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

PRESENTATION TO THE NUCLEAR WASTE TECHNICAL REVIEW BOARD

SUBJECT: RETARDATION OF GAS PHASE RADIONUCLIDES

PRESENTER: AREND MEIJER

PRESENTER'S TITLE: GEOCHEMIST
ORGANIZATION: LANL/GCX

PRESENTER'S TELEPHONE NUMBER: (505) 256-3769

JULY 12, 1994

RETARDATION OF GAS-PHASE RADIONUCIDES IN UZ

PRESENTATION OUTLINE

- GAS-PHASE SOURCE TERM
- GAS FLOW IN UZ - DATA AND MODELS
- RETARDATION MECHANISMS
- DATA AND MODELING NEEDS
- CONCLUSIONS

GAS-PHASE SOURCE TERM

- RADIONUCLIDES OF GREATEST CONCERN
  - ^{14}C, ^{129}I, ^{99}Tc, ^{79}Se
- IMPORTANT CHEMICAL SPECIES IN GAS-PHASE
  - CO_2, I_2, Tc_2O_7, SeO_2
- $^{14}CO_2$ MOST IMPORTANT GAS-PHASE RADIONUCLIDE
- APPROXIMATELY 2% OF $^{14}CO_2$ PRESENT IN LABILE FRACTION AVAILABLE FOR QUICK RELEASE AFTER FAILURE OF A WASTE PACKAGE
- TOTAL $^{14}CO_2$ INVENTORY APPROX. $1.3X10^3$ MOLES (VAN KONYNENBURG, 1989, 1992, 1993 and PARK, 1991)

MODELS OF GAS FLOW IN UZ

- BUOYANCY-DRIVEN ADVECTION (ROSS ET AL., 1992)
  - $^{14}CO_2$ TRANSPORTED TO SURFACE IN 0.5-2 X 10^3 YR. DEPENDING ON RETARDATION AND RELEASE TIMES
  - MODEL USED IN TSPA 93
  - PREDICTED RELEASES EXCEEDING EPA REGULATIONS
- BAROMETRIC PUMPING (NILSON ET AL., 1994)
  - $^{14}CO_2$ TRANSPORTED TO SURFACE IN 1-2X10^2 YR. DEPENDING ON BULK PERMEABILITY (1-50 DARCIES), RETARDATION AND RELEASE TIMES
- HOT REPOSITORY WILL INCREASE TRANSPORT RATE

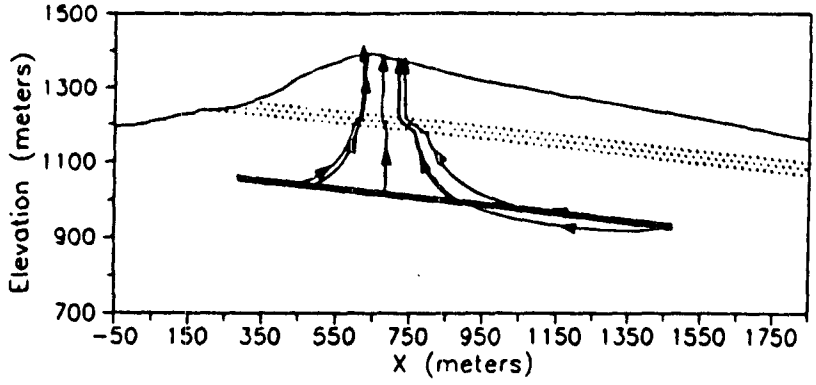


Figure 6a. Path lines with ambient temperature, 0.1× permeability contrast.

