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 and the environment.

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

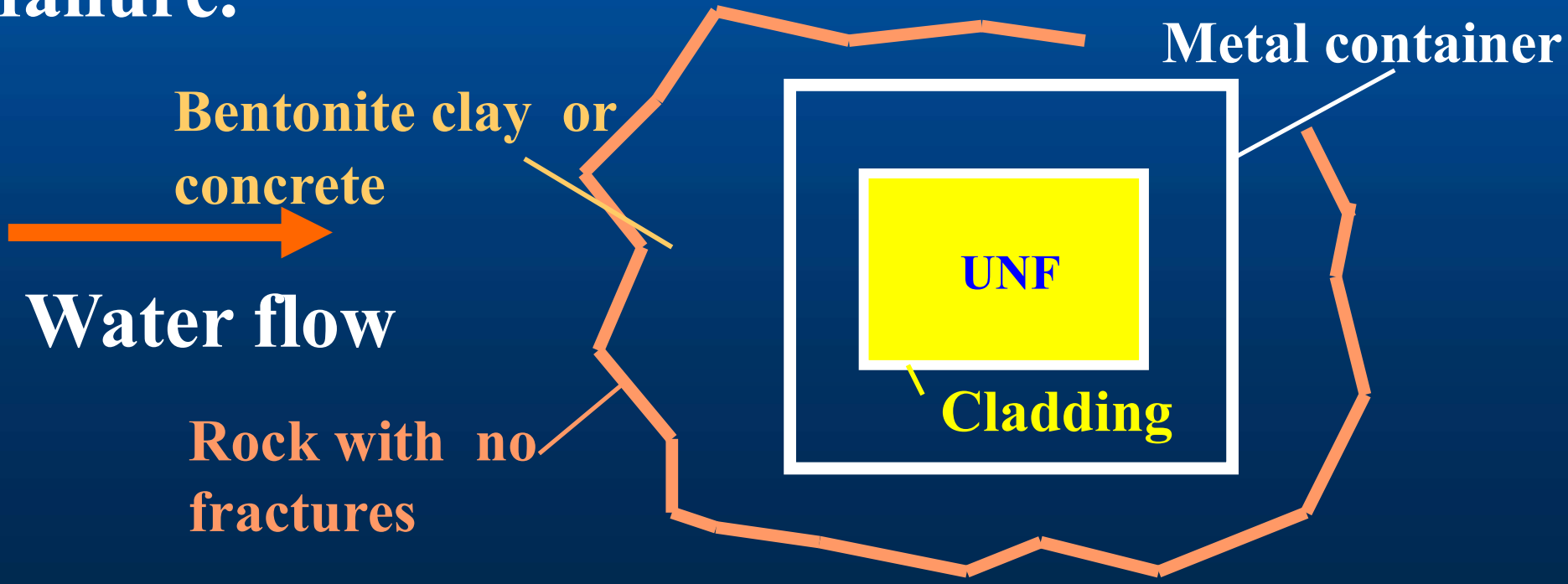
Metal Containers

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 (1:08)

Metal Corrosion

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 → oxides and other compounds

Metal corrosion: Iron

Many metals are initially in a neutral charge state.

