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Mr. John J. Linehan, Acting Chief
ATTN: D. Brooks
Repository Projects Branch
Division of Waste Management
U. S. Nuclear Regulatory Commission
Washington, D. C. 20555

Dear Mr. Linehan:

NATIONAL MEETING OF THE AMERICAN CHEMICAL SOCIETY

Please find enclosed the requested copies of the viewgraphs used in several presentations at the August, 1986 National meeting of the American Chemical Society. Contact M. J. Furman of my staff on FTS 444-7062 with any questions.

Sincerely,

J. J. Keating, Director
Basalt Waste Isolation Division

BWI:MJF

Enclosure

214

EFFECT OF IONIZING RADIATION ON WASTE PACKAGE PERFORMANCE: PROGRAM OVERVIEW

D.T. Reed

Waste Management Symposium
American Chemical Society Meeting

September 9, 1986

Rockwell Hanford Operations

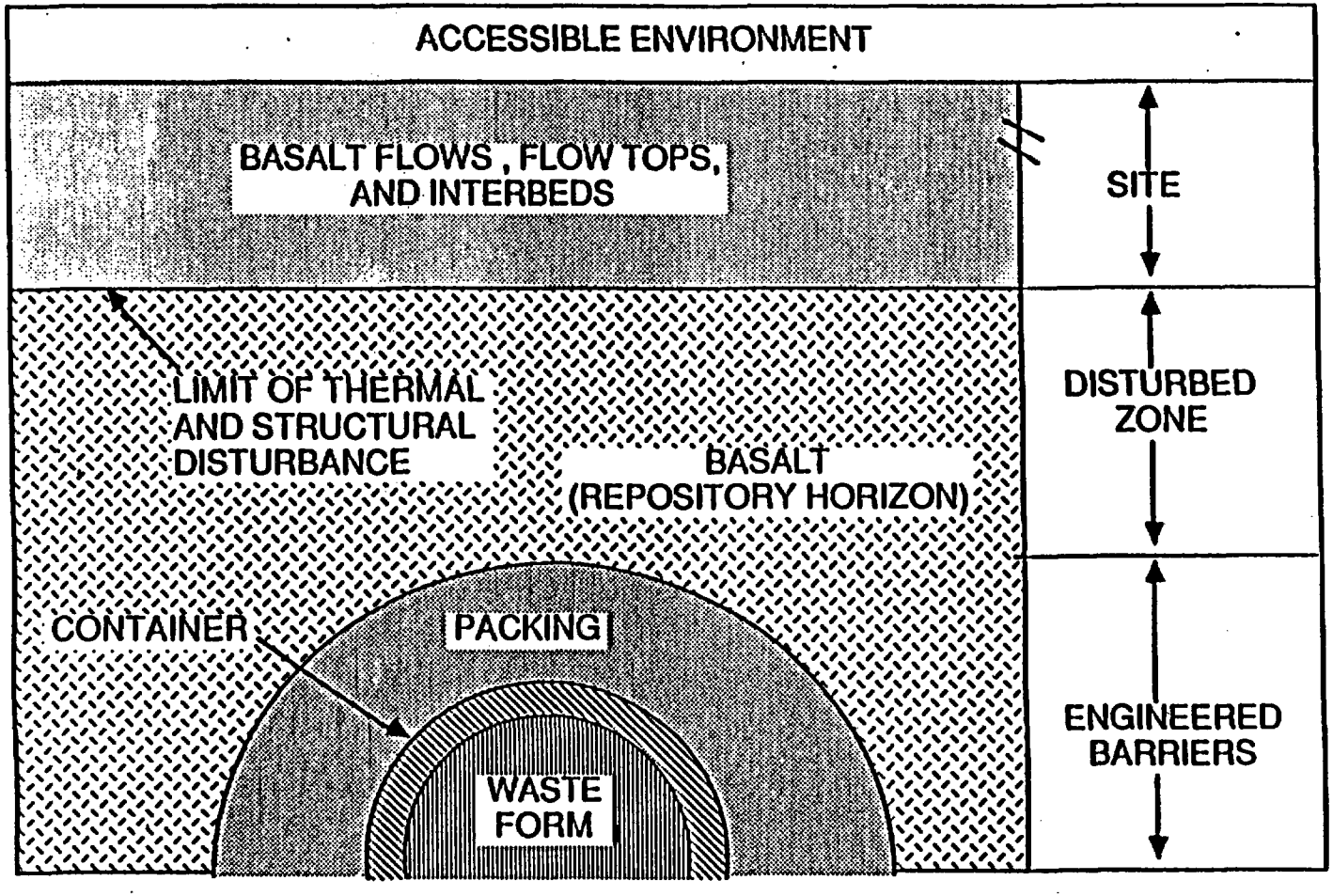
WP8608-M48

OVERVIEW

- Purpose for Investigation of Radiolytic Effects
- Radiation Environment
- Radiolysis Program
- Status of Major Issues