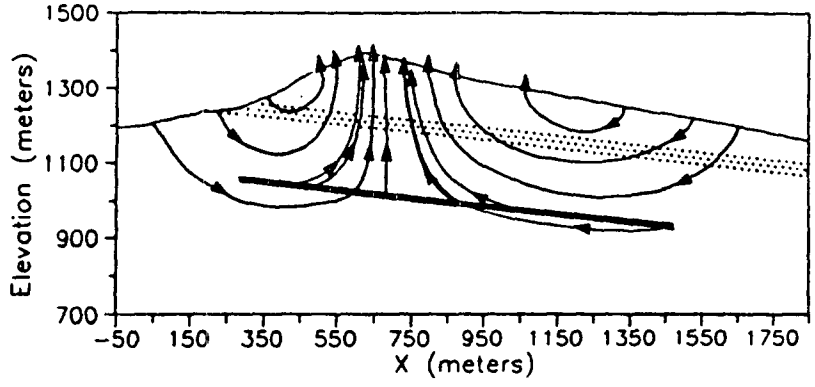
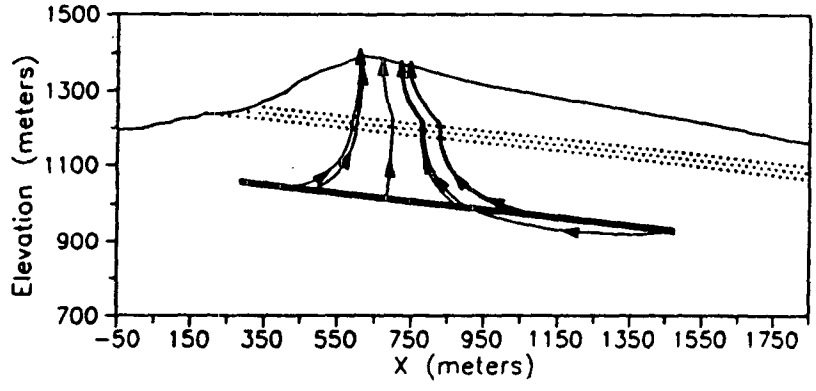


Figure 6b. Path lines with ambient temperature, no permeability contrast.



