Long-Term Stability of Waste Packages

“I could not be expected to feel much courage in the presence of the fearful fate that appeared to await me.”

—Henry Lawson in “Journey to the Center of the Earth” by Jules Verne.
Multiple Barriers

Most countries favor deep, geological burial of radioactive wastes because they would then pose no danger to human health.

Proposed designs include multiple barriers, each serving as a backup for when (not if) a previous barrier fails.
Metal Containers

Most of the radionuclides will spend their entire lives within the UNF because UNF itself dissolves slowly in water. Whether UNF is reprocessed or not, wastes will ultimately be placed in metal containers for disposal.

Will corrosion destroy the waste package before the radionuclides decay to harmless levels?
Overall Goal of Barriers

The goal of the metal containers and the multi-barrier concept is to isolate UNF long enough such that radioactive decay will lessen the burden placed on the next barrier after failure.
Swelling of bentonite clay

Sodium bentonite expands when wet, absorbing as much as several times its dry mass in water. The property of swelling on contact with water makes sodium bentonite useful as a sealant, because it provides a self-sealing, low-permeability barrier.

http://www.youtube.com/watch?v=yyCXp9eybrc
Main concern: contact with groundwater will corrode metal containers, depending on the dissolved oxygen content.

Corrosion is the disintegration of metal from chemical reactions; loss of electrons reacting with water and oxygen.

Metals $\rightarrow$ oxides and other compounds
Metal corrosion: Iron

Many metals are initially in a neutral charge state.

\[ \text{Fe}^0 + \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}^{3+} + \text{OH}^- \rightarrow \text{Fe(OH)}_3\downarrow \]

12 electrons short

\[ 4\text{Fe}^0 + 3\text{O}_2 + 6\text{H}_2\text{O} \rightarrow 4\text{Fe}^{3+} + \]
gains the 12 electrons

\[ 12\text{OH}^- \rightarrow 4\text{Fe(OH)}_3\downarrow \text{or} \]

\[ 4\text{FeO(OH)}\downarrow + 4\text{H}_2\text{O} \]
“Rust” most stable
**Metal corrosion: Zinc**

\[ 2\text{Zn}^0 + 2\text{H}_2\text{O} + \text{O}_2 \rightarrow 2\text{Zn}^{2+} + 4\text{OH}^- \rightarrow 2\text{Zn(OH)}_2 \downarrow \rightarrow \text{ZnO ("white rust") + H}_2\text{O} \]
Factors that affect corrosion

pH (controls the solubility of metals; acids will of course dissolve metals)

Oxygen and water (promotes corrosion)

Temperature (heat accelerates reactions)

Other ions such as chloride (Cl\(^{-}\))

\[
\text{Fe}^{3+} + 3\text{Cl}^{-} \rightarrow \text{FeCl}_3^0
\]

(drives reaction to the right)

Water flow rate (greater flow, great mass removal)
Factors that affect corrosion

After closure, all the oxygen will be consumed, and sulfide may become the primary corrosive agent:

$$\text{4Cu} + 2\text{HS}^- \rightarrow 2\text{Cu}_2\text{S} + \text{H}_2(\text{g})$$

Sulfide from the dissolution of sulfide minerals such as pyrite in the buffer zone and microbial reduction of sulfate ions.
Types of corrosion

Pitting

Crevice

Erosion

Uniform
Chemical passivation

Formation of a thin, non-reactive surface film (mostly oxides) that inhibits additional corrosion.

\[ \text{Cu}_2\text{O} \text{ (cuprite)} \]
\[ \text{CuSO}_4 \cdot 5\text{H}_2\text{O} \]
\[ \text{Cu}_2(\text{OH})_3\text{Cl} \]

Can prolong the stability of the waste package.
Anthropogenic Analogues

Bronze cannon recovered in 1982 from a Swedish shipwreck in 1676.

Had been buried in marine clay sediments for 306 years.

Corrosion rate: 0.15 μm/year (0.02 mills per year). If 2 inches (5.1 cm) thick, it would last for 100,000 years (100 Ka).
<table>
<thead>
<tr>
<th>Item</th>
<th>Age</th>
<th>Corrosion Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bronze chisel (Argentina)</td>
<td>800 years old</td>
<td>0.04 mpy</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(1.01 μm/year)</td>
</tr>
<tr>
<td>Bronze plate</td>
<td>550 years old</td>
<td>0.03 mpy</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.76 μm/year)</td>
</tr>
<tr>
<td>Copper-zinc bell</td>
<td>1,030 years old</td>
<td>0.007 mpy</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.18 μm/year)</td>
</tr>
<tr>
<td>Bronze relics in tombs (China)</td>
<td>3,000 years old</td>
<td>0.01 mpy</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.25 μm/year)</td>
</tr>
</tbody>
</table>
Anthropogenic Analogues

Iron and steel archeological artifacts yield 0.1 to 10 µm/year.

