U.S. DEPARTMENT OF ENERGY
OFFICE OF CIVILIAN RADIOACTIVE WASTE MANAGEMENT

PRESENTATION TO
THE NUCLEAR WASTE TECHNICAL REVIEW BOARD

SUBJECT: POTENTIAL EFFECTS OF ENGINEERED BARRIERS ON RADIONUCLIDE MIGRATION

PRESENTER: RICHARD A. VAN KONYNENBURG

PRESENTER'S TITLE AND ORGANIZATION: ENGINEER
UNIVERSITY OF CALIFORNIA,
LAWRENCE LIVERMORE NATIONAL LABORATORY

PRESENTER'S TELEPHONE NUMBER: (510) 422-0456

July 12, 1994

TOPICS TO BE DISCUSSED

- Engineered barriers and other man-made structures
- Composition of candidate materials
- Scenario for oxidation and corrosion
- Oxidation and corrosion products
- Significant radionuclides
- Projected effects of engineered barriers on radionuclide migration
- Conclusions

ENGINEERED BARRIERS AND OTHER MAN-MADE STRUCTURES

Waste Packages

- Metal Barriers (including multipurpose canisters and glass pour canisters)

- Alternate Ceramic Barriers

- Package Fillers (currently not planned to be used)

Packing Material - outside of packages (use currently undecided)

Backfill Material (currently not planned to be used)

Drift liners and inverts

COMPOSITION OF CANDIDATE METAL BARRIER MATERIALS

Components (Major-X, Minor-x)

	Fe	Ni	Cr	Mo	Ti	Cu	Mn
I. Highly corrosion-resistant							
Alloy 825 (Incoloy 825)	X	X	X	x	x	x	x
Alloy 825 hMo (NiCrFe 4221)	X	X	X	x	x	x	x
Alloy C-22 (Hastelloy C-22)	x	X	X	X			
Alloy C-4 (Hastelloy C-4)	x	X	X	X			x
Ti-Grade 12		x		x	X		
Ti-Grade 16					X		
II. Moderately corrosion-resistant							
Alloy 400 (Monel 400)	x	X				X	x
70-30 Copper-Nickel (CDA 715)	x	X				X	x
III. Corrosion-allowance							
Carbon steel - A516 (grade 55)	X						
Centrifugally-cast steel - A27 (grade 70-40)	X						
2-1/4 Cr-1 Mo alloy steel - A387 (grade 22)	X		x	x			x
IV. Glass pour canisters and multi-purpose canisters							
Austenitic stainless steel	X	X	X	x			x

CANDIDATE MATERIALS FOR COMPONENTS OTHER THAN METAL BARRIERS

I. Ceramics as alternate barriers

Al_2O_3
TiO_2

II. Package fillers

Iron or steel shot
Zinc – 4 Aluminum alloy
Glass beads
Magnetite

III. Packing materials (outside packages)

Magnetite
Bentonite

IV. Backfill

Crushed tuff
Quartzite sand
Basalt

V. Drift liners and inverts

Concrete
Shotcrete, perhaps with metal fibers
Rock bolts – steel, perhaps corrosion–resistant
Rebar–steel

EXPECTED SCENARIO FOR OXIDATION AND CORROSION OF METAL BARRIERS

The primary repository design case asumes a high waste loading (80-100 MTU/acre or 91-114 kW/acre initially).

With this loading, water is expected to be driven out of the repository zone by evaporation, and package surface temperatures will exceed the boiling point for long times.

Under these conditions aqueous corrosion could not occur. The initial degradation mode would be dry oxidation.

After cooling and return of liquid water, aqueous corrosion could occur on the pre-oxidized packages.

One should therefore expect oxidation products initially and corrosion products later. The initial oxidation products may be modified after the return of liquid water.

MAJOR OXIDATION AND CORROSION PRODUCTS EXPECTED FROM CANDIDATE METAL BARRIER MATERIALS

Carbon and alloy steels

$Fe(OH)_2$	ferrous hydroxide
$FeCO_3$	siderite
Fe_3O_4	magnetite
$FeO(OH) \cdot xH_2O$	ferrihydrite
γ-$FeOOH \cdot xH_2O$	limonite
γ-$FeOOH$	lepidocrocite
α-$FeOOH$	goethite
$Fe_2O_3 \cdot nH_2O$	hydrous ferric oxide
γ-Fe_2O_3	maghemite
α-Fe_2O_3	hematite

Monel and Copper-nickel

$Ni(OH)_2 \cdot H_2O$		perhaps mixed Cu-Ni oxides
NiO	bunsenite	
Ni_3O_4		
Cu_2O	cuprite	
CuO	tenorite	
$CuCO_3Cu(OH)_2$	malachite	

Corrosion–resistant metals

$NiO \cdot Cr_2O_3$	spinel	$Ni(OH)_2\ H_2O$	
TiO_2	rutile	NiO	bunsenite
MoO_2		Ni_3O_4	
MoO_3		$Cr(OH)_3$	Cr_2O_3