$Fe^0 + O_2 + H_2O \rightarrow Fe^{3+} + OH^- \rightarrow Fe(OH)_3\downarrow$

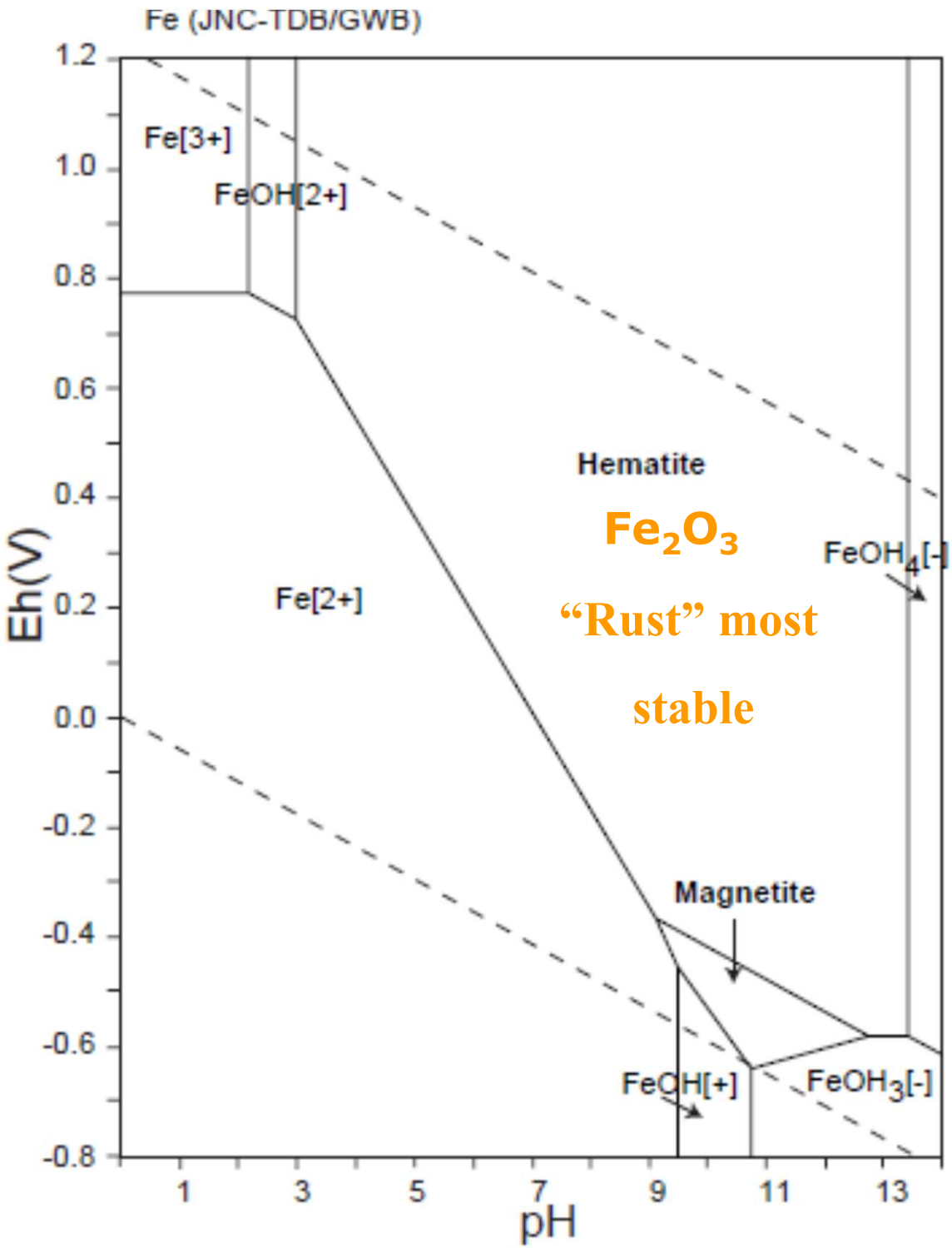
12 electrons short

$4Fe^0 + 3O_2 + 6H_2O \rightarrow 4Fe^{3+} +$

gains the 12 electrons

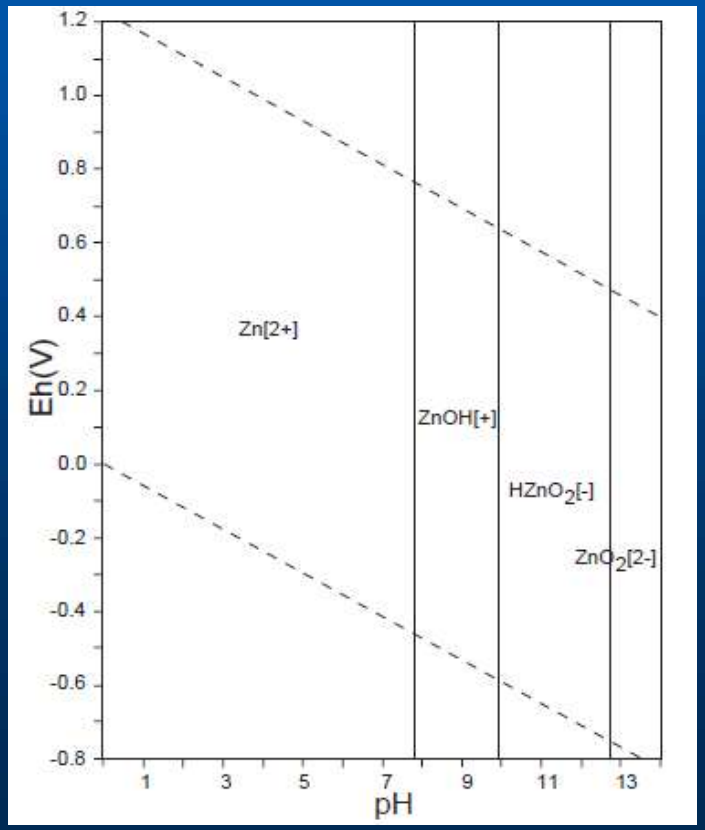
$12OH^- \rightarrow 4Fe(OH)_3\downarrow$ or

$4FeO(OH)\downarrow + 4H_2O$


Fe (JNC-TDB/GWB)
Fe[3+]
FeOH[2+]
Fe[2+]
Hematite
Fe_2O_3
"Rust" most stable
$FeOH_4[-]$
Magnetite
FeOH[+]
$FeOH_3[-]$
Eh(V)
pH
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
1
3
5
7
9
11
13

Metal corrosion: Zinc

$$2Zn^0 + 2H_2O + O_2 \rightarrow 2Zn^{2+} + 4OH^- \rightarrow$$
$$2Zn(OH)_2\downarrow \rightarrow ZnO \text{ (“white rust”)} + H_2O$$



