90 Sr Transport through the INTEC Vadose Zone
INTEC Contaminant Overview

Contaminants by Location

Tank Farm Soils
Injection Well
Perc Pond
Misc. Soil Sites
Liquid Releases
Total

(NCi or Kg)

U-234
Pu-240
Pu-239
Pu-238
Cs-137
Sr-90
H-3
I-129
U-234
Pu-239
Np-237
Pu-240
I-129

CONTAMINANT OVERVIEW
<table>
<thead>
<tr>
<th>Site Activity (Ci)</th>
<th>Service Waste (~25)</th>
<th>Former injection well 24.3 (total), 16 direct</th>
<th>OU 3-14 releases (&gt;18000)</th>
<th>OU 3-13 releases (&lt;1300)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPP-27</td>
<td>720</td>
<td>0.295</td>
<td>15,900</td>
<td>308.8</td>
</tr>
<tr>
<td>CPP-79 deep</td>
<td>874</td>
<td></td>
<td>918</td>
<td></td>
</tr>
<tr>
<td>CPP-31</td>
<td>918</td>
<td></td>
<td></td>
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<tr>
<td>soil sites</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>liquid releases</td>
<td></td>
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</tr>
<tr>
<td>Percolation ponds</td>
<td></td>
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</tr>
</tbody>
</table>
### CPP-31 Release

- Occurred in 1972
- During transfer of 2nd/3rd Cycle Raffinate
- Lost 70,000 liters (18,600 gallons) over 5 days

#### Raffinate Chemistry

<table>
<thead>
<tr>
<th>Component</th>
<th>Initial Concentration (mol/L)</th>
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<th>Component</th>
</tr>
</thead>
<tbody>
<tr>
<td>99-Tc</td>
<td>2.67E-05</td>
<td>90Sr</td>
<td>0.5</td>
</tr>
<tr>
<td>Cs (total)</td>
<td>1.74E-05 (15,900 Ci)</td>
<td>1.5</td>
<td>NR</td>
</tr>
<tr>
<td>Cs</td>
<td>2.02E-05</td>
<td>137Cs</td>
<td>4.5</td>
</tr>
<tr>
<td>Na+</td>
<td>5.83E-09</td>
<td>134Cs</td>
<td>1.5</td>
</tr>
<tr>
<td>Al+++</td>
<td>1.5</td>
<td>H+</td>
<td></td>
</tr>
<tr>
<td>Cs</td>
<td>2.02E-05 (16,000 Ci)</td>
<td></td>
<td></td>
</tr>
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<td>Cs</td>
<td>2.67E-05 (15,900 Ci)</td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>

#### Nonradioisotopes

- Occurred in 1972
Downward Transport

- Release occurred 1.75 meters below land surface (bbls)
- Alluvium is 13.5 meters thick
- Interbeds (and perched water) at INTEC exist at 30', 42', 85', and 116 meters
- Initial saturation in the alluvium ~30%
- Porosity 32%
- Additional 8 cm/yr (spatial average) anthropogenic water infiltration
- Average precipitation infiltration rate 18 cm/yr average

Additional 8 cm/yr (spatial average) anthropogenic water infiltration.

Alluvium is 13.5 meters thick.

Release occurred 1.75 meters below land surface (bbls).
Soil Data Near CPP-31

- 64 gamma logs taken in 2004 to depths of 12-14 meters
- One of the logged wells was cored and sent to the laboratory for $^{137}$Cs
- $^{137}$Cs-137 (pCi/g)
- Sr-90 (pCi/g)
- Soil Concentration (pCi/g)

2004 Analytical Data

Depth (meters)

0.00E+00 5.00E+06 1.00E+07 1.50E+07 2.00E+07 2.50E+07
0 2 4 6 8 10 12 14
Soil Column Notes:

- Initial $^{137}$Cs/$^{90}$Sr ratio = 1.16
- Highest $^{137}$Cs at 5-6 m (8,990,000 pCi/g)
- Highest $^{90}$Sr at 6.5-7.5 m (20,700,000 pCi/g)
- Distribution of $^{137}$Cs and $^{90}$Sr differ:
  - Gaussian $^{137}$Cs
  - 700,000 pCi/g $^{90}$Sr below the peak
  - 100 pCi/g $^{137}$Cs below the peak
  - Lateral movement of $^{90}$Sr $>$ $^{137}$Cs
  - Vertical offset does not support $V_{Sr}$ $>$ $V_{Cs}$
- Can't easily quantify the $^{90}$Sr
- 90% of $^{137}$Cs accounted for in alluvium