WP8608-M43

SPATIAL DIVISIONS OF A NUCLEAR WASTE REPOSITORY IN BASALT



WP8606-M27

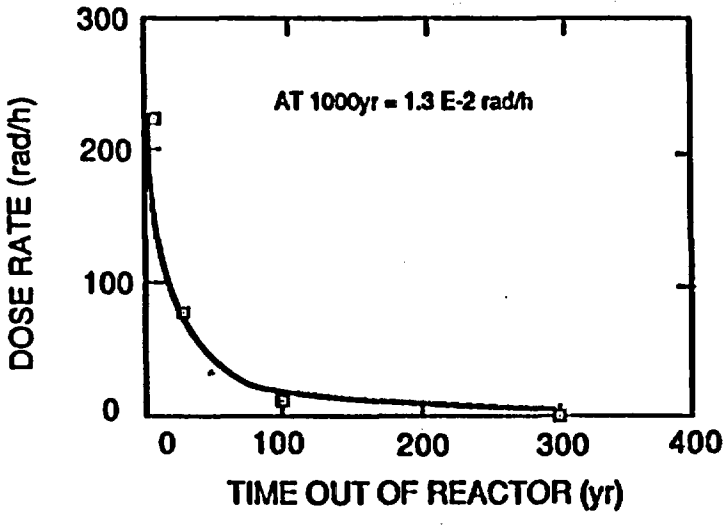
MAJOR RADIOLYTIC ISSUES

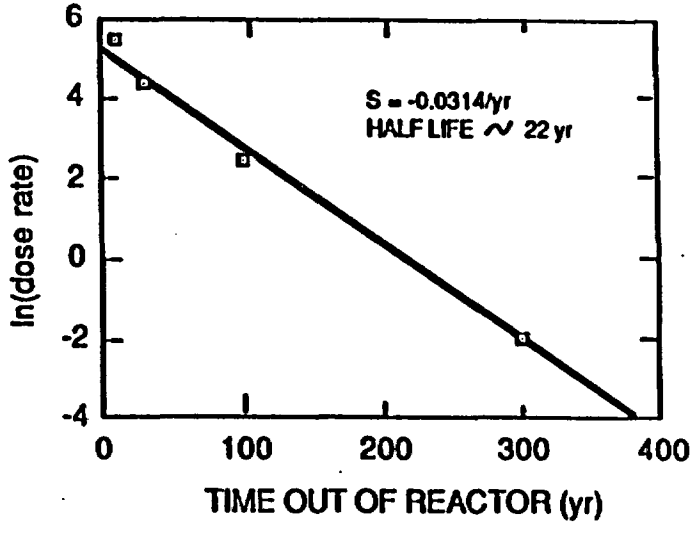
How will ionizing radiation affect performance of waste package?

1. Long term changes in bulk chemistry near the waste package
2. Solid damage to various components of the waste package
3. Corrosion of waste package components
4. Radionuclide speciation

WP8608-M44

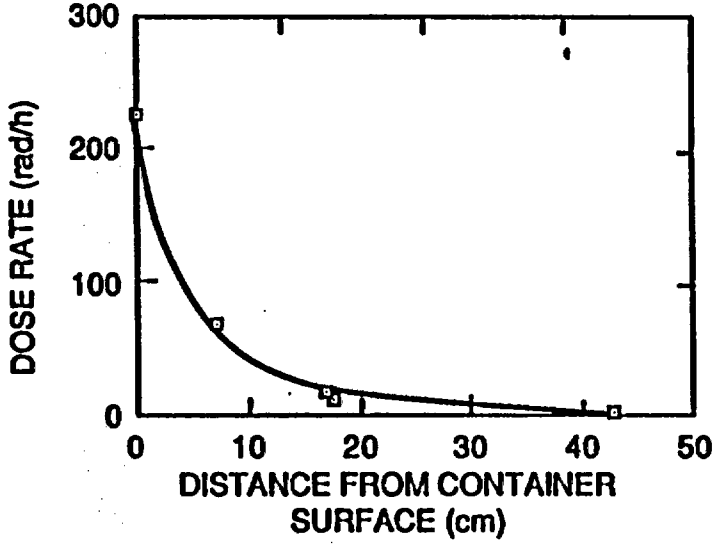
GAMMA DOSE RATE AS A FUNCTION OF TIME





WP8607-M164

GAMMA DOSE RATE AS A FUNCTION OF DISTANCE FROM THE OUTER CONTAINER SURFACE



Effective Attenuation Coeffecient = 0.164/cm

WP8607-M165

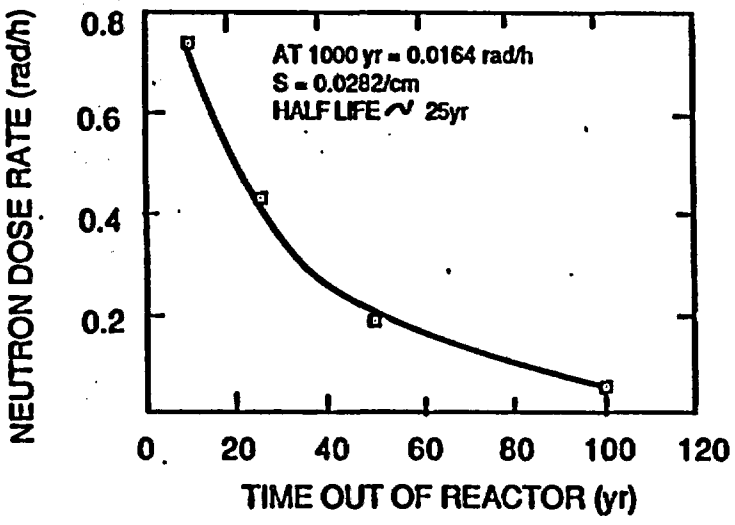
ESTIMATED RADIOLYTIC YIELDS IN THE AQUEOUS PHASE OF SATURATED PACKING MATERIAL

TIME	ENERGY DEPOSITED IN PACKING MATERIAL (MJ)	YIELDS (moles)			
		$-H_2O$	H_2O_2	OH	H_2
1st year	4.11	1.8	0.20	1.45	0.15
Year 50	0.85	0.38	0.041	0.30	0.031
Total (1,000 yr)	133.0	59.3	6.3	46.9	4.8

