SCIENTIFIC NOTE BOOK # 373E
Radiation Effect on the Chemistry of Near-Field Environment

by

Lietai Yang

Southwest Research Institute
Center for Nuclear Waste Regulatory Analyses
San Antonio, Texas

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1. INITIAL ENTRIES

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Project Staff: Lietai Yang / N. Sridhar

(This layout of computerized Scientific Notebook is designed by A. Ghosh to address the criteria of CNWRA QAP-001)

1.1. Objectives

The objective of this study is to make bounding calculations for the radiolysis effect of the chemistry in the Nearfield Environment (NFE) of the proposed high-level waste repository at Yucca Mountain, Nevada. The calculation will be conducted on the basis of the EDA II (Enhanced Design Alternative II) Waste Package for typical Waste Form, 21 Fuel Assembly PWR Fuel.

[October 28, 1999]

1.2.

Radiation Field Calculations/Estimations for EDA II Design

The dose rate along the radius direction of the VA (Viability Assessment) Design was calculated by S.Su and M.N. Haas[1]. Figure 1 shows the dimension of the Waste Package Transporter. Figure 2 shows

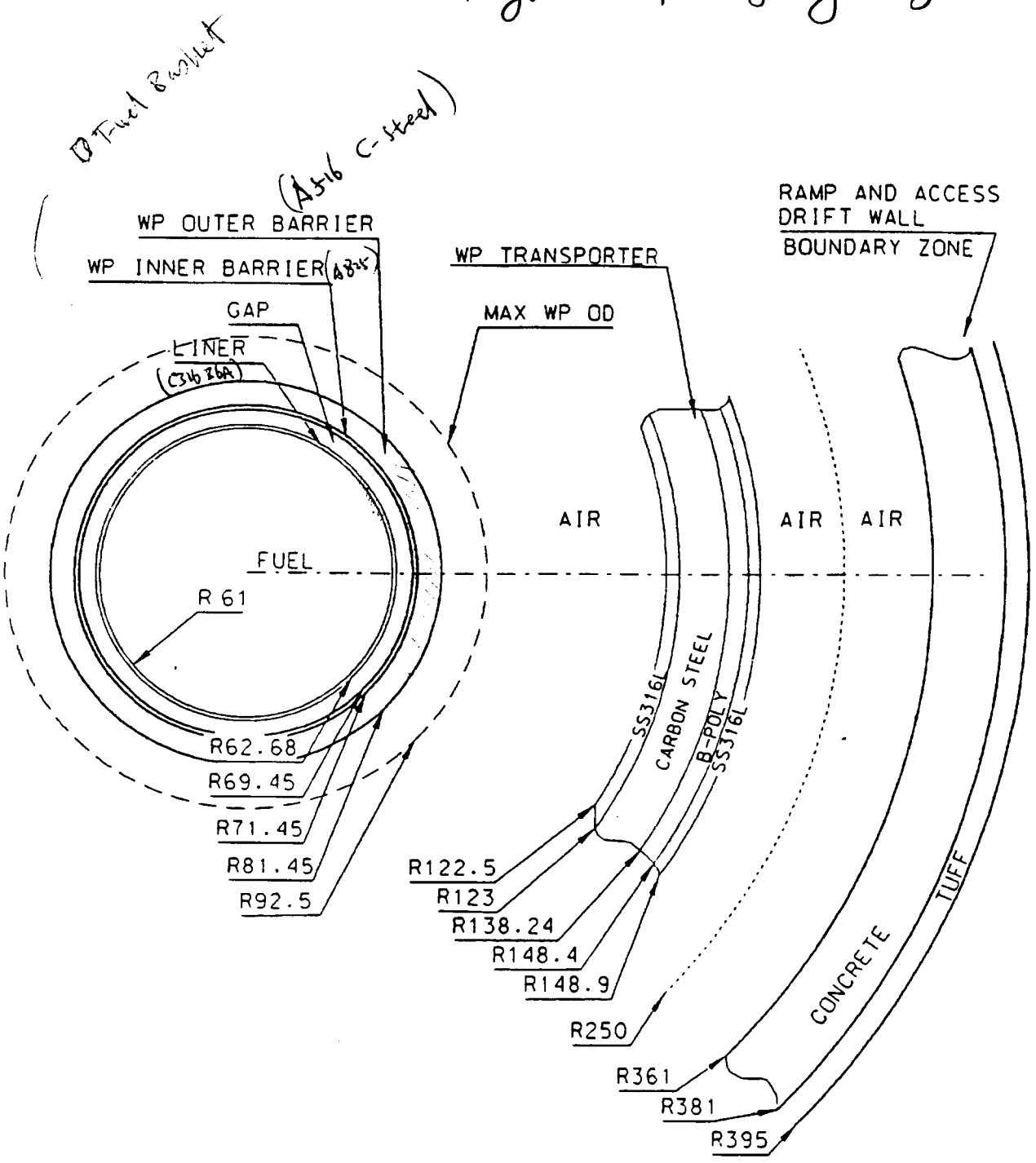
[1] S.Su and M.N. Haas, MGDS Subsurface Radiation Shielding Analysis (BCAE00000-01717-0200-00001 Rev 00, OCRWM (Office of Civilian Radioactive Waste Management) Report (1997). Note: MGDS stands for "Mined Geologic Disposal System"