Graphs show:

- Soil Concentration (pCi/g) vs. Depth (meters)
- $^{137}$Cs and $^{90}$Sr profiles
- Initial $^{137}$Cs/$^{90}$Sr Ratio = 1.16
Perched Water Concentrations @ 30 m (b/s)

Data taken in the perched water at 30 m

- 90Sr as high as 480,000 pCi/L
- Data taken in the perched water at 30 m

Matching 90Sr concentrations requires constant Kd = 0.2 mL/g

- Measured Kd range is 13-145 mL/g (Liszewski et al., 1998)
- Using Kd = 100 mL/g allows no 90Sr to leave the alluvium
- Using Kd = 0.2 mL/g leaves no 90Sr in the alluvium
- No coverage beneath CPP-31
- No peak concentration data
- No first arrival data

C(pCi/L)

Date

1/1/72 12/24/01
1/2/2/91 12/27/96 12/28/86 12/29/81 12/30/76 1/2/30/75

Well M-5-05

Well S-5-06

Well M-5-12

Well M-5-2
Observations

- Traditional Kd approach is only valid for steady state systems
- Infiltration (leak) events are transitory
- Plume movements are transitory
- Initiation (leak) events are transient
- Chemical evolution is transient
- Dynamic changes in geochemical evolution
- Mineralogy, hydrology, and laboratory observations of Cs and Sr

To evaluate the geochemical evolution we needed to consider:

- Tank farm releases underwent extreme changes in pore water chemistry
- Highly transient flow

Observations
<table>
<thead>
<tr>
<th>Mineral</th>
<th>Weight Percent by Source</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Clays</strong></td>
<td>1. (Bartholomay, et al. 1989)</td>
</tr>
<tr>
<td>0 - 22</td>
<td>19</td>
</tr>
<tr>
<td>0 - 0</td>
<td>6</td>
</tr>
<tr>
<td>0 - 14</td>
<td>8</td>
</tr>
<tr>
<td>3 - 12</td>
<td>7</td>
</tr>
<tr>
<td>0 - 13</td>
<td>12</td>
</tr>
<tr>
<td>0 - 18</td>
<td>12</td>
</tr>
<tr>
<td>16 - 21</td>
<td>16</td>
</tr>
<tr>
<td>45 - 56</td>
<td>33</td>
</tr>
</tbody>
</table>

- **K-Feldspar**
- **Calcite**
- **Pyroxene**
- **Plagioclase**
- **Dolomite**
- **Quartz**
- **Clays**

<table>
<thead>
<tr>
<th>Range (n=3)</th>
<th>Median (n=5)</th>
<th>2. (Liszewski, et al. 1997)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8 - 14</td>
<td>10</td>
<td>8 - 14</td>
</tr>
<tr>
<td>0 - 3</td>
<td>0</td>
<td>0 - 3</td>
</tr>
<tr>
<td>8 - 14</td>
<td>12</td>
<td>8 - 14</td>
</tr>
<tr>
<td>0 - 6</td>
<td>3</td>
<td>0 - 6</td>
</tr>
<tr>
<td>6 - 18</td>
<td>12</td>
<td>6 - 18</td>
</tr>
<tr>
<td>16 - 30</td>
<td>23</td>
<td>16 - 30</td>
</tr>
<tr>
<td>32 - 45</td>
<td>38</td>
<td>32 - 45</td>
</tr>
</tbody>
</table>

Weights Percent by Source
- Excavated, homogenized, 8 backfilled mix of overbank and channel deposits
- INTEC alluvium
- Overbank deposits
- Channel deposits

