Natural Analogues of Geological Repositories, WIPP, and UNF Reprocessing

“At first I saw absolutely nothing. When I was able to open my eyes, I stood still, far more stupefied than astonished.”

—Henry Lawson in “Journey to the Center of the Earth” by Jules Verne.
Can natural analogues be used as examples of long-term geological storage?

The Oklo Pit. Uranium mine in the Gabon Republic.

In circa 1970, U core samples were deficient wrt $^{235}\text{U}$. 
The Oklo Pit Mine

$^{235}\text{U}$ is normally 0.72%.

Some cores samples contained as little as 0.44% $^{235}\text{U}$. Why? Was some being stolen?

Follow-up analyses of core samples indicated the presence of more than 30 elements that usually occur as fission products.
In 1972, Francis Perrin concluded that, at one time, the Oklo site had yielded a self-sustaining nuclear chain reaction.

The Oklo Pit Mine

Evidence that, within a U-ore body, a natural reactor became critical, consumed about six tons of fuel during a 600,000 to 5 million-year period, and then the reaction ceased—all in Pre-Cambrian times (about 2 billion years [2 Ga] ago).
Uranium enrichment? Not needed.

About 17% $^{235}$U when the Earth was formed.

Two billion years ago (2 Ga), there would have been 3 to 4% $^{235}$U at Oklo.

Groundwater content at that time was about 12 to 15% (Brookins, 1983). About 400° C.
The Oklo Pit Mine
Fossil Reactor 15, located in Oklo, Gabon. U oxide remains are visible as the yellowish rock.
<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>Observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Americium</td>
<td>The yields from the reactions may have been limited.</td>
</tr>
<tr>
<td>Barium</td>
<td>Behavior of fissiogenic barite masked by naturally occurring barite.</td>
</tr>
<tr>
<td>Bismuth</td>
<td>$^{209}$Bi was derived from the decay of $^{237}$Np. Remained with the host UO$_2$ possibly as a sorbate (half-life of $^{237}$Np is $2.12 \times 10^6$ years).</td>
</tr>
<tr>
<td>Bromide</td>
<td>Assumed to have migrated from the host UO$_2$</td>
</tr>
<tr>
<td>Cadmium</td>
<td>Migrated from the host UO$_2$ possibly by volatilization.</td>
</tr>
<tr>
<td>Indium</td>
<td>$^{115}$In was likely retained (half-life of $4.4 \times 10^{14}$ years).</td>
</tr>
<tr>
<td>Iodine</td>
<td>Fissiogenic iodine was not retained.</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>About 80% of the fissiogenic Mo isotopes had migrated from the host UO$_2$ but were retained as a sulfide mineral within 1.5 m of the reactor zone in the sandstone gangue (the half-life of $^{100}$Mo is $8.5 \times 10^{18}$ years)</td>
</tr>
<tr>
<td>Neodymium</td>
<td>Retained in the host UO$_2$. Stable, fissiogenic $^{143}$Nd present in greater amounts than background levels.</td>
</tr>
<tr>
<td>Neptunium</td>
<td>Assumed to have been retained by sorption and solid solution with UO$_2$ as inferred by the presence of $^{209}$Bi.</td>
</tr>
</tbody>
</table>
Implications about storage

It appeared that many fission products remained in the ore body despite the movement of groundwater through the sandstone.

The presence of $^{99}\text{Ru}$ suggested that $^{99}\text{Tc}$ was once present (half-life of $2.12 \times 10^5$ years [212 Ka]).

Stable, deep storage for billions of years.
Cigar Lake, Saskatchewan

1.3 billion-year-old (1.3 Ga) U deposit

Currently 430 m below land surface

Contains about 8% U

Water saturated since hydrothermal formation.
Cigar Lake Deposit

Clay (illite) above the ore.

Clay layer may have provided long-term protection of UO$_2$. Groundwater flowed over the deposit and not through it.

Only chemical diffusion through the clay.

Dissolution of UO$_2$ limited by its solubility
Waste Isolation Pilot Project (WIPP)

Geological repository for transuranic wastes (TRU) Np, Pu, Am, Cm . . .
WIPP

10,240 acre (4,144 ha) site near Carlsbad, New Mexico
Disposal area 2,150 feet deep (655 m)
Waste disposal since 1999
DOE/defense/legacy-related wastes only
HLW and SNF not allowed

http://www.wipp.energy.gov/
Burial in Permian-Age Salt Deposits

Cross section showing major geologic units above and below the WIPP repository.
Origin of Salt

Evaporites: Minerals that precipitate from sea water as the water evaporates

By geological processes, a structural basin holding sea water can be isolated from the sea. As the water evaporates, minerals form. Carbonates then gypsum first because they are less soluble than halite or potash.
http://www.youtube.com/watch?v=3b036aKc8EY (6:52)
“Visitors to Carlsbad, N.M. are encouraged to visit the WIPP Experience Exhibit. Friendly staff are available to answer questions about this one-of-a-kind facility. Free 250-million-year-old (250 Ma) rock salt samples are available for all visitors.”

What about UNF?
UNF Reprocessing

An alternative to the “Once Through” Cycle.

Extract U and Pu from UNF, and leave the fission products.

Blend the extracted Pu with natural, enriched reprocessed or depleted U to make “mixed oxide” (MOX) fuel. PuO$_2$ can vary from 1.5 to 30% by weight.