RADIONUCLIDES HAVING HALF-LIVES >1000 YEARS, SIGNIFICANT INVENTORIES AND SOLUBILITIES, AND LOW SORPTION IN TUFF

Nuclide	Half-life (years)	Initial Inventory (Ci/MTU)	40CFR191 Release Limit (Ci/MTU)	Chemical Form Under Yucca Mountain Conditions
C-14	5.7×10^3	0.9	0.1	CO_2, HCO_3^-
Ni-59	7.6×10^4	2.78	1.0	Ni^{2+}
Se-79	$\leq 6.5 \times 10^4$	0.43	1.0	SeO_4^{2-}, SeO_3^{2-}
Tc-99	2.1×10^5	13.5	10.0	TcO_4^-
I-129	1.6×10^7	0.030	0.1	I^-, IO_3^-
U-234	2.5×10^5	1.36	0.1	
U-236	2.3×10^7	0.28	0.1	$UO_2(CO_3)_3^{4-}$ and others
U-238	4.5×10^9	0.28	0.1	
Np-237	2.1×10^6	0.35	0.1	$NpO_2CO_3^-$, NpO_2^+

PROJECTED EFFECTS OF ENGINEERED BARRIERS ON RADIONUCLIDE MIGRATION

1. Containment
2. Temperature Tailoring
3. Water Restriction
4. Redox Buffering
5. pH Buffering
6. Chemical Reactions with Wasteform Components or Radionuclides
7. Sorption of Radionuclides
8. Colloid Formation
9. Colloid Filtering
10. Diffusion Barrier Formation

CONTAINMENT

The primary purpose of the engineered barriers is to <u>prevent</u> migration of radionuclides by containing them.

The trend in recent years has been toward more robust packages and longer intended containment lifetimes.

Attempts to use engineered barriers to accomplish other goals (such as preventing collapse of drifts, restricting water ingress, or retarding radionuclide transport) should be carefully evaluated for detrimental impacts on containment lifetime, to insure that the overall system performance is optimized.

TEMPERATURE TAILORING

Use of packing and/or backfill would increase the waste package temperatures.

Advantage: Under unsaturated conditions, the higher package temperatures would produce lower relative humidiites at package surfaces, delaying the onset of aqueous corrosion.

Disadvantages: If emplaced too early, packing and/or backfill would produce excessive package temperatures, raising the oxidation rates and shortening containment lifetimes. Later installation would be difficult because of high drift temperatures.

WATER RESTRICTION

Backfill could produce a capillary barrier to prevent access of liquid water to the packages — Jim Conca will discuss this.

REDOX BUFFERING

Use of thick metal barriers and/or packing containing magnetite (Fe_3O_4) could hold down the oxidation potential near the packages for extended periods of time.

Advantage:

1. In the event of liquid water contact containment lifetimes would be extended.

2. Several of the radionuclides are less soluble or more strongly sorbed when in lower oxidation states (e.g. ^{99}Tc, ^{79}Se, and the actinides.

Question: How long could redox buffering be relied upon?

pH BUFFERING

Use of concrete or shotcrete would raise the pH in its vicinity.

Advantage: This would reduce the solubility of ^{59}Ni and the actinides, so long as the pH is not high enough to produce soluble hydroxide complexes.

Question: How long could it be relied upon? (Note that natural CO_2 will carbonate the concrete over time).

CHEMICAL REACTIONS WITH WASTEFORM COMPONENTS OR RADIONUCLIDES

Iron metal has been found to increase the dissolution rate of waste glass.

Consideration is currently being given to use of copper/nickel or Monel for glass waste package outer barriers.

Concrete that still contains portlandite [$Ca(OH)_2$] could trap $^{14}CO_2$ as calcite:

$$^{14}CO_2 + Ca(OH)_2 \rightarrow Ca^{14}CO_3 + H_2O$$

Questions: How long could this be relied upon? Would the timing of the release match the period of effective trapping?

SORPTION OF RADIONUCLIDES

The following minerals have been found to be effective sorbents for various species:

1. Oxides and hydroxides of Fe, Mn, Al, and Si.
2. Layer silicates such as smectites, illites, vermiculites, and kaolinites
3. Carbonate minerals
4. Zeolites

Iron (hydr)oxides would be produced by oxidation and corrosion of steel barriers.

These have been found to be effective sorbents for C, Ni, Se, U, and Np, from the earlier list of significant radionuclides, as well as many others.

Other sorbents could be selected for inclusion in packing or backfill, if used.

Sorbents would have to be able to tolerate the elevated temperatures initially and remain effective for later use.

Question: How long could sorbents be relied upon, in view of competition for sorption sites by various species?

COLLOID FORMATION

Pseudocolloids could be formed from waste package oxidation or corrosion products, or from packing or backfill materials.

COLLOID FILTERING

Colloids are commonly removed by sand filters in water treatment facilities.

Perhaps packing or backfill could be used for this purpose around or beneath waste packages.

DIFFUSION BARRIER FORMATION

Under unsaturated conditions, packing and/or backfill could serve as a diffusion barrier for radionuclides departing from packages.

Transport under these conditions would have to be studied and modeled.

Jim Conca will discuss this.

CONCLUSIONS

1. Engineered barriers offer significant potential beneficial effects on the retardation of radionuclide migration.

2. Benefits for retardation must be balanced against possible detrimental effects on containment lifetimes.

3. Accurate prediction of the long-term viability of potential beneficial effects is challenging.