Lu, Amter and Ross, 1991

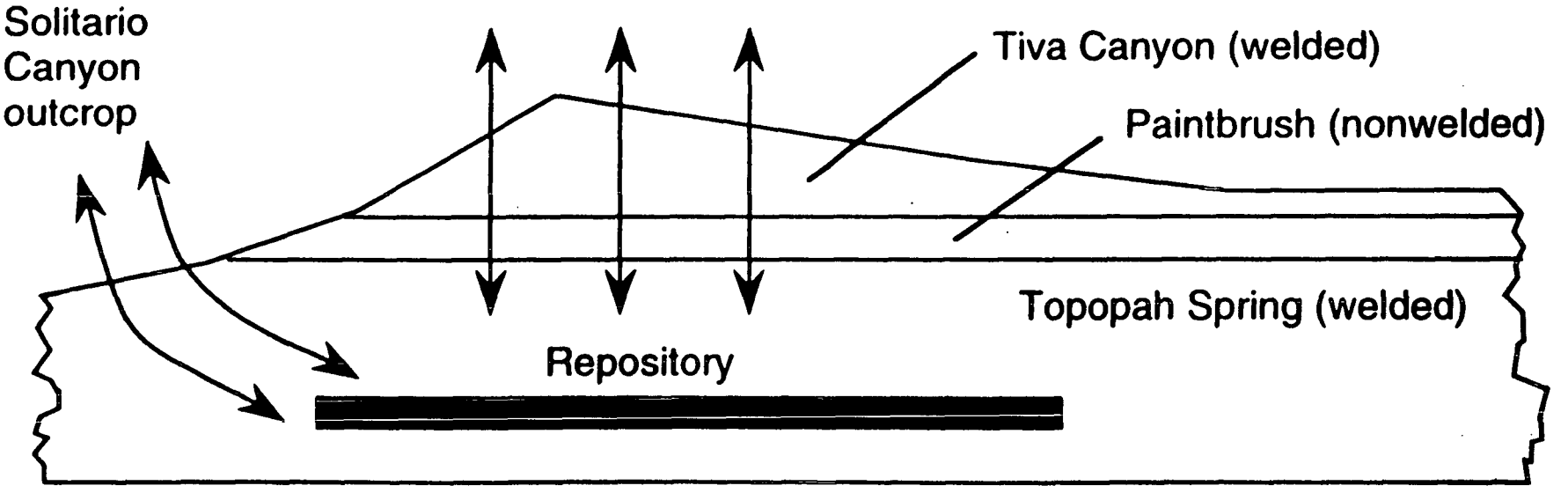


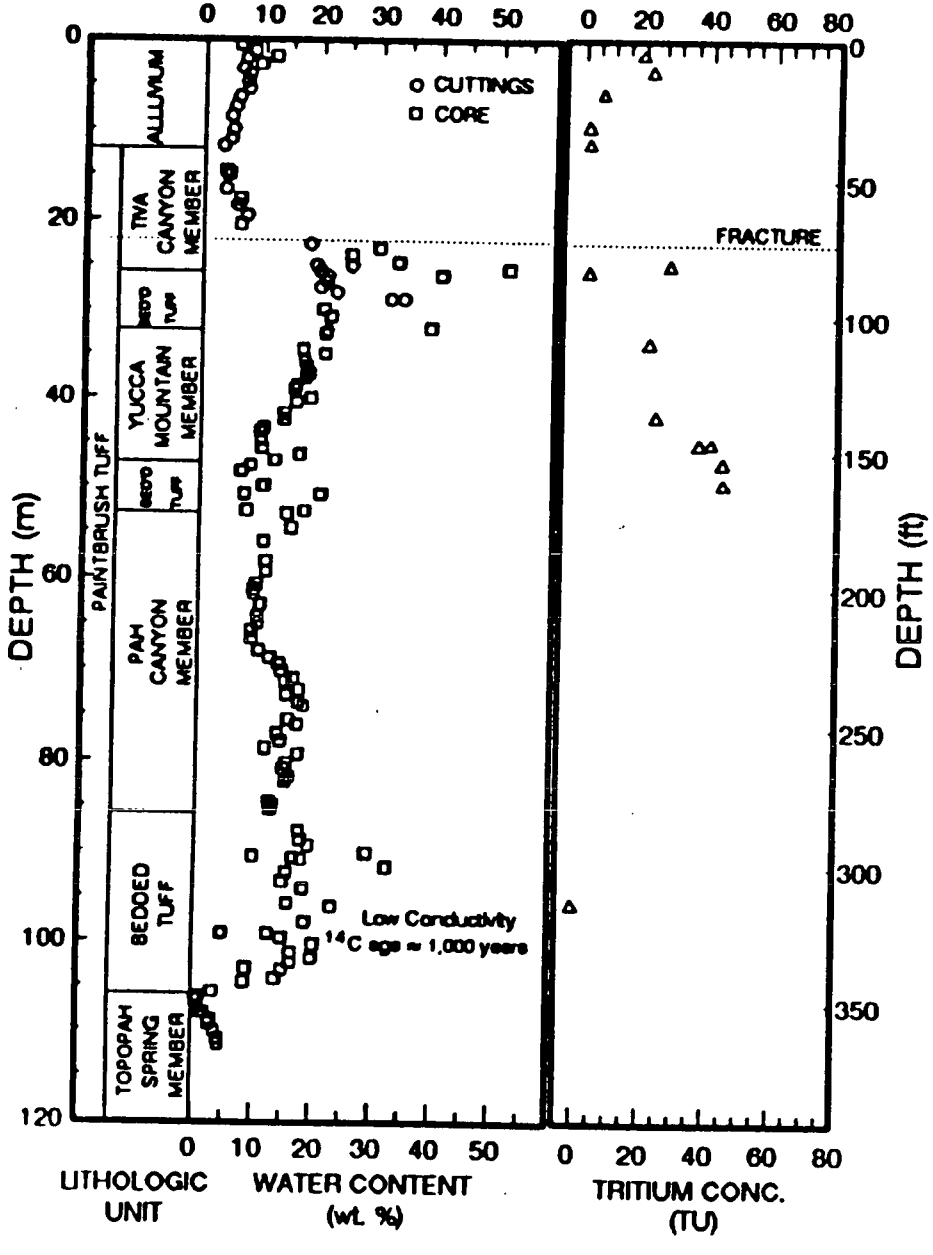
Figure 21-2. Schematic of proposed Yucca Mountain repository. Repository may breathe vertically through the paintbrush or horizontally through the Solitario Canyon outcrop.

NILSON ET AL. (1994)