Not new idea; was expected in the 1970s.
UNF Reprocessing

Banned by President Carter in 1977 because of Pu accessibility concerns. The ban was lifted by President Reagan in 1981.

Commercial reprocessing of UNF did not materialize long in the U.S.

Large-scale reprocessing of UNF developed in the UK and France.
Relevant Terms

*Extraction*. The transfer of solute(s) from one liquid phase to another.

Typically, the transfer of solutes from an aqueous, hydrophilic (“water loving”) phase to a hydrophobic (“water fearing”) phase composed of an organic solvent.
**Relevant Terms**

*Scrubbing*. The purification of an intermediate product such as the removal of fission products from the solvent that were co-extracted with uranium and plutonium.

*Stripping*. The back extraction; the transfer of solute(s) from the hydrophobic phase back into a hydrophilic aqueous phase for additional separations and recovery.
Early UNF reprocessing

The used fuel was first cooled for about 40 days. Then the aluminum cladding was dissolved in a hot sodium hydroxide-sodium nitrate solution (Gray, 1999). The fuel was then dissolved in a 60% nitric acid solution. The plutonium that was dissolved was reduced to $\text{Pu}^{4+}$ by the addition of sodium nitrite. The nitrite oxidized to nitrate, and the resulting electrons reduced the plutonium.
Early UNF reprocessing

Then bismuth nitrate and phosphoric acid were added to co-precipitate the plutonium:

\[
\text{Pu} \xrightarrow{\text{NaN_2O_2}} \text{Pu}^{4+} + \text{Bi(NO_3)_3} + H_3PO_4 \rightarrow \\
\text{BiPO}_4(\text{Pu}^{4+})\downarrow + 3\text{NO}_3^- + 3\text{H}^+ \quad (2.3)
\]

The precipitate was collected by centrifugation, then dissolved in nitric acid. The final product was refined to remove impurities such as fission products by
Modern UNF Reprocessing

Plutonium-Uranium Solvent Extraction (Purex) method invented in about 1954, and has become “the universal choice.”

Basics of the Purex Process:
It is a liquid-liquid extraction

UNF is physically broken down and dissolved in concentrated nitric acid yielding a dissolution liquor that contains U, Pu, and all the fission products.
The Purex Reaction

The acidic (~3 N HNO₃) solution is reacted with a solution containing 30% tributyl phosphate (TBP) dissolved in kerosene or dodecane.

TBP, is an organophosphorus compound with the formula CH₃CH₂CH₂CH₂CH₂O)₃PO.
We are mixing a hydrophilic solution ("water loving") with a hydrophobic ("water fearing") solution.
The Purex Reaction

$U^{4+}$ and $Pu^{4+}$, which are hydrophilic, react with TBP in the presence of nitrate to form organic-soluble complexes which are more hydrophobic.

$$Pu^{4+} + 4NO_3^- + 2TBP \rightarrow Pu(NO_3)_4 \cdot 2TBP$$

Fission products such as $Cs^+$ do not react with TBP as strongly and remain in solution.
Purex Reaction

Liquor $\rightarrow$

30% TBP in Kerosene
Hydrophobic liquid

$3 \text{N} \ HNO_3$
Hydrophilic liquid

Extract $\rightarrow$
U, Pu, some
Th, Np

$\leftarrow$ Raffinate

Fission products
(Waste)
Purex Reaction

Pu (IV) is then chemically reduced to Pu (III) by adding hydroxylamine (NH$_2$OH), and then extracted with 6-M nitric acid.

UO$_2^{2+}$ remains in the organic phase.

Multiple extraction cycles are required. Extracts can be further refined by the removal of Np and Th.
Commercial UNF reprocessing in the US


Used a three-cycle Purex process.

U and Pu-nitrate solutions were the end product.
West Valley Plant. New York.
West Valley Plant

NFS operated the site as a nuclear fuel reprocessing center from 1966 to 1972, and accepted radioactive waste for disposal until 1975.

During the operation of the plant, 640 tonnes of used reactor fuel were processed, resulting in 660,000 gallons (2,500 kL) of radioactive liquid waste.

The liquid waste is stored in underground waste tanks.
West Valley Plant

NFS also used a 15-acre (6 ha) area for the disposal of radioactive waste from commercial waste generators, and another 7-acre (2.8 ha) landfill was used to dispose of radioactive waste generated from reprocessing.

In 1976, NFS decided the costs and regulatory requirements of reprocessing made the venture impractical. Left lease to State of New York in 1980.
Contaminated soil and groundwater issues remain.
Commercial Reprocessing (almost)

The Nuclear Fuel Services facility was the first and only private plant in the United States to reprocess UNF.

General Electric completed its Midwest Fuel Recovery Plant at Morris, Illinois, in 1974, but immediately declared it inoperable and never used it.
Commercial Reprocessing (almost)

In 1970, Allied General Nuclear Services began constructing a 1,500 ton/year (1,360 tonnes/a) reprocessing plant at Barnwell, South Carolina. Because of the 1977 ban, the plant was not completed.

In the future, we may reconsider reprocessing of UNF, but what about the wastes such as waste acids containing fission and TRU products?
In Summary

http://www.youtube.com/watch?v=FMhruDLNwBI (4:41)