Greater rate: steels in aerated (oxidizing) sediments.

Corrosion depths ~ 2 cm in less than 10,000 years “unlikely”

Ni-Cr-Mo alloys

Ni-Cr-Mo alloys leading candidate for radioactive waste containers at Yucca Mountain

Alloy 22: 22% Cr, 13% Mn, 3% W, 3% Fe, 60% Ni

In order to mimic long-term exposure to corrosive environments, various short-term tests have been developed that use aggressive acids, chlorides, and elevated temperatures.
Examples of aggressive corrosion test solutions

ASTM G-28, Method A:
50 % H₂SO₄, 41.7 g/L Fe₂(SO₄)₃ • 9H₂O in boiling deionized water, 5-day exposure

“Green Death”
11.4% H₂SO₄ + 1.2% HCl + 1% FeCl₃ + 1% CuCl₂ in deionized water, 25ºC, exposure interval is a variable.
# Corrosion test results for Alloy 22 for industrial applications

<table>
<thead>
<tr>
<th>Media</th>
<th>Temperature (°C)</th>
<th>General corrosion (mpy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASTM 28A</td>
<td>100</td>
<td>36 (0.91 mm)</td>
</tr>
<tr>
<td>Green Death</td>
<td>100</td>
<td>4 (0.10 mm)</td>
</tr>
<tr>
<td>10% HNO₃</td>
<td>100</td>
<td>2 (0.05 mm)</td>
</tr>
<tr>
<td>50% H₂SO₄</td>
<td>100</td>
<td>308 (7.82 mm)</td>
</tr>
<tr>
<td>10% H₂SO₄ + 1% HCl</td>
<td>100</td>
<td>354 (9.00 mm)</td>
</tr>
</tbody>
</table>

from [www.corrosionlab.com](http://www.corrosionlab.com) and [www.specialmetals.com](http://www.specialmetals.com)
Standard corrosion rate for Alloy 22

For Yucca Mountain, however, using the Total-System Performance Assessment, a constant general corrosion rate of $10^{-5}$ cm/year (0.0004 mpy) has been used to assess outer container of Alloy 22. This rate is based on the long-term persistence of a passive film.

(Ahn et al., 2008. J. of Nuclear Materials, 379, 33-41)
The TSPA-VA was conducted by DOE to assess the behavior of the proposed high-level waste repository at Yucca Mountain. Final results were presented in 1998.

Among the many factors considered were rates of infiltration, radionuclide mobility, pore-water velocity, and chemical precipitation kinetics. Used a variety advection-dispersion-sorption and reactive-transport models, and . . .

*waste package corrosion.*
General Training On Methodologies For Geological Disposal in North America
IAEA Network of Centers of Excellence

Total System Performance Assessment for Yucca Mountain

Peter Swift
Yucca Mountain Lead Laboratory Chief Scientist
Sandia National Laboratories
14 November 2008

Corrosion versus decay of $^{241}$Am

Rate = $10^{-5}$ cm/year (0.0004 mpy)

Assume:
- instantaneous arrival of groundwater to 12-cm thick waste package.

<table>
<thead>
<tr>
<th>years</th>
<th>Half-life</th>
<th>% decayed</th>
<th>% corroded</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.23</td>
<td>14.8</td>
<td>0.01</td>
</tr>
<tr>
<td>432</td>
<td>1</td>
<td>50.0</td>
<td>0.04</td>
</tr>
<tr>
<td>2,160</td>
<td>5</td>
<td>97.0</td>
<td>0.18</td>
</tr>
<tr>
<td>4,320</td>
<td>10</td>
<td>99.9</td>
<td>0.36</td>
</tr>
</tbody>
</table>
Corrosion versus decay of $^{99}$Tc (half-life = 212,000 years)

Rate = $10^{-5}$ cm/year (0.0004 mpy)

Assume:
- Instantaneous arrival of groundwater to 12-cm thick waste package.

<table>
<thead>
<tr>
<th>Half-life</th>
<th>% decayed</th>
<th>% corroded</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>29</td>
<td>8.8</td>
</tr>
<tr>
<td>1</td>
<td>50</td>
<td>17.7</td>
</tr>
<tr>
<td>5</td>
<td>96.9</td>
<td>88.3</td>
</tr>
<tr>
<td>10</td>
<td>99.9</td>
<td>Failed</td>
</tr>
</tbody>
</table>
Conclusions of the TSPA Peer Review Panel (3rd Interm. Rep.)