* Yield values estimated for pure water at 200°C were used. These were:
  $G(-H_2O) = 4.3$, $G(OH) = 3.4$, $G(H_2O_2) = 0.46$ and $G(H_2) = 0.35$
* Mass of CSF steel container is 4194 Kg (75100 moles)

WP8607-M176

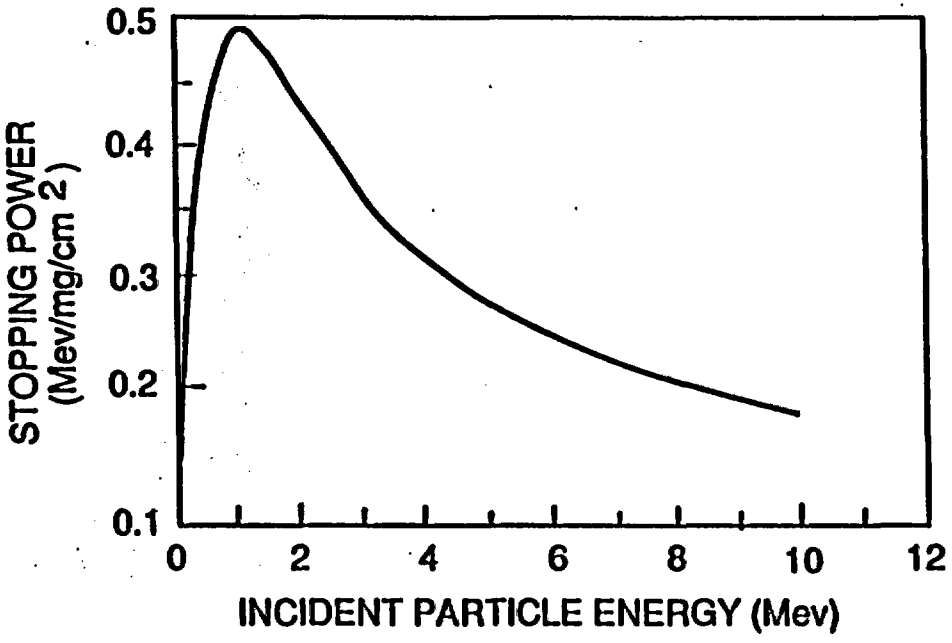
NEUTRON DOSE RATE AS A FUNCTION OF TIME



WP8607-M166

STOPPING POWER OF AN ALPHA PARTICLE IN A UO_2 MATRIX

(Calculated using data from Northcliffe and Schilling, 1970)



WP8606-M50

PROGRAM DESCRIPTION: RADIOLYSIS

PROGRAM	SUBCONTRACTOR
• Bulk chemistry	PNL and ANL
• Corrosion	HEDL
• Packing stability	ANL
• Radionuclide speciation	ANL ANL -LPAS PNL - STF

WP8608-M45

BULK CHEMISTRY: EXPERIMENTAL APPROACH

AQUEOUS

- SAMPLES: Synthetic groundwater + various combinations of container material, basalt , packing material and methane.

IRRADIATION CONDITIONS: Dose rate: 100 - 10,000 rad/h
Total Dose: up to 100 Mrad
Temperature: 100 - 250 C

ANALYSIS: Aqueous Composition - major cations, anions , dissolved organics

Solids: alteration mineral products
Dissolved gases: hydrocarbons, hydrogen, oxygen

MIXED PHASE

SAMPLES: Air / water / methane mixtures

IRRADIATION CONDITIONS: Same as Aqueous

ANALYSIS: GAS PHASE: nitrogen oxides, methane, hydrocarbons, hydrogen carbon oxides and oxygen

CONTAINER CORROSION EXPERIMENTAL APPROACH AQUEOUS

SAMPLES: Container material coupons encapsulated in packing material placed in a flow-through system.

IRRADIATION CONDITIONS: Dose Rate: 100 - 10,000 rad/h
Duration: 4 mo - 1 yr
Temperature: 100 - 250 C

ANALYSIS: Characterization of oxide layer
Weight loss determination
Major cation and anion concentrations
Dissolved gas composition

MIXED PHASE

SAMPLES: Container material coupons suspended in an air / steam / methane environment

IRRADIATION CONDITIONS: SAME

ANALYSIS: Gas phase composition
Solid surface of the coupon

WP8608-M59

RADIONUCLIDE SPECIATION EXPERIMENTAL APPROACH

1. SPENT FUEL TEST FACILITY

   APPROACH: Rocking autoclave experiments containing spent fuel with basalt/container material/GR-4

   ANALYSIS: Solid characterization
   Major cation and anion concentration
   Dissolved gases (planned)

2. SPECIATION STUDIES: IN-SITU SPECTROSCOPY

   APPROACH: Static experiments with different isotopes of the same element. Monitor concentration of that isotope as a function of time and presence of waste package components

   ANALYSIS: Laser photoacoustic spectroscopy
   Laser induced fluorescence

3. IRRADIATION OF RADIONUCLIDE SOLUTIONS

   APPROACH: Irradiate radionuclide solutions. Determine qualitative effect of radiolytic products on dissolved species.