Factors that affect corrosion

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

2. Oxygen and water (promotes corrosion).

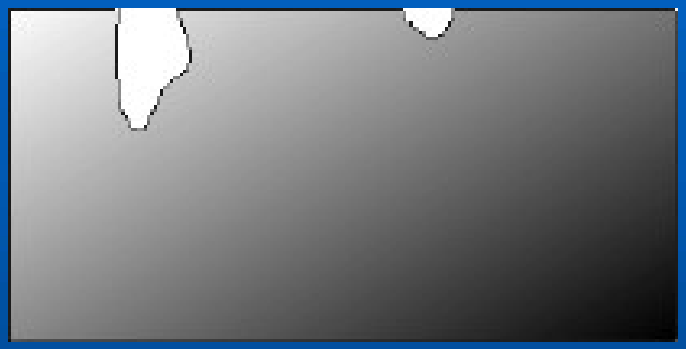
3. Temperature (heat accelerates reactions).

Factors that affect corrosion

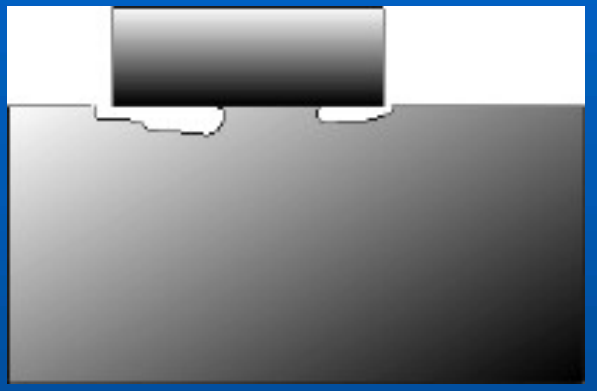
4. Other ions such as chloride (Cl^-) $Fe^{3+} + 3Cl^- \rightarrow FeCl_3^0$ (drives reaction to the right).

5. Water flow rate (greater flow, great mass removal).

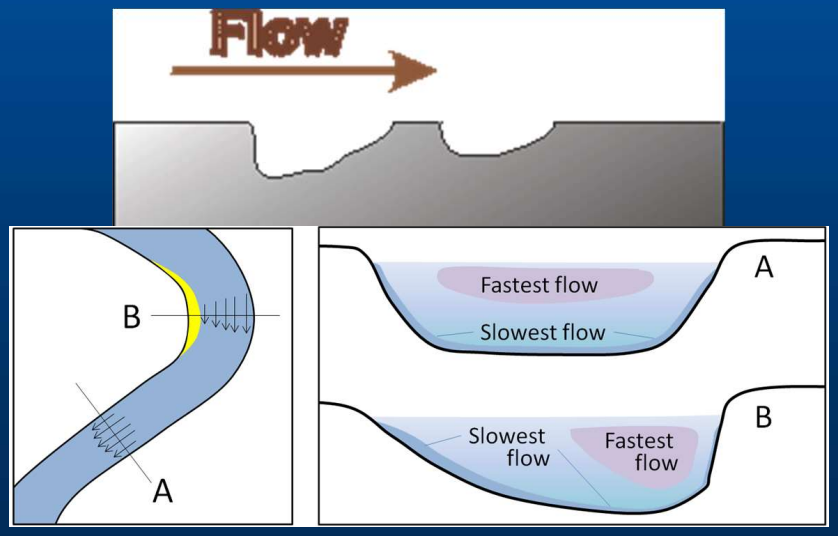
Types of corrosion



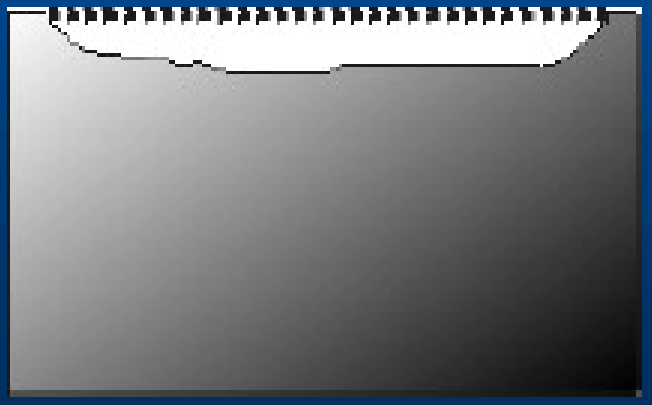
Pitting



Crevice



Erosion



Uniform

Factors that affect corrosion

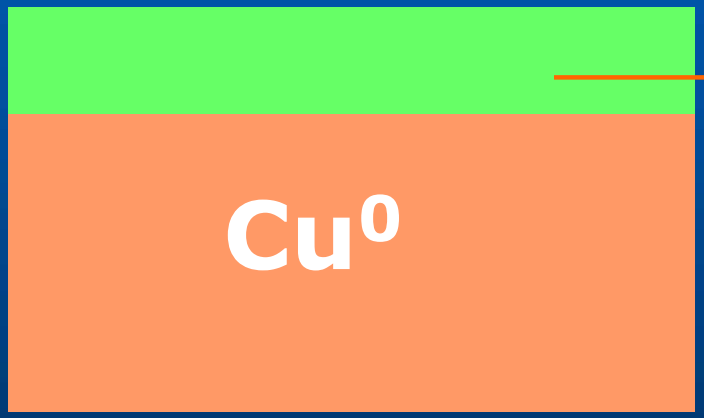
After closure of disposal site, all the oxygen may be consumed, and sulfide may become the primary corrosive agent:

$$4Cu + 2HS^- \rightarrow 2Cu_2S + H_{2\,(g)}$$

Sulfide from the dissolution of sulfide minerals such as pyrite in rocks and microbial reduction of sulfate ions.