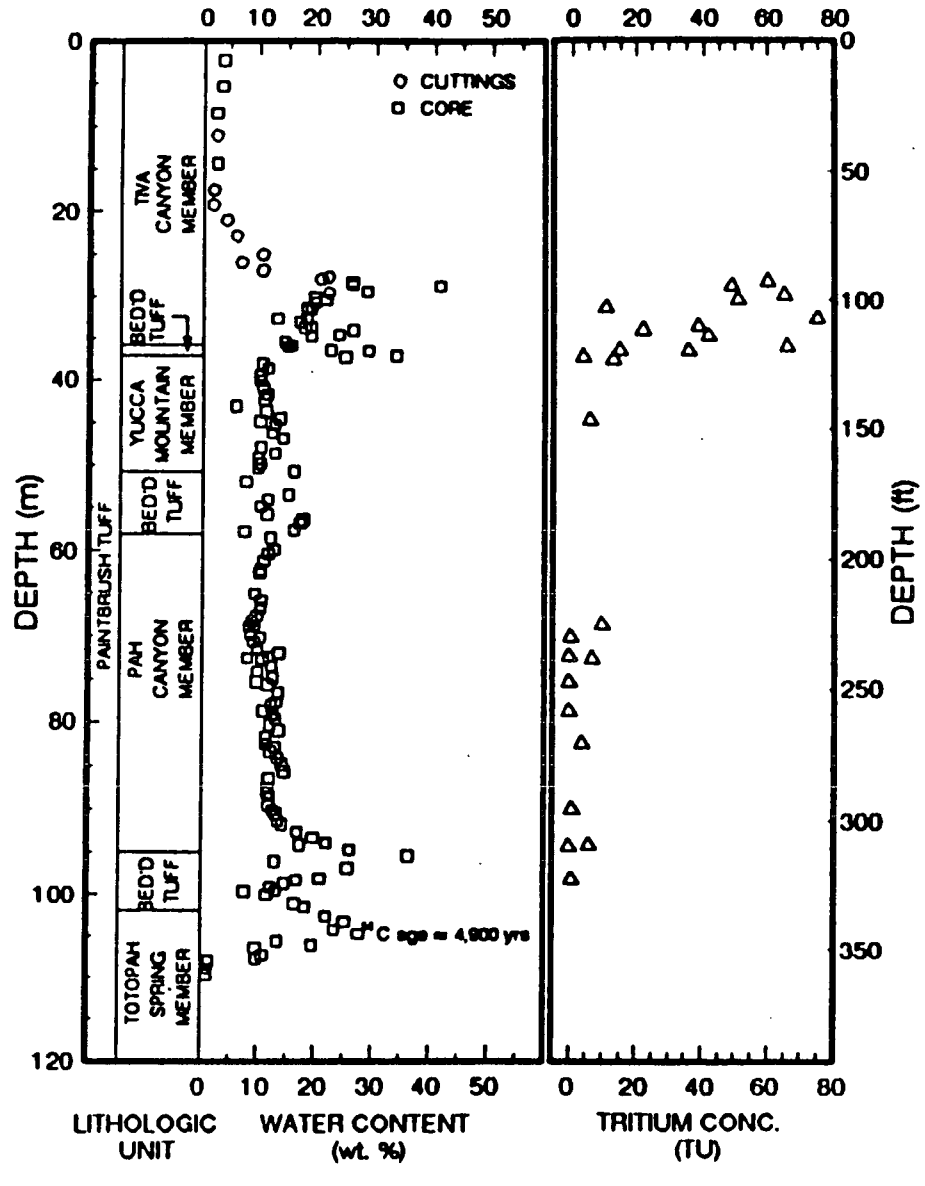
GAS-FLOW IN UZ - ISOTOPIC EVIDENCE

- ISOTOPIC DATA SUGGESTS 2 FLOW REGIMES
  - "Shallow" (<50m) and "Deeper" (>50m)
- "SHALLOW" REGIME SHOWS BOMB-PULSE ^{3}H AND ^{36}Cl ABOVE PAH CANYON MEMBER
- "DEEPER" REGIME SHOWS LINEAR DECREASE IN $^{14}CO_2$ WITH INCREASING DEPTH SUGGESTING DOWNWARD TRANSPORT
- GAS-PHASE AND AQUEOUS-PHASE $^{14}CO_2$ "AGES" (1-10X10^3 YR) ARE ON AVERAGE MUCH YOUNGER THAN AQUEOUS-PHASE ^{36}Cl "AGES" (<50-750X10^5 YR)