Content of Figure 1 is in the Insert for Figure 1 (Next Page).

L. Yang.

Figure 1 Dimension of a Typical VA Waste Package

Insert for Page 2, Figure 1, J. Yang.



ALL DIMENSIONS ARE IN CENTIMETERS

FIGURE 7.5-1
WASTE PACKAGE TRANSPORTER RADIAL SHIELD MODEL

CAD FILE: t:\repss\nucl\flg\ssnu0005.flg

2 shows the radial dose rate profile for waste package transporter. The gamma dose rates are 35.5 rem/h and 7.6E4 rem/h for Wp outside surface and inside respectively. The neutron dose rates are 4.3 and 33 rem/h for WP outside surface and inside respectively.

Differences Between the designs of EDA II and VA

Figure 3 shows the EDA II design. In EDA II design, the there are a 5 cm SS316 inside shell and a 2cm C-22 alloy outside shell. Further more, the EDA II design has a drip shield over the WP container.

Dose rate of the EDA II WP

Compared with the VA design, the only differences between the new container and the VA container are (1) the total thickness of the new container is less than that of VA design (2 cm A825 inner barrier and 10 cm A516 carbon steel barrier); (2) the materials of the new container are different. Therefore, the radial dose rate profile can be obtained from Figure 2 based on the shielding property differences between the EDA II and Va designs.

Shielding properties of the materials used in the EDA II and the VA designs

The shielding properties of the VA and the EDA II materials are given in Figure 4.

The total attennuation coefficient for laminated shield can be calculated using the following equation[2]:

$$\mu t = \sum \left(\left(\frac{\mu}{\rho} \right)_i \rho_i t_i \right) \qquad (1)$$

where μ is the mean linear attenuation coefficient, t the total thickness, $(\mu/\rho)_i$ the mass attenuation coefficient of the ith component, ρ_i the density of the ith component, and t_i the thickness of the ith component shield.