Chemical passivation

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



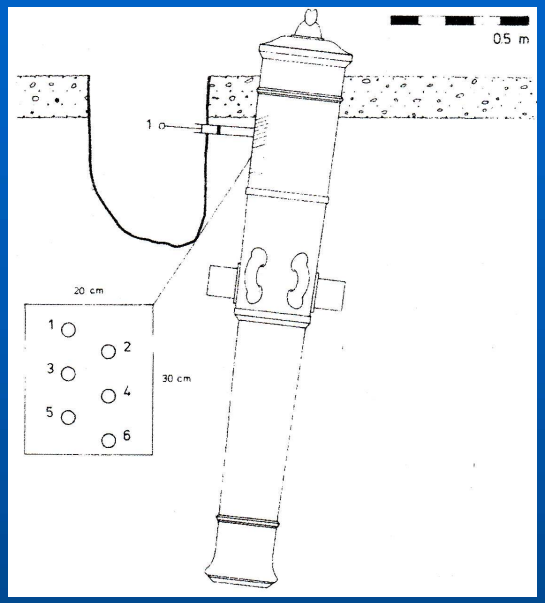
Cu_2O (cuprite)

$CuSO_4 \cdot 5H_2O$

$Cu_2(OH)_3Cl$

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 mils* per year). If 2 inches (5.1 cm) thick, it would last for 100,000 years (100 Ka).

*1/1000 of an inch

Anthropogenic Analogues

Bronze chisel (Argentina)	800 years old	0.04 mpy (1.01 µm/year)
Bronze plate	550 years old	0.03 mpy (0.76 µm/year)
Copper-zinc bell	1,030 years old	0.007 mpy (0.18 µm/year)
Bronze relics in tombs (China)	3,000 years old	0.01 mpy (0.25 µm/year)

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"

(from Bennett and Gens. 2008. *J. of Nuclear Materials*, 279, 1-8)

Ni-Cr-Mo alloys

Ni-Cr-Mo alloys are the 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% H_2SO_4, 41.7 g/L $Fe_2(SO_4)_3 \cdot 9H_2O$ in boiling deionized water, 5-day exposure

"Green Death"

11.4% H_2SO_4 + 1.2% HCl + 1% $FeCl_3$ + 1% $CuCl_2$ in deionized water, 25°C, exposure interval is a variable.

Corrosion test results for Alloy 22 for industrial applications

Media	Temperature (°C)	General corrosion (mpy)
ASTM 28A	100	36 (0.91 mm)
Green Death	100	4 (0.10 mm)
10% HNO_3	100	2 (0.05 mm)
50% H_2SO_4	100	308 (7.82 mm)
10% H_2SO_4 + 1% HCl	100	354 (9.00 mm)

from www.corrosionlab.com and 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 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 Total-System Performance Assessment-Viability Assessment (TSPA-VA)

The TSPA-VA was conducted by DOE to assess the behavior of the proposed high-level waste repository at Yucca Mountain.

Among the many factors considered were rates of infiltration, radionuclide mobility, pore-water velocity, and chemical precipitation kinetics and . . .

waste package corrosion.

Sandia National Laboratories

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

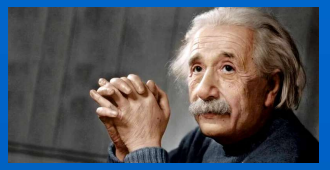
Sandia National Laboratories

14 November 2008

PA 1994, PA 1995, Viability Assessment 1997, PA Site Recommendation, and License Application 2010

for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Corrosion versus decay: A thought experiment



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

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

years	Half-life	% decayed	% corroded

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.

years	Half-life	% decayed	% corroded
100	0.23	14.8	0.01
432	1	50.0	0.04
2,160	5	97.0	0.18
4,320	10	99.9	0.36

Corrosion versus decay of ^{99}Tc (half-life = 212,000 years)