Mineralogical

Extractions, homogenized, 8 backfilled mix of overbank and channel deposits.
<table>
<thead>
<tr>
<th>Component</th>
<th>Initial Concentration (mol/L)</th>
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<th>Initial Concentration (mol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H+</td>
<td>5.83E-09</td>
<td>134Cs</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>137Cs</td>
<td>4.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CS (total)</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sr</td>
<td>2.02E-05 (16,000 Ci)</td>
</tr>
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<td></td>
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<td>2.02E-05 (16,000 Ci)</td>
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<td></td>
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<tr>
<td></td>
<td>2.67E-05</td>
<td>99Tc</td>
<td></td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Non Radionucleides</th>
<th>Radiouclides</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raffinate Composition</td>
<td></td>
</tr>
<tr>
<td>Component</td>
<td>Concentration (mole/L)</td>
</tr>
<tr>
<td>-----------</td>
<td>-----------------------</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>3.64E-03</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>2.2E-04</td>
</tr>
<tr>
<td>Na⁺</td>
<td>2.2E-04</td>
</tr>
<tr>
<td>H⁺</td>
<td>1.64E-03</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>5.36E-08 (7.30)</td>
</tr>
</tbody>
</table>

**Perched- and Infiltration-Water Composition**
Acid to rapidly react with calcite:
- dissolves calcite
- increases the pH of the influxing solution
- supersaturates the influxing solution with respect to Aluminum -- forming gibbsite
- releases gas-phase CO$_2$
- decreases the pore-water pH

Acid to slowly react with alumino-silicate minerals:
- alumino-silicate minerals may be inert if pH is buffered rapidly
- reactions may be neglected

Potential impact on hydrologic properties:

\[
\begin{align*}
\text{Calcium carbonate (CaCO}_3\text{)} & + \text{Nitric acid (HNO}_3\text{)} \\
& \rightarrow \text{Calcium nitrate (Ca(NO}_3\text{)}_2\text{)} + \text{Carbon dioxide (CO}_2\text{)} + \text{Water (H}_2\text{O)}
\end{align*}
\]
Ion Exchange

Sr and Cs characterized by low ionic potential (valence/ionic radius)

Exchange occurs rapidly for both species

Sr exchanges primarily on planar sites on clays

Cs exchanges on frayed edge and planar sites

- edge sites are stronger bonding than planar sites
- bonded stronger at low concentration, weaker at high concentration
- not easily released from the edge sites

Exchange occurs rapidly for both species

Sr and Cs characterized by low ionic potential (valence/ionic radius)
Ion exchange model parameters

- Cation Exchange Capacity (CEC) -- solid media property -- strong function of soil type
  - INTEC specific values are not available
    - INL values are available from Liszewski, Bartholomay, Hawkins and Short, USGS
    - literature is pretty consistent for order and relative magnitude
      - $\text{Cs}^+ < \text{Sr}^2+ < \text{Ca}^{2+} < \text{Mg}^{2+} < \text{K}^+ < \text{NH}_4^+ < \text{Na}^+ < \text{H}^+$

- Selectivity Coefficients
  - INL values are available from Liszewski, Bartholomay, Hawkins and Short, USGS
  - INTEC specific values are not available
  - spatially variable (depositional environment)
  - solid media property -- strong function of soil type

- Ion exchange capacity (CEC)
How Good are the Sr-90 Parameters for Ion Exchange?

Comparison of Batch Experiment to Hawkins & Short (1965) Data
Comparison for 137Cs Using 2 Exchange Sites
One-Dimensional Simulation Results

- Initial (pre-release) water saturation of ~30% (after equilibration)
- Water flux and water content allowed to reach steady state (multiphase)
- Layered media:
  - alluvium thickness 13 m
  - basalt underneath
  - hydraulic properties taken from the OU 3-14 RI/BRA/FS model
- Boundary conditions:
  - 18 cm/yr infiltration at top
  - 18,600 gallons over 5 days during simulated release, released at 1.75 meters
  - saturated bottom boundary (perched water)
- Domain size: 60 m x 30 m x 18 m

- Roughly equal to gamma distribution from 1970's data
1-D Simulation Results

- Calcite and pH distributions
  - Calcite buffers pH rapidly
  - Transient drop in pH from dissolution
    - Returns to neutral once dissolution dissipates
    - Alumino-silicate dissolution is minor

Calcite (volume fraction)

- 1 week
- 1 yr
- 2 yr
- 5.0
- 5.5
- 6.0
- 6.5
- 7.0
- 7.5
- 8.0

Elevation above basalt (m)