   ANALYSIS: Oxidation state-specific separations
   Laser spectroscopy

WP8608-M61

AQUEOUS CHEMISTRY
SUMMARY OF OBSERVATIONS

Major cation/anion concentration: No effect
possible exception: carbonate

pH : have not separated out geochemical from radiolytic effect

Dissolved Organics: will be generated to a varying extent depending on dose rate, total dose and waste package components. Have not been characterized.

Organic Polymers: are generated under certain conditions. Are not expected under repository-relevant conditions.

Oxygen formation: not observed

Nitric acid formation: not observed

** over 70 gamma irradiation experiments have been completed

EFFECT OF IONIZING RADIATION ON CORROSION

1. Radiation induced damage to container material
2. Radiation induced damage/alteration of protective layer
3. Radiolytic generation of corrodants in aqueous medium
    a. Formation of oxidants
    b. Products that indirectly affect corrosion

WP8607-156

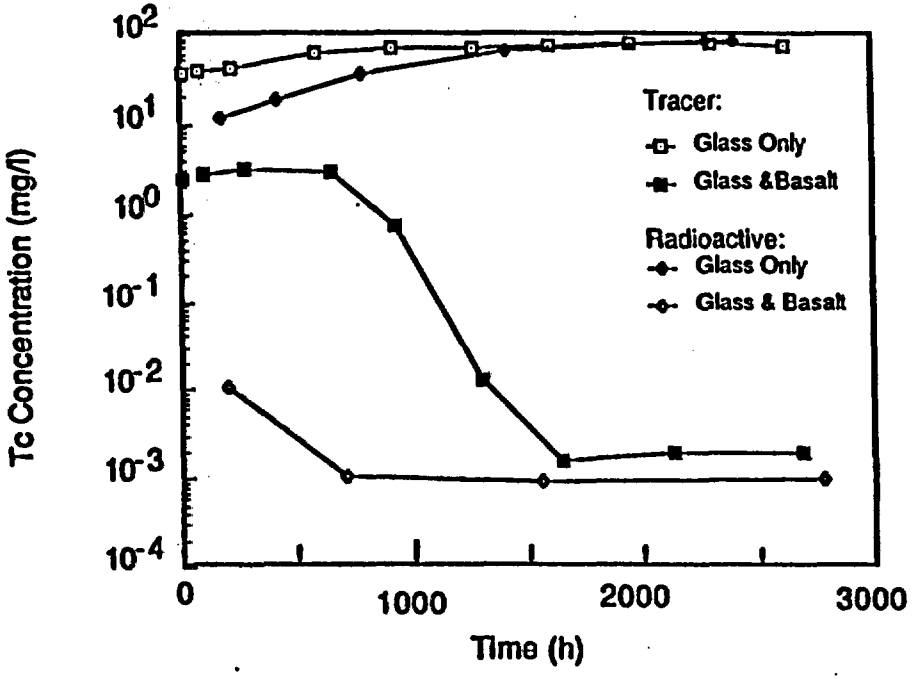
COMPARISON OF AMOUNT OF RADIOLYTIC CORROSION PREDICTED BY CRITERION WITH EXPERIMENTAL RESULTS

EXPERIMENTAL CONDITIONS	AMOUNT OF CORROSION OBSERVED (mg)		RADIOLYTIC CORROSION PREDICTED BY CRITERION (mg)
	Aqueous	Radiolytic	
100° C carbon steel/GR-4 Dose rate = 2.18 E3 rad/h Total dose = 6.3 Mrad Duration = 4 months	48.02	1.38	32.0 - only 3.7% of this observed
250° C carbon steel/GR-4 Dose rate = 3.0 E5 rad/h Tatal dose = 2000 Mrad Avg. duration = 8.9 months	84.2	45.4	10,200 - only 0.44% of this observed

WP8607-M174

COMPARISON OF FULLY RADIOACTIVE AND TRACER DOPED GLASS EXPERIMENTS

BOTH ARE AT 200 C AND 30 MPa; RADIATION LEVEL IS 1000 rad/h. DATA IS FROM UNPUBLISHED WORK AT PNL (REPRODUCED BY PERMISSION OF J.R. BURNELL).



WP8608-M58

EFFECT OF IONIZING RADIATION ON THE REDOX ENVIRONMENT

Containment period: oxidation front will not be generated

1. Effect of ionizing radiation will be very local
2. Yield of oxidants will be very small with respect to reducing agents present in the waste package

Controlled Release (Isolation) Period

1. Potential for a local environment within the container does exist -- oxygen formation, poor communication with host environment
2. Effect will still be relatively small and localized -- reducing agents still present, most radionuclides in the waste form are in a reduced state

WP8608-M63

NATURAL ANALOGS: APPLICATION TO PREDICTION OF LONG-TERM RADIONUCLIDE ISOLATION IN A NUCLEAR WASTE REPOSITORY IN BASALT

J.R. Burnell
D.E.Grandstaff
M.L. Cummings

Rockwell Hanford Operations

WP8607-M7

RESPONSIBILITIES

OF BASALT WASTE ISOLATION PROJECT INCLUDE

A. Define the geochemical environment of the waste package for the postclosure period

B. Predict the amount of radionuclides which would be released from the waste package after a container breach

GEOCHEMICAL ENVIRONMENT AT T AND P OF CONCERN WILL LARGELY BE CONTROLLED BY BASALT - THE PREDOMINANT SOLID COMPONENT OF THE REPOSITORY

CONSEQUENTLY,

The BWIP is involved in a large-scale experimental program to investigate the hydrothermal behavior of basalt and its synergistic interactions with other waste package components.