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

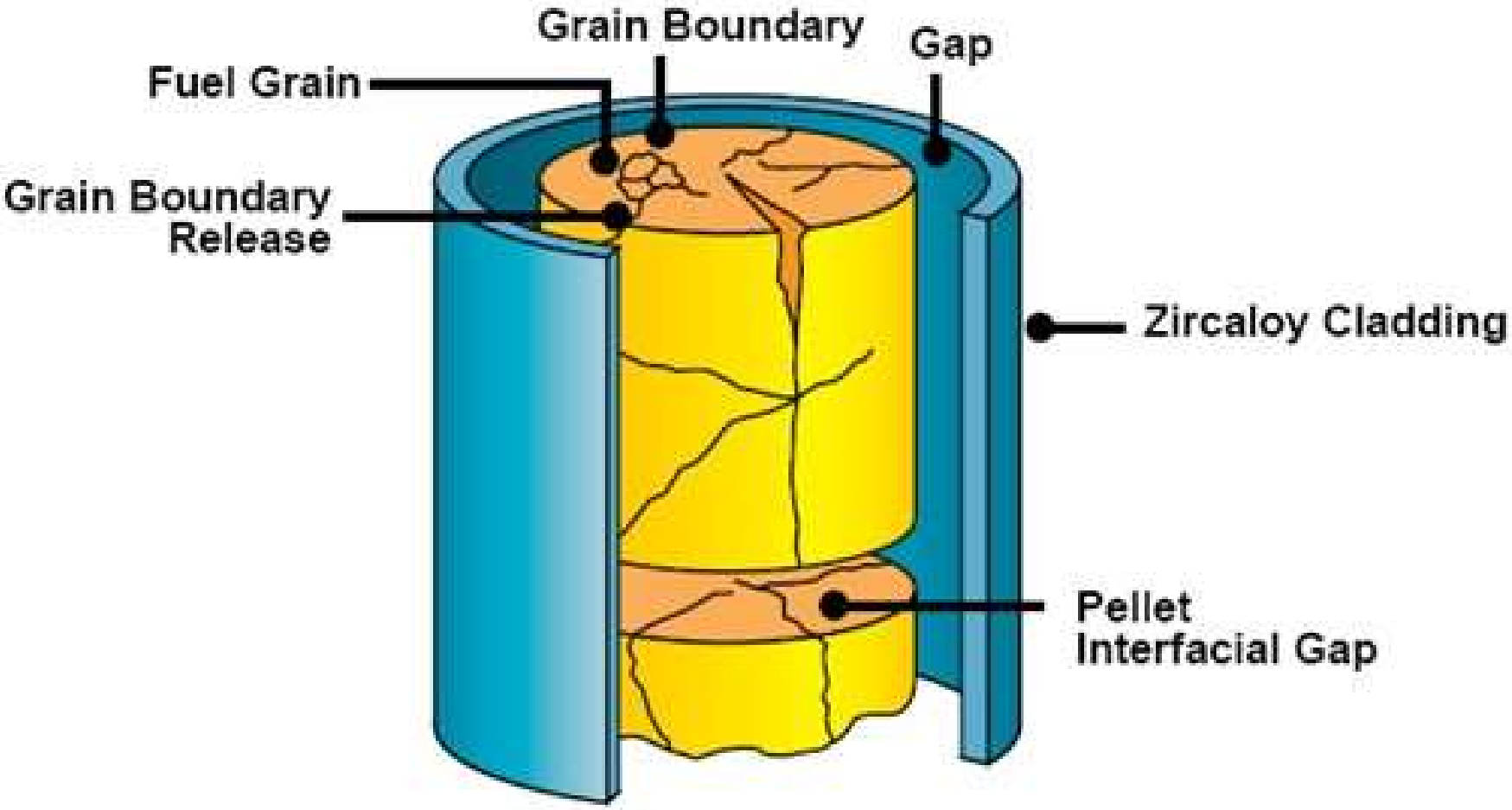
Assume: instantaneous arrival of groundwater to 12-cm thick waste package.

Half-life	% decayed	% corroded
0.5	29	8.8
1	50	17.7
5	96.9	88.3
10	99.9	Failed

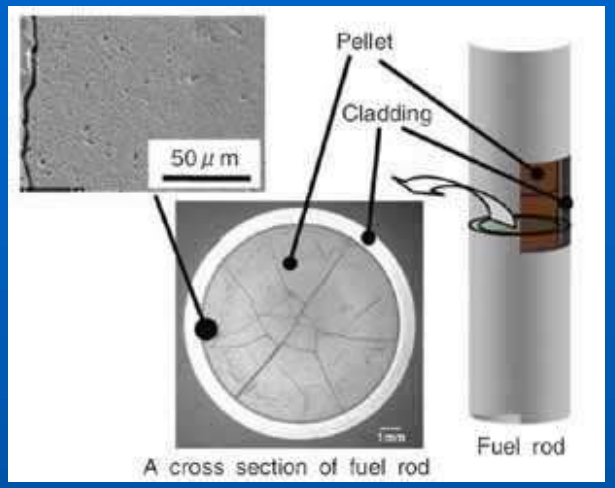
Conclusions of the TSPA Peer Review Panel (3rd Interm. Rep.)

"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)."