WELL UZ-4

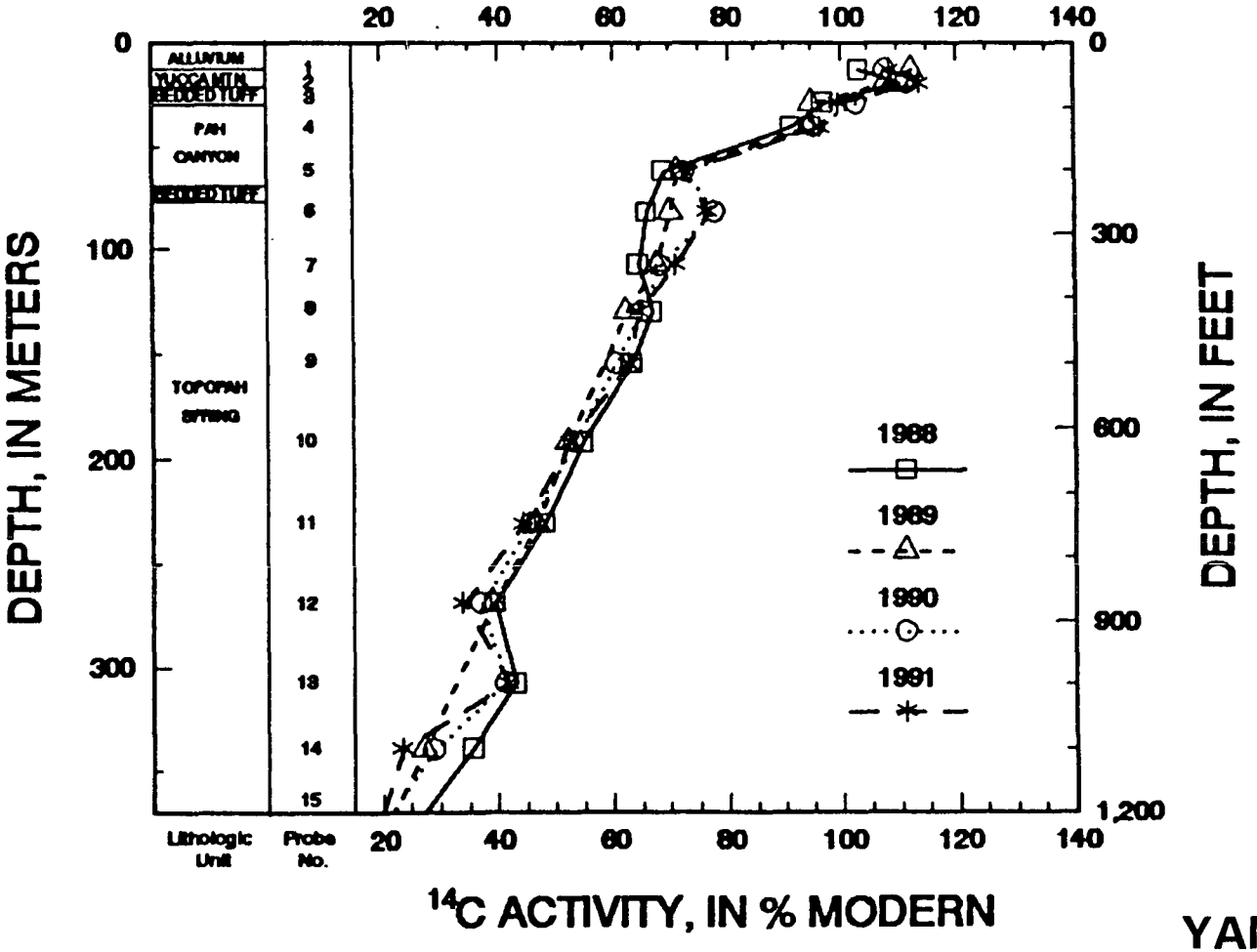


WELL UZ-5



YANG ET AL., 1993

WELL UZ-1



YANG, 1992

POTENTIAL $^{14}CO_2$ RETARDATION MECHANISMS

- LOW REDOX POTENTIAL IN ENGINEERED BARRIER
- SORPTION ONTO METAL OXIDES AND OXYHYDROXIDES
- COPRECIPITATION AS $CaCO_3$ IN CEMENT/CONCRETE
- COPRECIPITATION AS $CaCO_3$ DURING DRYOUT PHASE
- ISOTOPE EXCHANGE WITH HCO_3^- IN UZ PORE WATER
- ISOTOPE EXCHANGE WITH $Ca^{12}CO_3$ IN CEMENT
- ISOTOPE EXCHANGE WITH $Ca^{12}CO_3$ IN DRY-OUT ZONE