- Batch experiments using various configurations of waste form, groundwater, basalt, container material

- Temperatures 85 to 250 ^{o}C

- Flow-through experiments, in which groundwater is pumped at a controlled rate through configurations of waste package materials

WP8608-M10

SOLUTION CONCENTRATIONS OF RADIONUCLIDES ARE MONITORED AS A FUNCTION OF TIME

- Anticipate that hydrothermal reaction will produce secondary phases
- These secondary phases will incorporate radionuclides
- The mobility of the radionuclides thus incorporated will be controlled then by the solubility of the incorporating phase

We want to measure the solubility-controlled concentration as input to transport models

QUESTION:

ARE THE PHASES FORMED IN LABORATORY STABLE FOR 10,000 YEARS?

OR

IN ANALOGOUS NATURAL BASALT-GROUNDWATER SYSTEMS, DO HYDROTHERMAL CONDITIONS RESULT IN THE SAME MINERAL ASSEMBLAGES AS WE SEE IN THE LAB?

LOCATE ANALOG:

Need to find analogous situation in natural systems where system evolution is longer and compare

- No natural system compares one-to-one with waste package
- Must be selective
- Choose specific parameters to analogize

NATURAL ANALOGS OF ANTICIPATED SYSTEM ARE USEFUL FOR THIS CONCERN.

APPROACH:

1. Decide on a question to pursue
2. Locate a reasonable-appearing analogy
3. Demonstrate validity of analogy
4. Answer the question

WHAT PARAMETERS CAN BE ANALOGIZED?

- Temperature
- Pressure
- Groundwater composition
- Groundwater flux
- Solid phases
  - Basalt
  - Wasteform
  - Steel or copper
- Redox conditions
- Radiolysis

WP8608-M15

8.0.

GRANDE RONDE BASALT NATURAL ANALOG

ANALOGOUS PARAMETERS:

Basalt - Same phases and chemical composition as repository

Temperature - Estimated same range

Pressure - Similar low values

Groundwater Composition - Unknown but probably similar (both buffered by basalts)

Groundwater flux - Unknown

Redox - Range may include repository relevant conditions

Radiation - Not analogous

Age - Apparently concurrent with eruption of Grande Ronde basalts, so 12 - 14 MYBP

WP8608-M16

- STUDY IS A CONCURRENT ATTEMPT TO DEMONSTRATE THE ANALOGY AND TO ANSWER THE QUESTIONS
- CURRENTLY ATTEMPTING TO DEFINE CLOSELY
  - Temperature range of reaction
  - Fluid chemistry during reaction
- ALSO STUDYING ALTERATION MINERAL PHASES - ARE THEY THE SAME AS FORMED IN THE LABORATORY?
- OTHER LINES OF INVESTIGATION:
  - Evaluate leaching and transport of trace elements (Cs, Ce, Sm, Th, U, Rare Earth Elements) from the basalt by hydrothermal solutions
  - Estimate redox conditions of the alteration system and the mobility of elements as a function of redox state

WP8608-M17

ICELANDIC GEOTHERMAL FIELDS

- Just beginning

- Basalts of Iceland are similar chemically to those of the Columbia River Plateau

- Vast amount of data available through Icelandic Geologic Survey including abundant down - hole information

WP8608-M18

ICELANDIC ANALOGY

- Temperatures - encompass the same range
- Groundwaters - very similar in Krafla field
- Basalt - very similar in composition
- Redox - variable
- Radiation - not analogous

To demonstrate the analogy:

Currently using experiments with basalt from Krafla geothermal field in same fashion as Grande Ronde basalts.

Question:

Do the Krafla basalts behave the same as Grande Ronde basalts in the lab?

If they do,we can possible extrapolate and use the large-scale data from the Iceland geothermal fields

GEOCHEMICAL BEHAVIOR OF RADIONUCLIDES IN A NUCLEAR WASTE REPOSITORY IN BASALT

G.S. Barney

Presentation to the American Chemical Society

September 9, 1986

Rockwell Hanford Operations

WP8608-M36

OVERVIEW OF PRESENTATION

- Use of radionuclide chemical information
- Description of important radionuclides and chemical processes
- Geochemical parameters that affect radionuclide behavior
- Solubility and sorption behavior of radionuclides
- Description of sorption mechanisms
- Future work