Grain Boundary
Gap
Fuel Grain
Grain Boundary
Release
Zircaloy Cladding
Pellet
Interfacial Gap

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 hot melting point (1,930° C, 3,506° 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

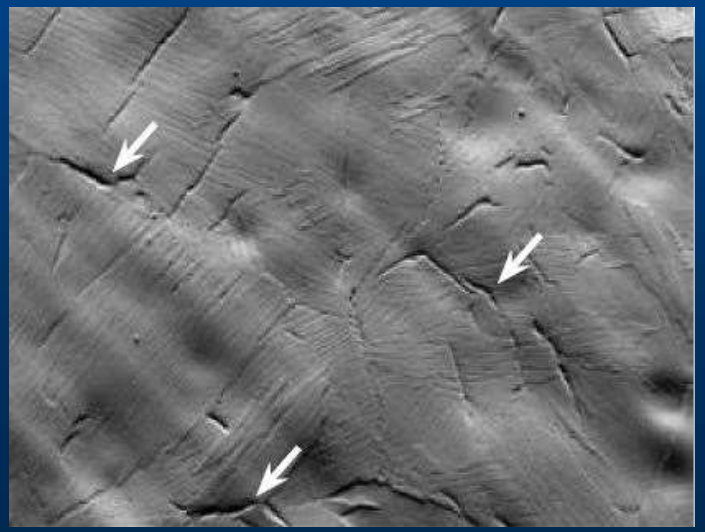
Enhanced corrosion resistance.

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

Hydrogen embrittlement

Zirconium reacts with hot water to form hydrogen: $Zr + 2H_2O \rightarrow ZrO_2 + 2H_2\uparrow$

The hydrogen diffuses within 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

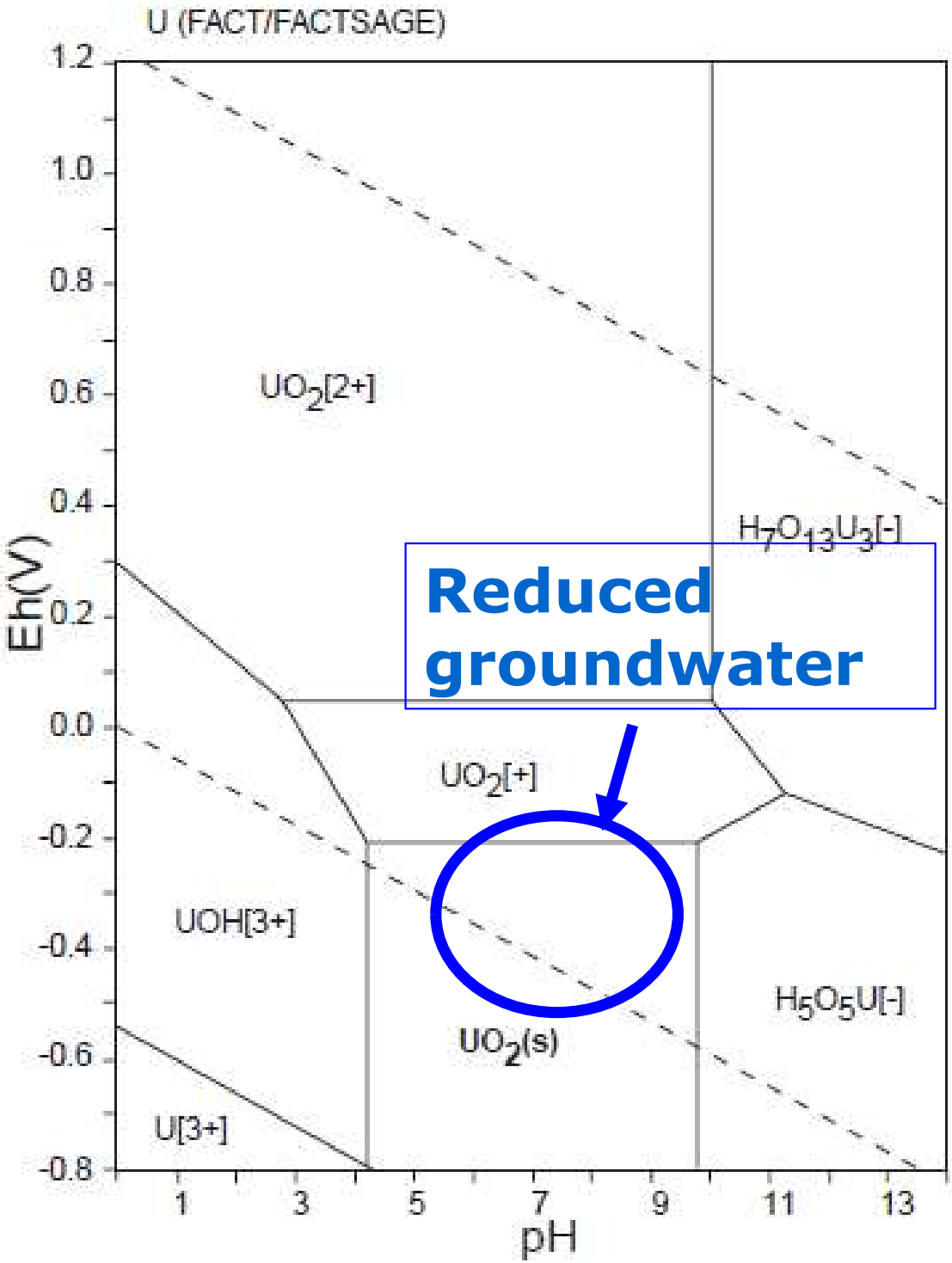
The corrosion/dissolution of spent fuel by groundwater.