After placement of the waste packages, there will be a “hot, dry period during which the surface temperatures of the waste packages exceed boiling . . . [for] several hundred to several thousand years.”

“The earliest failures of the waste packages will occur as a result of corrosion pits at [about] 3,000 years.”
Conclusions of the TSPA Peer Review Panel (3rd Interim. Rep.)

“About 1% of the waste packages will be breached at 10,000 years (10 Ka).”

However, for spent fuel, no credit was given to the cladding. The cladding will corrode, but will delay spent fuel breaching. “Ten percent of the cladding is estimated to have failed by 200,000 years (200 Ka).”
Waste Package Degradation

From Performance Assessment-Viability Assessment 1997
Corrosion of the cladding around UNF

Zircaloy is frequently used for cladding of fuel rods. A tube with that is about 1 mm thick.

Zirconium (Zr) has a very small absorption cross section for thermal neutrons. Also has a high melting point ($1,930 \degree C, 3,506\degree F$)

Zirconium is resistant to corrosion in sulfuric acid ($H_2SO_4$), nitric acid ($HNO_3$), and hydrochloric acid ($HCl$)
Zirconium and Zircaloy

Zirconium only sparingly soluble in water. About 5 µg/L in 10^{-4} M LiOH at 572° F (300° C) (Qui et al., 2008).

Zircaloy 2: 98.25% Zr, 1.45% Sn, 0.10% Cr, 0.14% Fe, 0.06% Ni and 0.01% Hf

Enhanced corrosion resistance.

Zircaloy reacts with O_2 to form a passivation layer of ZrO_2.
Waste Form Degradation

- Pits Penetrate CRM
- Water Enters Waste Package
- CAM Corrosion Products and Mineral Precipitates
  CAM is Penetrated by Corrosion
- Crevice under CAM
- Deep Pit in CRM
- Uranium Dioxide (UO2) Fuel
- Zircaloy Cladding
- Fuel Grain
- Grain Boundary
- Gap
- Grain Boundary Release
- Zircaloy Cladding
- Pellet Interfacial Gap
Corrosion of fuel cladding

The rate of corrosion of the cladding increases with temperature.

\[ \Delta w = A e^{(-b/\text{temp}) \times \text{time}} \]

<table>
<thead>
<tr>
<th>Temperature (° C)</th>
<th>Thickness loss (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>0.008</td>
</tr>
<tr>
<td>300</td>
<td>0.1</td>
</tr>
<tr>
<td>350</td>
<td>1.0</td>
</tr>
<tr>
<td>400</td>
<td>6.3</td>
</tr>
</tbody>
</table>

“Corrosion may exceed thickness in less than 300 years” (Fraker, 1989)
Hydrogen embrittlement

Zirconium reacts with hot water to form hydrogen: $\text{Zr} + 2\text{H}_2\text{O} \rightarrow \text{ZrO}_2 + 2\text{H}_2$

The hydrogen diffuses with the zirconium and forms Zr hydrides (ZrH, ZrH$_2$, ZrH$_4$). The metal then becomes embrittled (ductility decreases) and it fractures easily. Cracks begin to form in the zirconium hydride platelets and are propagated through the metal.
After the failure of all the barriers

The corrosion/dissolution of spent fuel by groundwater.

The ultimate dispersion of the fission and activation products and actinides in spent fuel requires that they be leached from the exposed fuel pellets and transported from the disposal site by moving groundwater.
Groundwater reaches the fuel . . . then what?

Recall that used fuel is basically UO$_2$.

Under reducing (oxygen poor) pH neutral water the solubility of UO$_2$ is about $3 \times 10^{-9}$ mole/L or about 0.8 µg/L.

In the presence of oxygen:

$$\text{UO}_2 \rightarrow \text{U}_4\text{O}_8 \rightarrow \text{UO}_2^{2+}$$
Reduced groundwater
But will the radionuclides leach into groundwater?

Based on geochemical principles and limited observations . . .

The radionuclides produced by neutron capture in the zircaloy cladding will be “presumably incorporated within the oxide [layer].” Wiles, 2002.

Radionuclides having an ionic radius $\pm 15\%$ of U (IV) will remain in the crystal structure as a “solid solution” (homogeneous crystalline solid). They cannot leach and migrate until the fuel itself dissolves.
241\textsuperscript{Am}, 239\textsuperscript{Pu}, 242\textsuperscript{Pu}, 93\textsuperscript{Zr}, 242\textsuperscript{Cm}, 94\textsuperscript{Nb}, 151\textsuperscript{Sm}, 113\textsuperscript{m}Cd and others
Will radionuclides leach into groundwater?

Non-volatile radionuclides such as Tc, Pd, and Ru that do not form solid solutions with U form microphases at grain boundaries, and are still trapped within the lattice.