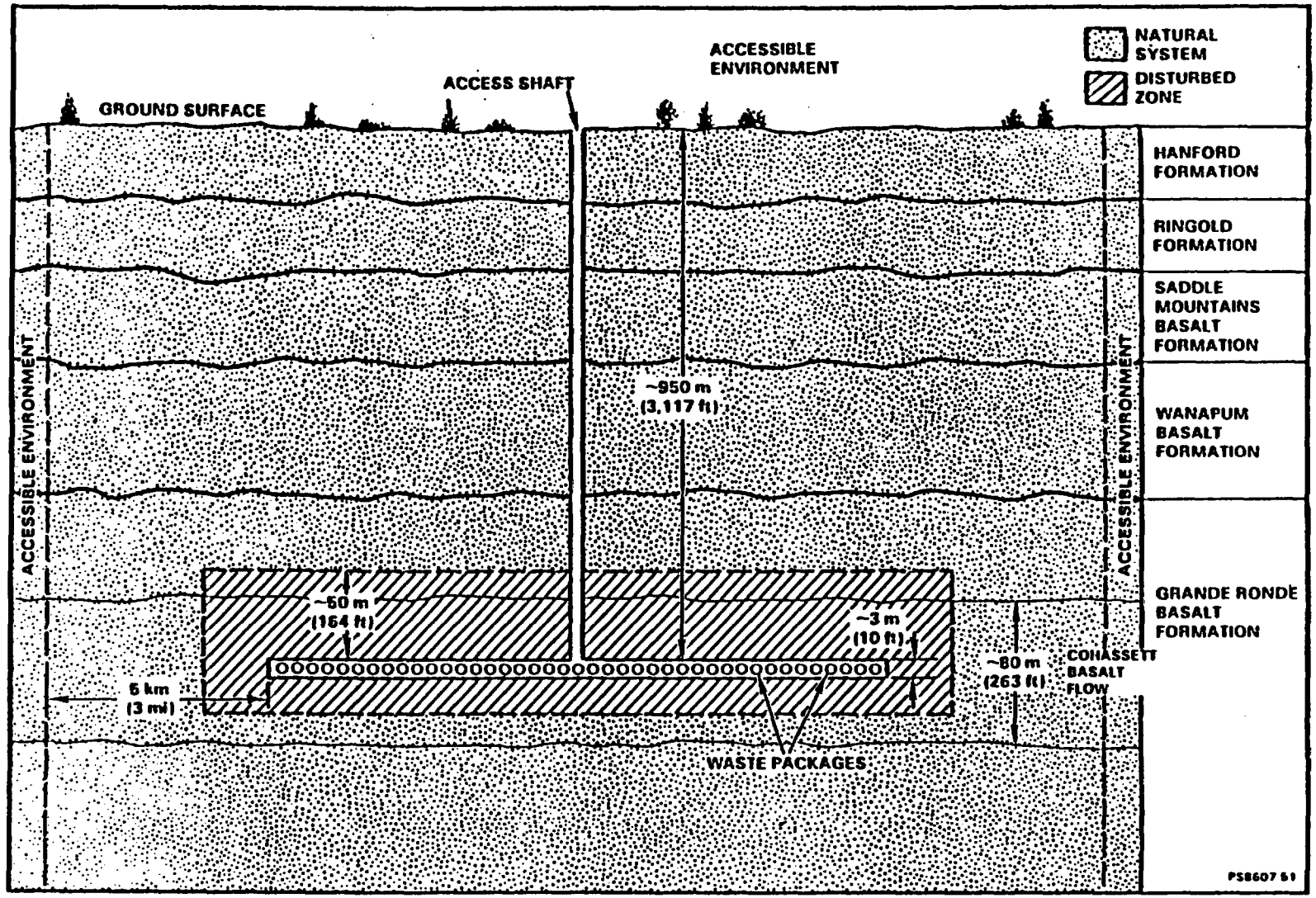
WP8608-M54

UTILIZATION OF CHEMICAL DATA ON RADIONUCLIDES

- Overall purpose is to predict release and transport of waste radionuclides from a basalt repository

- Develop models of radionuclide dissolution and sorption under expected conditions for release and transport models

WP8608-M53


NATURAL SYSTEM
DISTURBED ZONE
ACCESSIBLE ENVIRONMENT
ACCESS SHAFT
GROUND SURFACE
HANFORD FORMATION
RINGOLD FORMATION
SADDLE MOUNTAINS BASALT FORMATION
WANAPUM BASALT FORMATION
GRANDE RONDE BASALT FORMATION
ACCESSIBLE ENVIRONMENT
ACCESSIBLE ENVIRONMENT
~950 m (3,117 ft)
~50 m (164 ft)
~3 m (10 ft)
~80 m (263 ft)
COHASSETT BASALT FLOW
5 km (3 mi)
WASTE PACKAGES
PS8607 51

GEOCHEMICAL PROCESSES THAT CONTROL RADIONUCLIDE BEHAVIOR

RADIONUCLIDE REACTIONS	RELATED PROCESSES
• Dissolution/Precipitation • Sorption/Desorption • Complexation • Redox Reactions	• Groundwater Reactions with Engineered Barriers and Host Rock • Radiolysis

WP8608-M37

GEOCHEMICAL PARAMETERS THAT AFFECT RADIONUCLIDE BEHAVIOR

- GROUNDWATER COMPOSITION
    1. Major and Trace Inorganic Components
    2. Organic Components
    3. Dissolved Gases
- pH
- REDOX POTENTIAL
- ENGINEERED BARRIERS AND HOST ROCK COMPOSITION
    1. Mineralogy
    2. Surface Area
    3. Cation Exchange Capacity
    4. Redox Capacity