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 uranium oxide.

Under reducing (oxygen poor) pH neutral water the solubility of UO_2 is about 3×10^{-9} mole/L or about 0.8 µg/L.


U (FACT/FACTSAGE)
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
Eh(V)
1
3
5
7
9
11
13
pH
UO2[2+]
H7O13U3[-]
Reduced groundwater
UO2[+]
UOH[3+]
H5O5U[-]
UO2(s)
U[3+]

But will the radionuclides leach into groundwater?

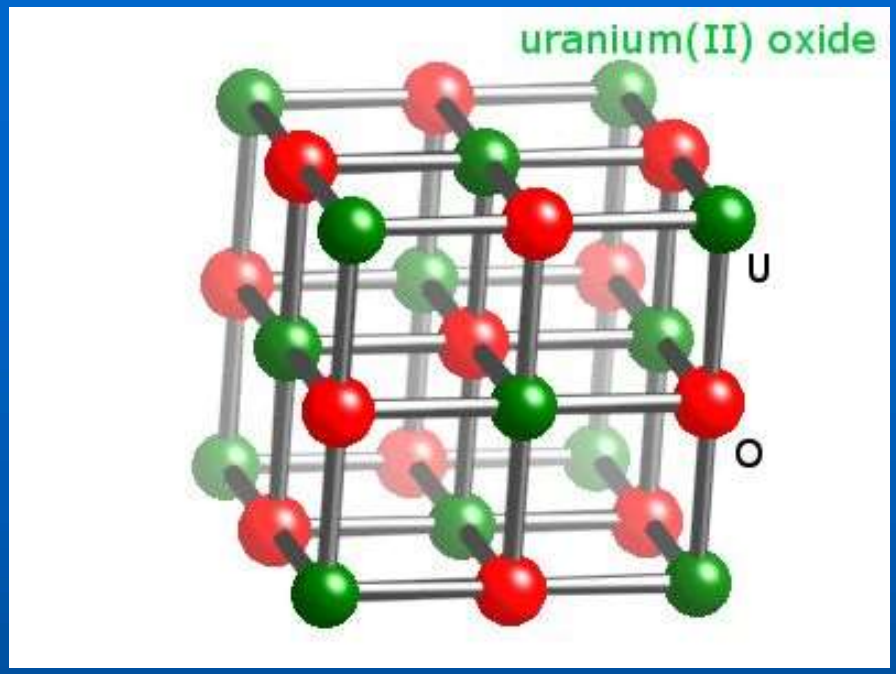
The radionuclides produced by neutron capture in the zircaloy cladding will be "presumably incorporated within the oxide [layer]." Wiles, 2002*.

*The Chemistry of Nuclear Fuel Waste Disposal by D. R. Wiles. 2002. Polytechnic International Press, Montreal, Canada. 10 chapters, 182 p.

But will the radionuclides leach into groundwater?

Radionuclides having an ionic radius ± 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.

***The Chemistry of Nuclear Fuel Waste Disposal by D. R. Wiles. 2002. Polytechnic International Press, Montreal, Canada. 10 chapters, 182 p.**



^{241}Am, ^{239}Pu, ^{242}Pu, ^{93}Zr, ^{242}Cm, ^{94}Nb, ^{151}Sm, ^{113m}Cd and others