During the operation of a reactor, the ceramic pellets develop cracks and grain boundaries. The cladding holds the fuel bundle together.
Which radionuclides leach into groundwater?

Gas-phase radionuclides (Kr, Xe, Cl and I) can diffuse from the used fuel and accumulate in grain boundaries, cracks, and the gap between the fuel and the cladding.

“Instant Release Group” (Canadian concept): those radionuclides that are predicted to be relatively leachable when groundwater is in contact with the exposed used fuel.
**THE PERIODIC TABLE OF THE ELEMENTS**

<table>
<thead>
<tr>
<th></th>
<th>H</th>
<th>Li</th>
<th>Be</th>
<th>B</th>
<th></th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>F</th>
<th>Ne</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>Mg</td>
<td>Al</td>
<td></td>
<td></td>
<td></td>
<td>Si</td>
<td>P</td>
<td>S</td>
<td>Cl</td>
<td>Ar</td>
</tr>
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<td>Sc</td>
<td>Ti</td>
<td>V</td>
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<td>Mn</td>
<td>Fe</td>
<td>Co</td>
<td>Ni</td>
<td>Cu</td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td>Zn</td>
<td>Ga</td>
<td>Ge</td>
<td>As</td>
<td>Se</td>
</tr>
<tr>
<td></td>
<td>Rb</td>
<td>Sr</td>
<td>Y</td>
<td>Zr</td>
<td>Nb</td>
<td>Mo</td>
<td>Tc</td>
<td>Ru</td>
<td>Rh</td>
<td>Pd</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>Ag</td>
<td>Cd</td>
<td>In</td>
<td>Sn</td>
<td>Sb</td>
</tr>
<tr>
<td>Cs</td>
<td>Ba</td>
<td>*</td>
<td>Hf</td>
<td>Ta</td>
<td>W</td>
<td>Re</td>
<td>Os</td>
<td>Ir</td>
<td>Pt</td>
<td>Au</td>
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<tr>
<td>Fr</td>
<td>Ra</td>
<td>**</td>
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</tr>
</tbody>
</table>

* The Lanthanide (Rare Earth) Elements

<table>
<thead>
<tr>
<th>La</th>
<th>Ce</th>
<th>Pr</th>
<th>Nd</th>
<th>Pm</th>
<th>Sm</th>
<th>Eu</th>
<th>Gd</th>
<th>Tb</th>
<th>Dy</th>
<th>Ho</th>
<th>Er</th>
<th>Tm</th>
<th>Yb</th>
<th>Lu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ac</td>
<td>Th</td>
<td>Pa</td>
<td>U</td>
<td>Np</td>
<td>Pu</td>
<td>Am</td>
<td>Cm</td>
<td>Bk</td>
<td>Cf</td>
<td>Es</td>
<td>Fm</td>
<td>Md</td>
<td>No</td>
<td>Lw</td>
</tr>
</tbody>
</table>

** The Actinide (Transuranic) Elements

*Figure 4.6 – Radionuclides included in the Instant Release group.*
How much of each radionuclide will leach?

Experimentally, about 8 to 10% of each member of the Instant Release Group may be released to groundwater (Source? Updates?)

Specifically, the Group consists of $^3\text{H}$, $^{14}\text{C}$, $^{36}\text{Cl}$, $^{39}\text{Ar}$, $^{40}\text{K}$, $^{42}\text{Ar}$, $^{79}\text{Se}$, $^{81}\text{Kr}$, $^{85}\text{Kr}$, $^{90}\text{Sr}$, $^{99}\text{Tc}$, $^{126}\text{Sn}$, $^{129}\text{I}$, $^{135}\text{Cs}$, and $^{137}\text{Cs}$

However . . .
Consider the time needed for

1. Groundwater to re-saturate the disposal site.
2. The corrosion of the waste package.
3. The corrosion of the cladding.
4. Groundwater to transport the radionuclides to the surface or to wells.

Consider also the impacts of subsurface attenuation such as sorption and precipitation—geological barriers.

In a time frame of thousands of years, many members of the Instant Release Group would decay way.
Only $^{36}\text{Cl}$ and $^{129}\text{I}$?

Using a Canadian plan for SNF disposal in granite, D. R. Wiles came to the conclusion that in 10,000 years (10 ka), only two radionuclides would escape and move away from the disposal site after all barriers had failed:

$^{36}\text{Cl}^-$ an anion with a half-life of 310,000 years (310 ka) ($\beta$ decay)

$^{129}\text{I}^-$ an anion with a half-life of 17,000,000 years (17 Ma) ($\beta$ decay)

Wiles assumed that $^{99}\text{Tc}$ would precipitate under reducing conditions.