WP8608-M38

KEY RADIONUCLIDES IN WASTE AFTER 1,000 YEARS DECAY

ELEMENT	ISOTOPE	INVENTORY/EPA RELEASE LIMIT
Americium	^{241}Am	14,300
Plutonium	^{240}Pu	6,490
Uranium	^{234}U	40.8
Carbon	^{14}C	21.6
Neptunium	^{237}Np	17.4
Curium	^{245}Cm	17.4
Nickel	^{59}Ni	6.34
Zirconium	^{93}Zr	3.32
Thorium	^{230}Th	3.31
Niobium	^{94}Nb	2.18
Technetium	^{99}Tc	2.10
Tin	^{126}Sn	1.46
Cesium	^{135}Cs	0.765
Selenium	^{79}Se	0.710
Iodine	^{129}I	0.568

WP8608-M39

EFFECTS OF RADIONUCLIDE SPECIES ON DISSOLUTION AND SORPTION REACTIONS

COMPLEXATION REACTION:

$$M^{2+} + X^{-} = MX^{+}$$

DISSOLUTION REACTION:

$$M(OH)_2 = M^{2+} + 2OH^{-}$$

SORPTION REACTION:

$$M^{2+} + [\text{Surface}] = [\text{Surface}] - M^{2+}$$

WP8608-M40

REPRESENTATIVE FORMATION CONSTANTS FOR 1:1 ACTINIDE COMPLEXES WITH GROUNDWATER LIGANDS

ACTINIDE OXIDATION STATE	Log K_1			
	OH^-	CO_3^{2-}	F^-	SO_4^{2-}
III (An^{3+})	7.5	6.5	3.0	2.0
IV (An^{4+})	12.5	---	8.5	2.5
V (AnO_2^+)	5.0	6.0	6.0	2.0
VI (AnO_2^{2+})	8.5	10	3.0	2.0

WP8608-M46

EXPECTED REDOX REACTIONS OF RADIONUCLIDES IN A BASALT ENVIRONMENT

ELEMENT	REDUCTANT(S)	EXPECTED OXIDATION STATE
Plutonium	Basalt, Organics	Pu(IV) or Pu(III)
Uranium	Basalt	U(IV)
Neptunium	Basalt, Organics	Np(IV)
Technetium	Basalt	Tc(IV)
Selenium	Basalt	Se(-II) or Se(0)

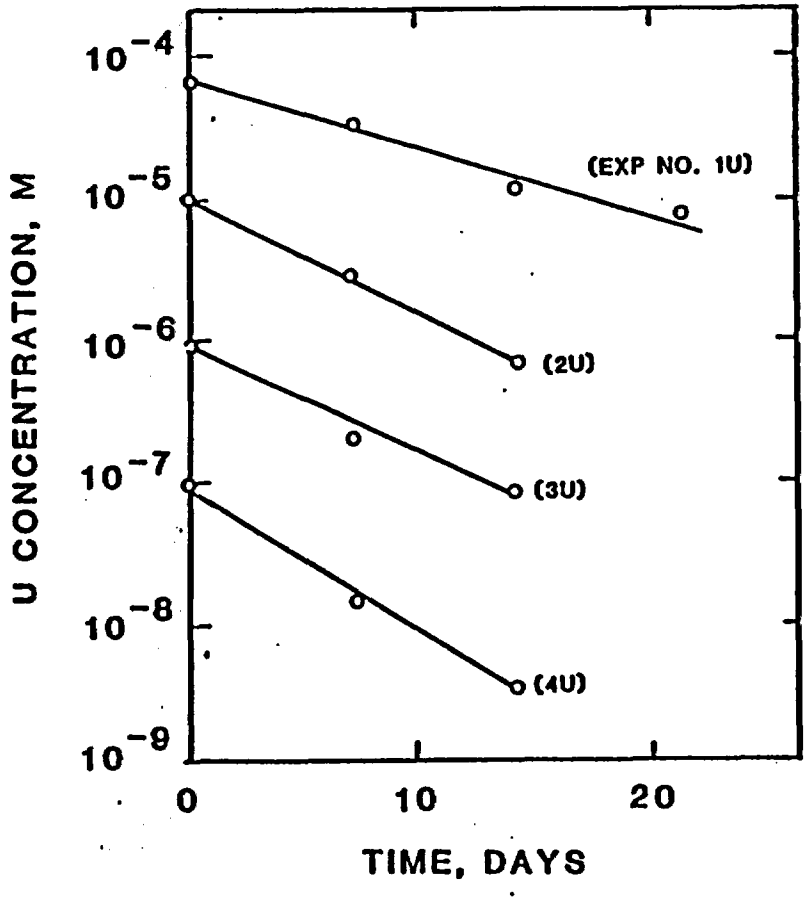
WP8608-M41

SOLUBILITY OF RADIONUCLIDES IN BASALT GROUNDWATER

ELEMENT	PROBABLE SOLID PHASE	SOLUBILITY (M)	
		OBSERVED	CALCULATED
Americium	$Am(OH)_3$	10^{-11} to 10^{-10}	10^{-9} to 10^{-6}
Plutonium	$PuO_2 \cdot xH_2O$	10^{-10} to 10^{-9}	10^{-11} to 10^{-6}
Uranium	UO_2	10^{-6} to 10^{-5}	10^{-11} to 10^{-6}
Neptunium	$NpO_2 \cdot xH_2O$	10^{-5} to 10^{-4}	10^{-11} to 10^{-9}
Technetium	$TcO_2 \cdot xH_2O$	10^{-8} to 10^{-7}	———
Carbon	$CaCO_3$	10^{-4} to 10^{-3}	———
Selenium	Se^o, CaSe	10^{-5} to 10^{-4}	10^{-8} to 10^{-6}