LOW REDOX POTENTIAL IN ENGINEERED BARRIER

- UZ GAS PHASE AT POTENTIAL REPOSITORY HORIZON LEVEL CURRENTLY HAS ATMOSPHERIC OXYGEN CONTENT
- RADIOLYSIS TENDS TO PRODUCE OXIDIZING AGENTS (E.G., H_2O_2, HNO_3, ETC)
- EVEN TRACE AMOUNTS OF O_2 RESULT IN THE PRODUCTION OF CO_2 IN FUEL MAINTAINED IN ARGON
- EXISTENCE OF SUFFICIENTLY REDUCING CONDITIONS TO PREVENT THE FORMATION OF CO_2 AFTER WASTE PACKAGE FAILURE CONSIDERED UNLIKELY SCENARIO
- OXIDATION RATE OF FUEL WILL RETARD RELEASE OF ALL BUT INITIAL "QUICK-RELEASE" FRACTION (CODELL AND WESCOTT, 1992)

SORPTION ONTO METAL OXIDES

- WASTE PACKAGES TO CONTAIN APPROX. 5 m^3 CARBON STEEL EACH. 2,000 WASTE PACKAGES = 1.0 X 10^4 m^3.
- ASSUME OXIDATION RESULTS IN OXIDE PHASE WITH 10m^2/g SURFACE AREA
- ACCORDING TO van GEEN ET AL. (1994), CO_2 SURFACE COVERAGE ON GOETHITE = 3.8 X 10^{-6} M/m^2
- TOTAL CO_2 RESERVOIR ON OXIDIZED CORROSSION ALLOWANCE LAYER = 3 X 10^6 M
- TOTAL $^{14}CO_2$ INVENTORY IN REPOSITORY = 1.3 X 10^3 M

COPRECIPITATION WITH $Ca^{12}CO_3$ IN CONCRETE AND DRY-OUT ZONE

- CARBONATION OF CEMENT/CONCRETE BY ATMOSPHERIC CO_2 WILL LIKELY BE NEAR MAXIMUM AT TIME REPOSITORY IS SEALED
- COPRECIPITATION OF $Ca^{14}CO_3$ WITH $Ca^{12}CO_3$ IN ROCK UNITS SURROUNDING REPOSITORY DURING DRY-OUT IS POSSIBLE BUT VERY DEPENDENT ON WASTE PACKAGE FAILURE TIMES
- COPRECIPITATION OF $^{14}CO_3$ IN CARBONATE MINERALS PROBABLY NOT A SIGNIFICANT RETARDATION MECHANISM

MAGNITUDES OF ^{12}C AND ^{14}C RESERVOIRS

- TOTAL $^{14}CO_2$ INVENTORY IN WASTE IS $1.3X10^3$ MOLES
- AQUEOUS ^{12}C RESERVOIR ON ORDER OF 1.0×10^9 MOLES IN THE UZ ABOVE THE POTENTIAL REPOSITORY. THIS PROVIDES A RETARDATION FACTOR RANGING FROM 40-180 AS A FUNCTION OF TEMP. INCLUDED IN TSPA 93.
- CARBONATE MINERALS PRECIPITATED AS A RESULT OF NEAR-FIELD DRY-OUT WILL PROVIDE A SMALLER (MINERAL SURFACE) EXCHANGE RESERVOIR COMPARED TO THE DISPLACED AQUEOUS RESERVOIR
- TOTAL ^{12}C RESERVOIR PRESENT IN CEMENT/CONCRETE IS ON ORDER OF $1\text{-}2X10^8$ MOLES BUT ONLY A PORTION OF THIS (i.e., SURFACES) AVAILABLE FOR EXCHANGE

CARBON ISOTOPE EXCHANGE KINETICS ON SOLID CARBONATE MINERALS

- EXPERIMENTS BY MOZETO ET AL. (1984) INDICATE CARBON ISOTOPE EXCHANGE ON CALCITE IS A 2-STEP PROCESS - ADSORPTION (HRS) AND ISOTOPE EXCHANGE
- ISOTOPE EXCHANGE MECHANISM DOMINATED BY RECRYSTALLIZATION OF CALCITE SURFACE LAYERS
- AQUEOUS PHASE REQUIRED FOR RECRYSTALLIZATION PROCESS TO OPERATE. EXTENDED DRY-OUT PERIOD WILL INHIBIT EXCHANGE PROCESS ON MINERAL SURFACES
- FRACTION OF TOTAL (SOLID) CARBONATE ^{12}C RESERVOIRS AVAILABLE FOR ISOTOPE EXCHANGE UNCERTAIN