- 0
- 2.5
- 5
- 7.5
- 10
- 12.5

pH

- 0
- 2.5
- 5
- 7.5
- 10
- 12.5

Elevation above basalt (m)
SOLUTION SPECIES AT 2.03 YRS

- Sodium retarded relative to NO₃⁻ and Ca²⁺
- Calcium is kept in solution and moves faster than nitrate and Sr-90
- Sodium knocks calcium off clays and drives exchange reactions where Na⁺ retarded relative to NO₃⁻ and Ca²⁺
- Strontium is kept in solution and moves slightly slower than nitrate at 1 yr is about 4% in solution
Distribution of Sr species at 2.03 yrs

- Sr transport is multimodal
- High aqueous concentrations correspond to low exchange concentration
- Sr²⁺ and Sr(NO₃)⁺ are the primary aqueous species
Distribution of exchangeable cations at 2.03 and 8.05 yrs

- Elevated leading edge calcium concentrations enhance Sr migration
- Sr exchange is preferred to Ca -- leaves more Sr on exchange sites
- Calcium is replaced by sodium (high sodium, low calcium)
- High exchange species == low aqueous species

Elevated leading edge cation concentrations enhance Sr migration

<table>
<thead>
<tr>
<th>Elevation above basalt (m)</th>
<th>SrX2 Conc (mole/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.0E+00</td>
</tr>
<tr>
<td></td>
<td>3.0E-02</td>
</tr>
<tr>
<td></td>
<td>6.0E-02</td>
</tr>
<tr>
<td></td>
<td>9.0E-02</td>
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<tr>
<td></td>
<td>1.2E-01</td>
</tr>
<tr>
<td></td>
<td>1.5E-01</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Elevation above basalt (m)</th>
<th>NaX and CaX2 Conc (mole/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NaX</td>
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<tr>
<td></td>
<td>CaX2</td>
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<td>SrX2</td>
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<td>0.0E+00</td>
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<td>3.0E-02</td>
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</tr>
</tbody>
</table>
Concentration of cations in solution at 8.05 yrs

Elevated aqueous concentrations at 30-40 ft corresponds to elevated concentration on the cation exchange sites.

Bulk of the Sr is deep in the column. Elevated aqueous concentrations at 30-40 ft corresponds to elevated concentration on the cation exchange sites.
Ion exchange results in a spatially and temporally variable partitioning:

\[
\left( \frac{\ln q}{\phi} S \right)^{10S} \frac{spv}{C} = p \cdot K_d
\]

Predicted Sf \( K_d \)
3-D SIMULATION RESULTS FOR CPP-31

Krigged log-10 (Cs-137) soil concentrations (corrected to 1972) pCi/g
Water Saturation 1, 5, and 17 months post CPP-31 release
Aqueous Species 12 Months Post CPP-31 Release
SR-90 on exchange sites 1, 2, and 3 years post CPP-31 release
Effective partitioning at 0.5, 1.5, and 17.5 years post CPP-31 release
Summary measures

(A) SrNO₃ in Aqueous phase

(B) Sr⁹⁰⁺ in Aqueous phase

(C) SrCO₃ in Aqueous phase

(D) SrOH⁻ in Aqueous

(E) Total Sr⁹⁰ in pore water

(F) Sr⁹⁰ total in Aqueous phase

(G) Cumulative Leaving Alluvium

(H) Flux Rate Out of the Alluvium

(I) Activity−weighted Kd on exchange sites
Where are we?

This model explains early arrival in perched water and soil concentrations. It does not correspond to observed 1977 ratios of $^{137}\text{Cs}/^{90}\text{Sr}$: core taken near CPP-31 by Rhodes et al.

- Suggests multiple processes are still occurring.
- Probably different in the perched water and alluvium.

This model explains early arrival in perched water and soil concentrations.
Final Observations

- Infiltration rates
- Topology/distribution of interbeds
- Geochemical processes in sediments
- Evolution of the surface releases

Predicted aquifer concentrations:
- 110 concentrations ~ 300,000 pCi/L
- >17,000 Ci total
- Catastrophic releases

CPP-31 and CPP-79
- The MCL is 8 pCi/L
- SRPA 90% ~ 900 pCi/L
- Over 20 years
- 16 Ci of 90 Sr

Direct injection of