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

PRESENTATION TO
THE NUCLEAR WASTE TECHNICAL REVIEW BOARD

SUBJECT: RADIATION-CHEMICAL EFFECTS

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Corrosion Products Identified

Cu	Cu_2O: always major product Nitrate phase: present at low RH CuO: minor component at 100% RH
Cu/Ni	Cu_2O: major product at 100% RH Nitrate phase: major product at low RH CuO: minor product at 100% RH
Al-bronze	Cu_2O: major product at 100% RH Nitrate phase: major product at low RH CuO: minor phase at 100% RH
Alloy 825	No significant corrosion

Preliminary Corrosion Experiments

Test Method

- Materials: Alloy 825
  CDA102, oxygen-free copper
  CDA613, 7% Al-bronze
  CDA715, 70/30 copper-nickel
- One coupon of each material in each vessel
- 0, 15, 100% relative humidity, floating total pressure
- Temperatures of 90, 120, 150, and 200°C
- One month duration, 7 x 10^4 rad/h dose rate
- Product analysis: weight loss and gain measurements, XRD, SEM/EDS analysis of corrosion products

Summary and Conclusions

- Gamma radiation will be present at dose rates as high as the 10^4 rad/hr range.

- Radiation-chemical effects will depend strongly on the humidity.

- Nitric acid, hydrogen peroxide, and ammonia can be formed, depending on environmental conditions.

- Radiation-chemical products can have significant effects on corrosion of copper-based candidate container materials:

  - Formation of $Cu_2NO_3(OH)_3$
  - Pitting

- No radiation-chemical effects were observed on corrosion of Alloy 825.

- Longer-term tests are needed to confirm and extend these results.

Others Who Have Contributed to Radiation-Chemical Studies

most work done here

D.T. REED
V. SWAYAMBUNATHAN
B.S. TANI
J.K. BATES — ARGONNE NATIONAL LABORATORY
W.L. EBERT
T.J. GERDING

copper in γ-ray

W.H. YUNKER — WESTINGHOUSE-HANFORD CO.

R.S. GLASS — LAWRENCE LIVERMORE NATIONAL LABORATORY
G.E. OVERTURF III

Environments Used in Corrosion Testing of Waste Containers Candidate Materials

Expected and Bounding

1. Water vapor

2. Air--water vapor mixtures

3. Liquid water solutions
   - Well J-13 water
   - Simulated J-13 water
   - Concentrated solutions

4. Two-phase (moist air and liquid water solutions)

Radiation-Chemical Effects

Types of radiation and dose rate

Range of elemental composition of environment

Radiation-chemical effects on environments of interest

- Water vapor
- Dry air
- Moist air
- Liquid water
- Two-phase (moist air and liquid water)

Interaction of radiation-chemical products with candidate container materials

- Moist air
- Liquid water solutions

TYPES OF RADIATION EMITTED BY HIGH-LEVEL WASTE

From fission products:

- Beta particles
- Gamma rays
- (Neutrinos)

From actinides:

- Alpha particles
- Nuclei recoiling from alpha emissions
- Neutrons
- Fission fragment nuclei
- Beta particles
- Gamma rays
- (Neutrinos)