DATA AND MODELING NEEDS

- NEED EXPERIMENTAL DETERMINATION OF CARBON ISOTOPE EXCHANGE RATES AND CAPACITIES ON CARBONATES IN CONCRETE TO BE USED IN REPOSITORY AND POSSIBLY ON OXIDIZED CORROSION ALLOWANCE LAYER TO BE USED IN WASTE PACKAGES
- NEED ADDITIONAL EXPERIMENTAL DATA ON WATER/GAS CARBON ISOTOPE EXCHANGE KINETICS
- NEED MORE DETAILED GAS FLOW MODELS THAT EXPLAIN SITE CHARACTERIZATION DATA AND BETTER QUANTIFY CARBON ISOTOPE EXCHANGE REACTIONS

CONCLUSIONS

- UZ AQUEOUS PHASE LARGEST POTENTIAL $^{14}CO_2$ EXCHANGE RESERVOIR
- DRY-OUT ASSOCIATED WITH "HOT REPOSITORY" WILL SUBSTANTIALLY DECREASE SIZE OF AQUEOUS PHASE RESERVOIR FOR THOUSANDS OF YEARS
- ISOTOPE EXCHANGE OF $^{14}CO_2$ WITH $^{12}CO_2$ ON SURFACES OF CARBONATE MINERALS WILL PROVIDE ADDITIONAL EXCHANGE RESERVOIR ALTHOUGH PROBABLY SMALLER THAN "DISPLACED" AQUEOUS RESERVOIR

CONCLUSIONS (cont'd)

- TSPA93 USED CURRENT AQUEOUS RESERVOIR FOR $^{14}CO_2$ RETARDATION. RELEASE RATE CALCULATED EXCEEDED EPA REGULATIONS.
- "HOT REPOSITORY" MAY LEAD TO LARGER $^{14}CO_2$ RELEASES BECAUSE OF POSSIBLE DECREASES IN SIZES OF EXCHANGE RESERVOIRS.
- EXPERIMENTAL DATA REQUIRED TO EVALUATE ALTERNATE EXCHANGE RESERVOIRS
- ADDITIONAL MODELING REQUIRED TO IMPROVE CORRESPONDENCE WITH SITE CHARACTERIZATION DATA AND TO EVALUATE CAPACITY OF NON-AQUEOUS RESERVOIRS

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

PRESENTATION TO THE NUCLEAR WASTE TECHNICAL REVIEW BOARD

SUBJECT: REVIEW OF GASEOUS ISOTOPES

PRESENTER: RICHARD A. VAN KONYNENBURG

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

PRESENTER'S TELEPHONE NUMBER: (415) 422-0456

DECEMBER 11-12, 1989

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

PRESENTATION TO THE NUCLEAR WASTE TECHNICAL REVIEW BOARD

SUBJECT: GASEOUS AND SEMI-VOLATILE RADIONUCLIDES

PRESENTER: DR. U-SUN PARK

PRESENTER'S TITLE AND ORGANIZATION: SENIOR STAFF ENGINEER
SCIENCE APPLICATIONS INTERNATIONAL CORPORATION
LAS VEGAS, NEVADA

PRESENTER'S TELEPHONE NUMBER: (702) 794-7643

REGISTRY HOTEL, DENVER, COLORADO
JUNE 25-27, 1991

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

NUCLEAR WASTE TECHNICAL REVIEW BOARD
FULL BOARD MEETING

SUBJECT: CARBON-14 RELEASES

PRESENTER: DR. RICHARD A. VAN KONYNENBURG

PRESENTER'S TITLE AND ORGANIZATION: ENGINEER
LAWRENCE LIVERMORE NATIONAL LABORATORY (LLNL)
LIVERMORE, CALIFORNIA

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

PLAZA SUITE HOTEL • LAS VEGAS, NEVADA
OCTOBER 14 - 16, 1992

ENVIRONMENTAL TRANSPORT OF GASEOUS RELEASES OF RADIONUCLIDES

Richard A. Van Konynenburg
Lawrence Livermore National Laboratory

Meeting of the
National Academy of Sciences'
Committee on the Technical Bases for
Yucca Mountain Standards

