-B-5 Reverse Well Location

200 East Area
216-B-5 Reverse Well Location

- 200 East - B Plant Reverse Well
- 200 East - B Plant Retention Basin
216-B-5 Reverse Well

- Consisted of 241-B-361 Settling Tank and 20-cm diameter well
- Liquid overflow from the settling tank was introduced into the aquifer
- Bismuth phosphate process (B Plant)
- 23 million liters of plutonium bearing waste (37 Ci Pu) disposed (1945-1947) – ~150g Pu-239 and 0.3g Pu-241
- Treatability test completed in 1995 (DOE/RL-95-59)
  - Plutonium “essentially immobile”
  - Pilot-scale pump-and-treat ineffective and discontinued
216-B-5 Reverse Well

Figure 3-3. Artist's Concept of 216-B-5 Reverse Well and 241-B-361 Settling Tank.

Cross-Section of Pu-239/240 Distribution in the Vicinity of the 216-B-5 Reverse Well (contours are in μCi/kg) (Source: DOE/RL-95-59 (1996), Figure F-4)

Majority of the plutonium remains in the sediments near the original disposal location
Am-241 from Decay of Disposed Pu-241

Ratio of Pu-239/240 to Am-241 similar at varying depth.

Suggests that their subsurface migration is correlated.

Am remained with Pu

Plutonium-239/240 and Americium-241 in Sediment Collected from Well 299-E28-23 (Smith 1979)
Summary of 200 Area Groundwater Monitoring Results for Pu-239/240 and Am-241 (1980 – Present)

- Groundwater monitoring of Pu, Am, and gross alpha is routinely conducted. For example, for the 200 East/West wells since 1980:
  - Pu-239/240: 1,737 distinct samples from 316 wells
  - Am-241: 691 distinct samples from 170 wells
- Nearly all of the Pu-239/240 detection results are in the immediate vicinity of 216-B-5 Reverse Well where Pu solutions were directly injected into the aquifer from 1945 to 1947.
- Only a handful of samples have detected Pu in the vicinity of the 216-Z-9 Trench, and all are below the MCL.
- Similarly, nearly all of the Am-241 detection results are in these same two locations with most being associated with the 216-B-5 Reverse Well.
- All Am-241 samples are below the MCL of 15 pCi/L.
200 West Area Plutonium Sites

- 231 - Z Building
- Z-9 Trench
- Plutonium Finishing Plant
- Z-12 Crib
- Z-18 Crib
- Z-1A Tile Field
216-Z-1A Tile Field

- Utilized 1964-1969
- Received overflow liquid waste from 216-Z-1, -2, and -3 cribs
- Most Pu from 6 million liters of acidic waste from Plutonium Reclamation Facility (1964-1969)
216-Z-1A Tile Field

North-south cross section through the center of the 216-Z-1A Tile Field and distribution of waste (top), and plan view of 216-Z-1A Tile Field and distribution of waste (bottom) (Dots indicate well locations).
216-Z-1A Tile Field – Pu and Am Distribution in Sediment Collected from Well 299-W18-149 (Price et al. 1979)

- Very High Concentrations in Near Surface Sediments
- Am-241/Pu-239,240 ratio increases with depth
- Migration of Pu and Am not correlated
- Suggests that Am was partially mobilized from Pu particles (due to acidic waste stream) in the near surface sediments and transported into the deeper sediments
216-Z-12 Crib

- Large quantities of low-salt, alkaline waste (281 million liters)
  - Major process was the conversion of plutonium oxide to plutonium tetrafluoride
  - Essentially a dilute hydrofluoric acid with Pu ions
  - Neutralized to pH 10 and sent to 241-Z-361 Settling Tank
- Large disposal area (546 m²)
High concentrations of both Pu and Am in the top layers of sediment.

Significant concentrations of both Pu and Am in deep silt layer.

Pu with Am may indicate particles transported (not an acidic waste stream like Z-1A).

Volumes discharged to 216-Z-12 Crib or 216-Z-1A Tile Field too low for lateral spreading (Kasper).
216-Z-9 Trench

- Samples obtained and analyzed from the top of the disposal area and from deep subsurface cores

- Acidic, high-salt, organic-rich RECUPLEX waste
  - Co-contaminants (CCl₄, TBP, DBBP, DBP, MBP), lard oil, nitrate

- Pu penetrated deep into the subsurface
216-Z-9 Trench

Figure 3.6. Construction Details for the 216-Z-9 Trench (after Ridgway et al. 1971)
Pu, Am, and tributyl phosphate (TBP) concentrations as a function of depth measured in soil samples from Well 299-W15-48

Am could have been separated from Pu and migrated deeper into the subsurface.
Pu, Am, and TBP concentrations as a function of depth measured in soil samples from Well 299-W15-46 (symbols at same depth represent duplicate analyses)

Am could have been separated from Pu and penetrated deeper into the subsurface.
Support through DOE Office of Biological and Environmental Research (BER) through the Subsurface Biogeochemical Research Program, Science Focus Area at Pacific Northwest National Laboratory (PNNL)

Methods were applied to samples from
- Surface Sediments (top 30cm) samples from the 216-Z-9 trench
- Deep Sediments samples from the 216-Z-9 trench
  - Two cores drilled 2004 - 2006
  - W15-46 (down gradient)
  - W15-48 (slant borehole)

Imaging based on nanometer-scale secondary-ion mass spectrometry (nanoSIMS) analysis from Lawrence Livermore National Laboratory.
Synopsis of Results from Advanced Studies

▶ Shallow sediment results
  ■ Large Pu particles found
    ○ Discharged directly from Z Plant
  ■ Very small particles also present
    ○ Dissolution under acid conditions and re-precipitation as Pu-PO$_4$-SiO$_2$ (?)

▶ Deep sediment results
  ■ Pu apparently migrates at low concentration in an acidic solution.
  ■ Interacts with the more basic sediment particles and precipitates from the solution (removed) to the particle surfaces.
  ■ Consistent with the observation of Am separation from Pu during migration – Pu particles dissolve allowing more mobile Am to separate.