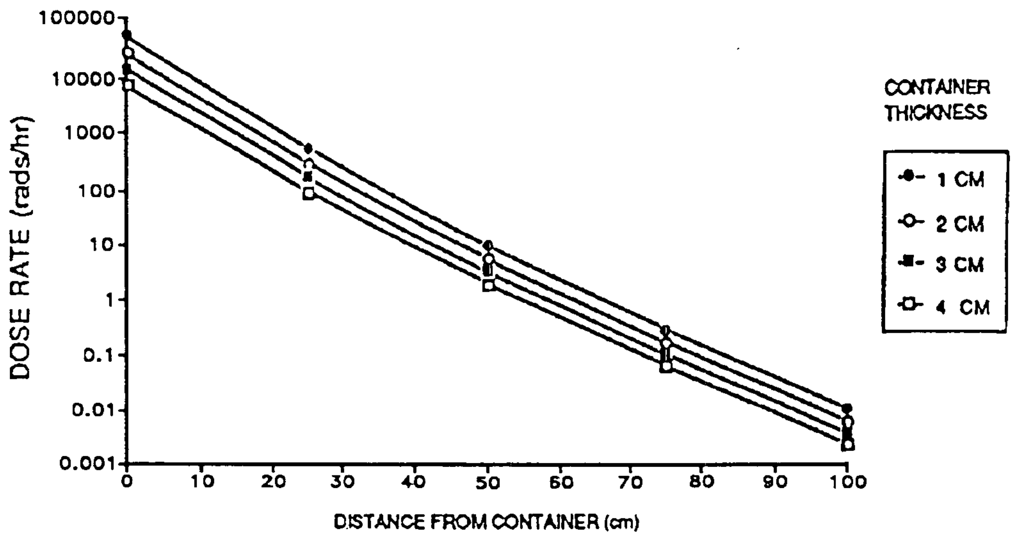
• A WIDE VARIETY OF TYPES OF RADIATION ARE EMITTED

APPROXIMATE RANGES OF EMITTED RADIATION IN CONTAINER MATERIAL

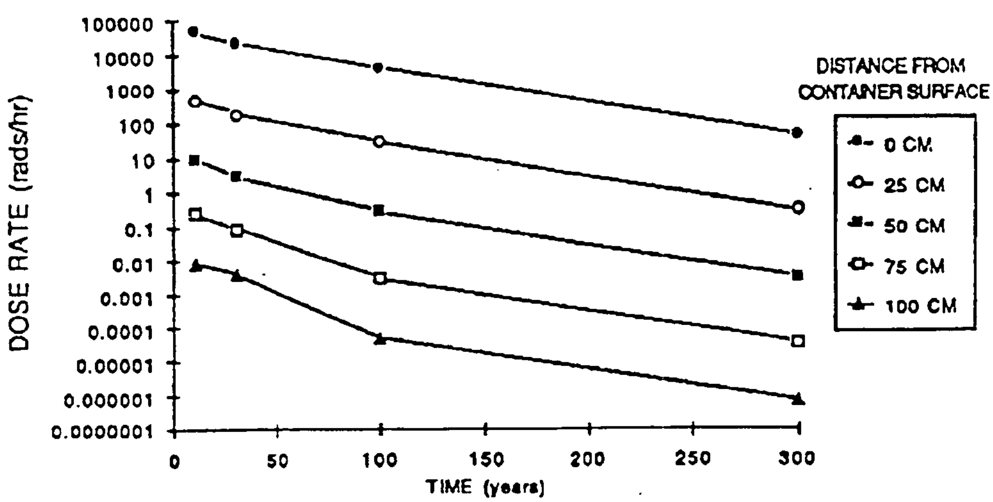
		Range (mm)
1.	Alpha recoil Nuclei	10^{-5}
2.	Alpha particles	10^{-2}
3.	Fission fragments	10^{-2}
4.	Beta particles	1
	Container Wall Thickness	10
5.	Gamma rays	10^2 to 10^3
6.	Neutrons	10^2 to 10^3
7.	Neutrinos	very large

- **ONLY GAMMA RAYS AND NEUTRONS COULD DELIVER SIGNIFICANT DOSES OUTSIDE THE CONTAINERS**

GAMMA RAY DOSE RATES OUTSIDE OF CONTAINERS



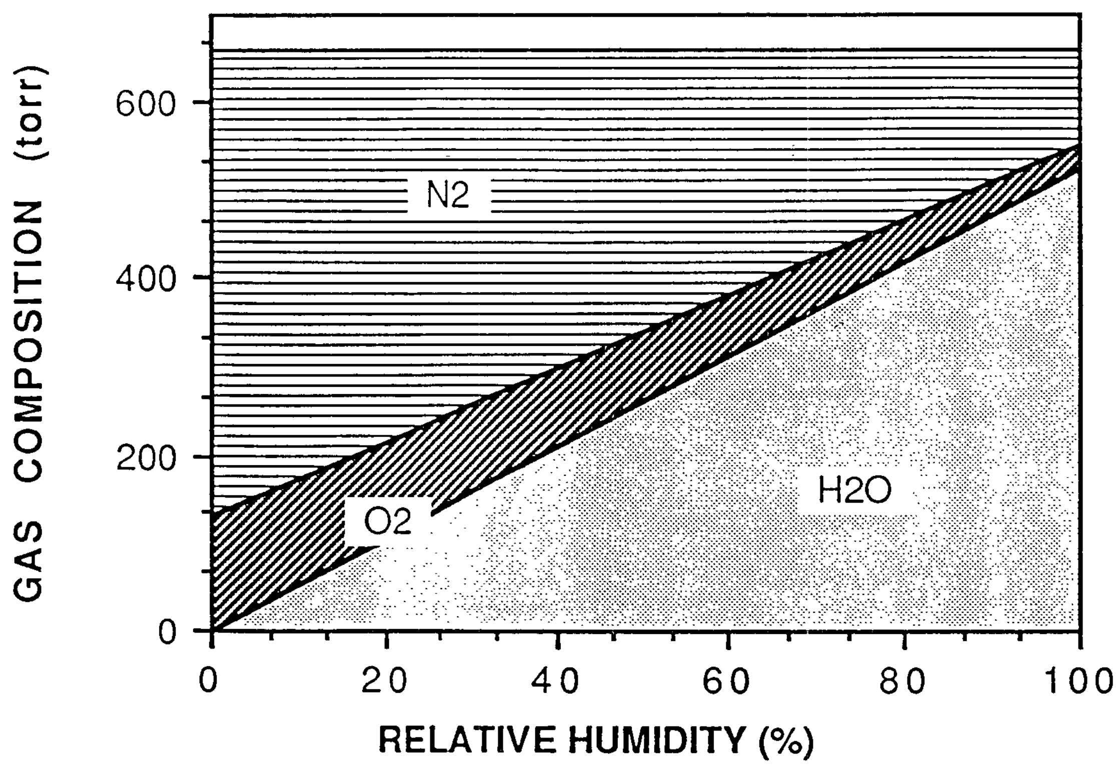
Dose rate as a function of distance from container and container thickness. Ten year old spent fuel at 33,000 Mwd burnup used.