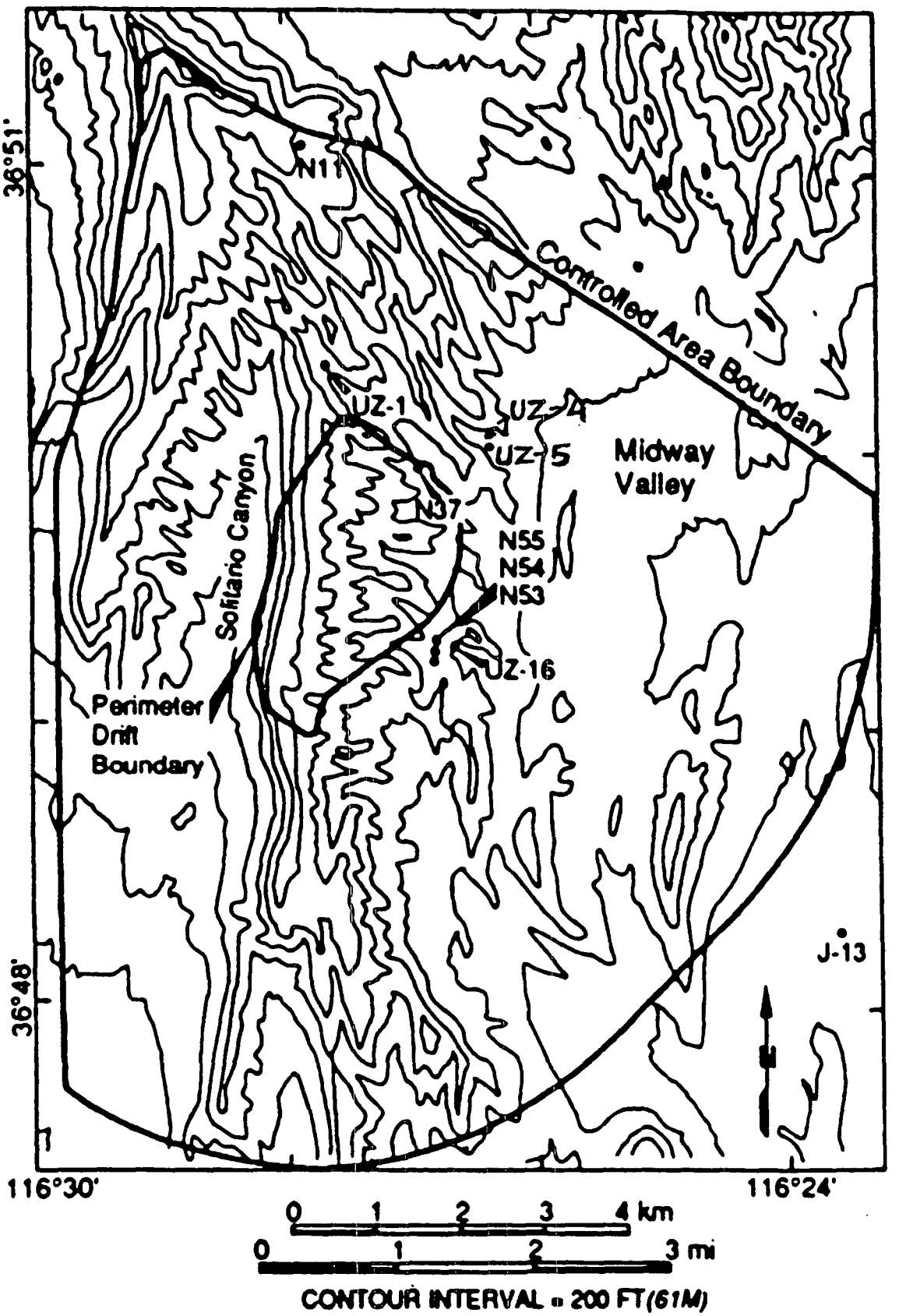
Las Vegas, Nevada

August 26, 1993

NRC Analysis of C-14 Releases at the Yucca Mountain site for Iterative Performance Assessment, Phase 2

by Richard Codell and
Rex Wescott
U.S. Nuclear Regulatory Commission

for the High-Level Waste/Carbon-14 Subcommittee
of the SAB Radiation Advisory Committee
June 16-17, 1992, Arlington VA


36°51'
36°48'
116°30'
116°24'
N11
Controlled Area Boundary
UZ-1
UZ-4
UZ-5
Midway
Valley
N37
N55
N54
N53
Solitario Canyon
UZ-16
Perimeter
Drift
Boundary
J-13
0 1 2 3 4 km
0 1 2 3 mi
CONTOUR INTERVAL = 200 FT(61M)