WP8608-M42

RATE CURVES FOR URANIUM(VI) SORPTION ON ALTERED PACKING MATERIAL



WP8503-108

DISTRIBUTION COEFFICIENTS FOR RADIONUCLIDE SORPTION ON BASALT SECONDARY MINERALS

ELEMENT	OXIDATION STATE	MEASURED K_d RANGE (m/Lg)
Americium	(III)	400 - >5,000
Plutonium	(IV)	700 - > 5,000
Uranium	(IV)	100 - 1,500
	(VI)	10 - 150
Neptunium	(IV)	400 - 1,500
	(V)	150 - 250
Technetium	(IV)	150 - 500
	(VII)	0
Selenium	(VII)	10 - 100
	(IV)	0.2 - 10
Carbon	(IV)	0
Iodine	(VI)	0
Zirconium	(IV)	100 - 700

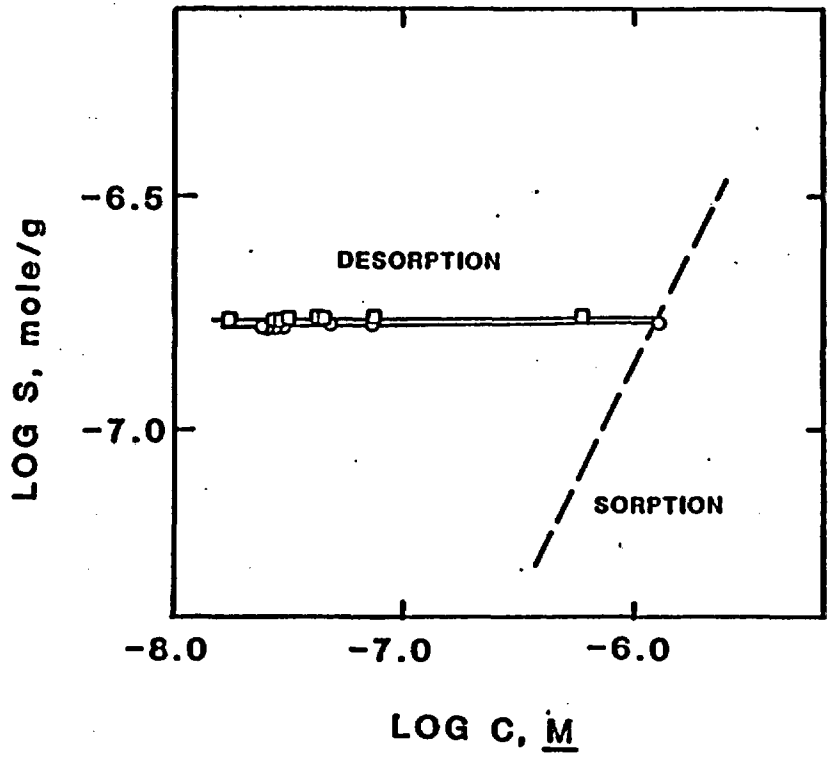
WP8608-M49

EFFECT OF CARBONATE CONCENTRATION ON K_d VALUES OF URANIUM, NEPTUNIUM, AND TECHNETIUM

RADIONUCLIDE		K_d values for solutions, mL/g	
		Without CO_3^{2-}	With 0.01M CO_3^{2-}
^{233}U	[U(IV)]	1,480 ± 870	100 ± 43
^{237}Np	[Np(IV)]	1,470 ± 810	29 ± 13
^{99}Tc	[Tc(IV)]	130 ± 110	1.5 ± 0.9

WP8608-M47

DESORPTION ISOTHERM FOR NEPTUNIUM DESORPTION FROM ALTERED PACKING MATERIAL



WP8503-95

RADIONUCLIDE SORPTION MECHANISMS

SURFACE COMPLEX FORMATION	ION EXCHANGE
Americium	Cesium
Plutonium	Strontium
Uranium	Radium
Neptunium	
Technetium	
Selenium	
Zirconium	

WP8608-M55

PLANS FOR FUTURE WORK

- Determine chemical behavior of additional radionuclides (e.g. nickel, zirconium, thorium)
- Measure sorption characteristics of additional solids (e.g. packing materials, corrosion products, colloids)
- Determine effects of organic ligands
- Field tests to determine applicability of laboratory data

WP8608-M52

SUMMARY OF RADIONUCLIDE BEHAVIOR IN A BASALT REPOSITORY

ACTINIDES

1. Exist in lower oxidation states (IV) or (III)
2. Hydroxyl and carbonate complex species predominate
3. Low solubilities (10^{-4} to 10^{-11})
4. Strongly sorbed by surface complex formation
5. Low mobility in groundwater

CARBON AND IODINE

1. Exist as anions in groundwater
2. Relatively high solubilities
3. No measurable sorption
4. High mobility in groundwater

TECHNETIUM AND SELENIUM

1. Exist in lower oxidation states, Tc(IV), Se^{o}, Se(-II)
2. Tc forms strong carbonate complexes
3. Low solubilities (10^{-4} to 10^{-8})
4. Strongly sorbed
5. Low obility for Tc, higher for Se

WP8608-M56