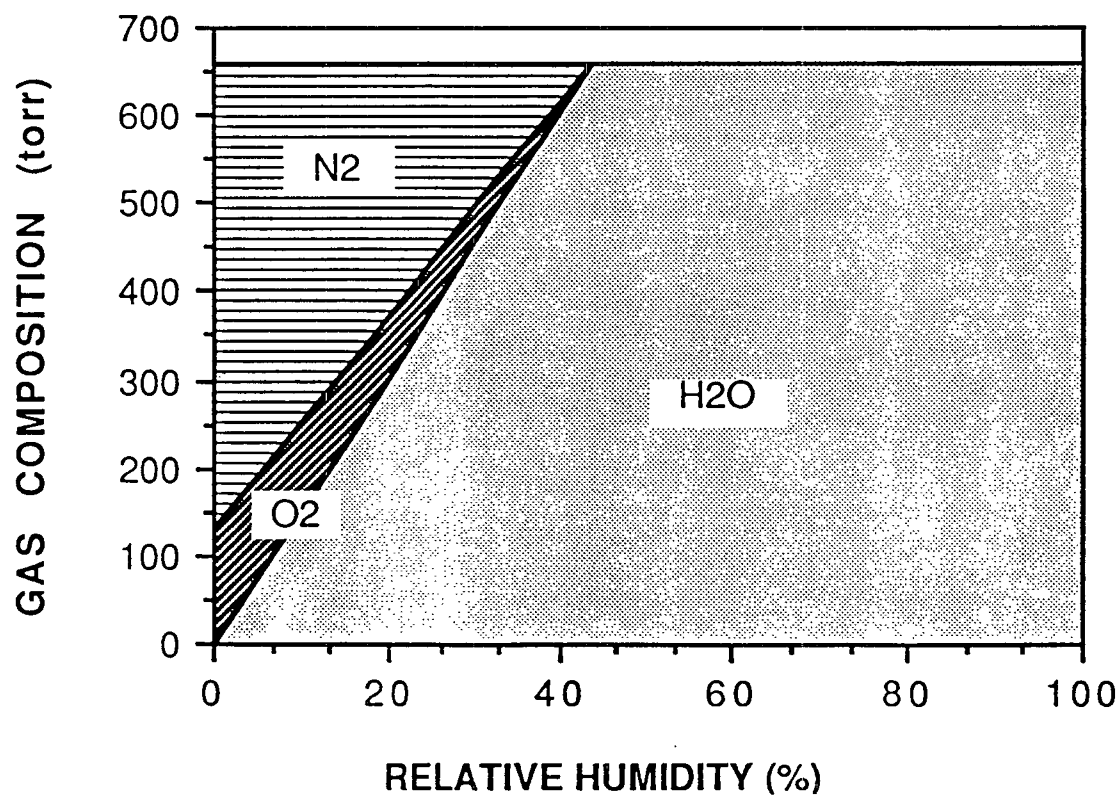
Dose rate as a function of time out of reactor and distance from container surface. Source burnup at 33,000 Mwd.

(Calculation by Reed and Underberg, 1986)

GAS PHASE COMPOSITION AT 90°C



COMPOSITION OF THE GAS PHASE AT 120°C



Radiation-Chemical Effects on Environments of Interest

1. Water Vapor

   a. Small steady-state concentrations of H_2, O_2, and H_2O_2 are produced.

   b. If catalytic materials such as Cu or MnO_2 are present, H_2O_2 decomposes to H_2O and O_2.

2. Dry Air

   a. N_2O, O_3, and N_2O_5 are produced.

   b. O_3 decomposes and converts N_2O_5 to NO_2.

   c. Long-term products are N_2O and NO_2.

   d. N_2O is chemically stable, but NO_2 is reactive, with Cu for example.

Radiation-Chemical Effects on Environments of Interest (continued)

3. Moist Air

   a. At room temp. and low humidity, products are N_2O, O_3, and HNO_3.
   b. At high humidity, ammonia is observed.

4. Liquid Water

   a. For pure water in a closed system, small steadystate concentrations of H_2, O_2, and H_2O_2 are produced
   b. If solutes are present or system is open, net radiolysis to H_2 and O_2 occurs.

5. Two-phase (Moist Air and Liquid Water)

   a. Nitrogen from air is fixed as NO_2^- and NO_3^- ions in the water.
   b. H^+ ions are produced in equivalent amounts.
   c. pH drops unless buffer is present, for example HCO_3^-.
   d. Radiolysis of water to H_2 and O_2 occurs, particulary if solutes are present.