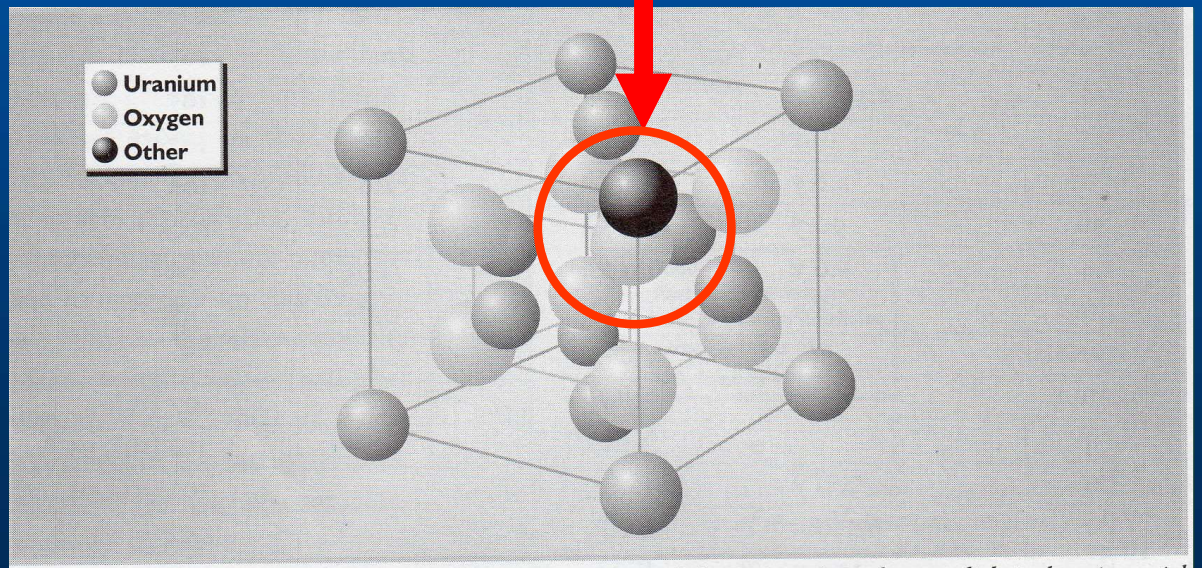
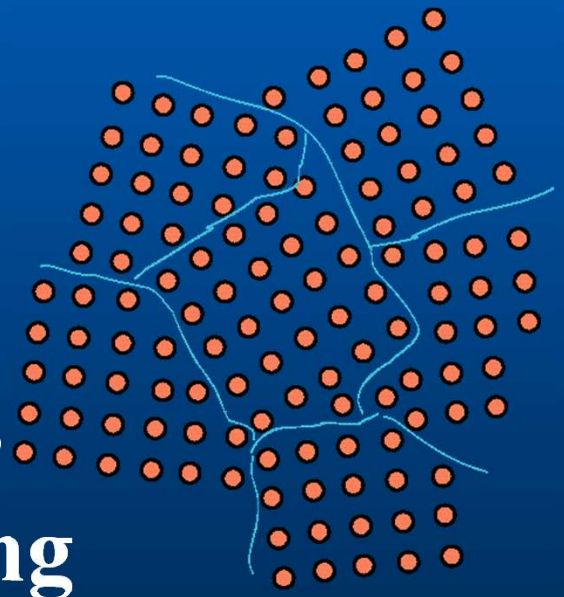


Figure 4.4 – Uranium dioxide lattice showing an atom of plutonium (or other nuclide in keeping with Goldschmidt's rule) replacing a uranium atom

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: those radionuclides that are predicted to be relatively leachable when groundwater is in contact with the exposed used fuel.

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."

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

However, . . .

Consider the time needed for:

1. Groundwater to re-saturate the disposal site (100 to 1,000 years).

2. The corrosion of the waste package (1,000 to 10,000 years).

3. The corrosion of the cladding (10,000 to 100,000 years).

Consider the time needed for:

4. The dissolution of the SNF (1,000 years)

5. Groundwater to transport the radionuclides to the surface or to wells (100,000+ years).

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.

What radionuclides would be left?

The last radionuclides

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:

$^{36}Cl^-$ and $^{129}I^-$. Why?

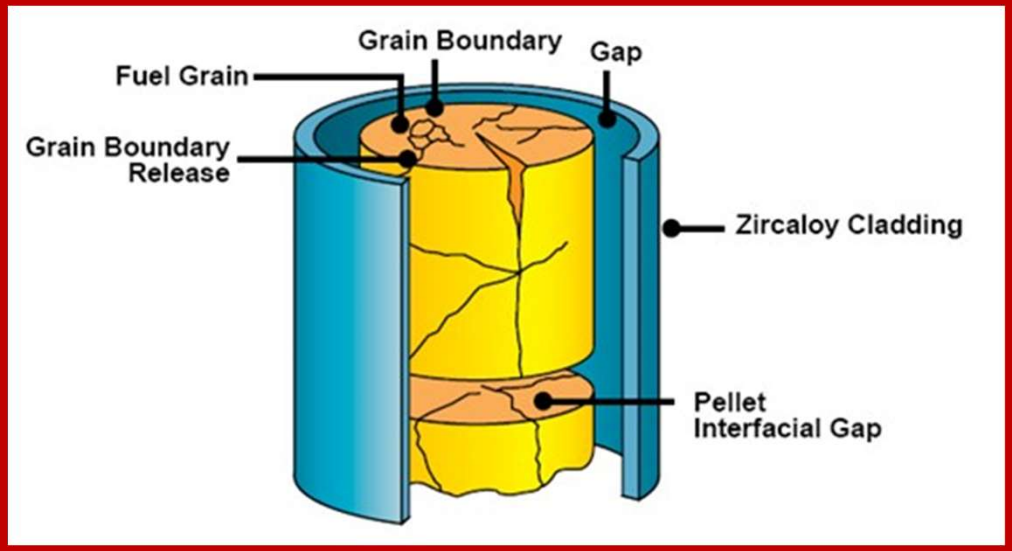
The last radionuclides

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

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

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

Questions?


Grain Boundary
Gap
Fuel Grain
Grain Boundary Release
Zircaloy Cladding
Pellet Interfacial Gap