[2]Etherington, Ed 1958 Page 7-71

assumed the same

Fig. 7.5-2 Radial Dose Rate Profile for Waste Package Transporter

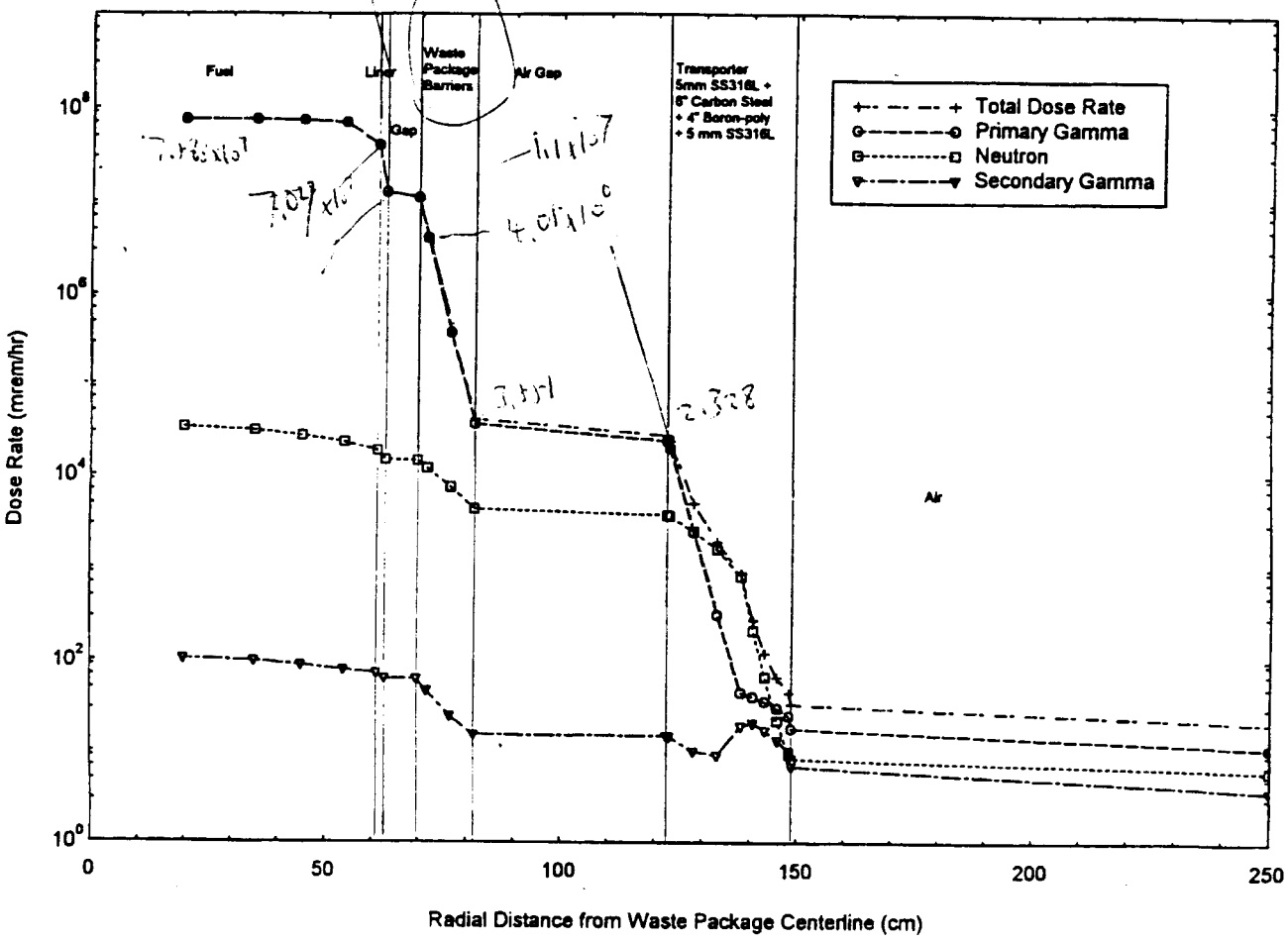


Figure 2 Radial Dose Profile

Numerical value see Insert after this page.

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Insert for Page 4 (after Page 4)

TABLE 7.5-2
RADIAL DOSE RATE PROFILE FOR WASTE PACKAGE TRANSPORTER

RADIAL DOSE RATE RESULTS FOR WASTE PACKAGE TRANSPORTER									
Region	Radial Dist. (cm)	Dose Rate (mrem/hr)				Fractional Standard Deviation			
		Neutron	Primary G	Second. G	Total	Neutron	Primary G	Second. G	Total
		tsprt01n.out	tsprt01g.out	tsprt01n.out	calculated	tsprt01n.out	tsprt01g.out	tsprt01n.out	calculated
Fuel	20.00	3.298E+04	7.588E+07	1.031E+02	7.591E+07	0.0071	0.0242	0.0168	0.0242
	35.00	3.002E+04	7.490E+07	9.794E+01	7.493E+07	0.0054	0.0156	0.0140	0.0156
	45.00	2.652E+04	7.399E+07	8.795E+01	7.402E+07	0.0048	0.0117	0.0127	0.0117
	54.00	2.254E+04	7.027E+07	7.771E+01	7.029E+07	0.0048	0.0089	0.0120	0.0089
Liner	61.00	1.820E+04	4.019E+07	7.126E+01	4.021E+07	0.0050	0.0103	0.0132	0.0103
Gap	62.68	1.443E+04	1.251E+07	6.252E+01	1.252E+07	0.0051	0.0095	0.0166	0.0095
	69.45	1.400E+04	1.102E+07	6.136E+01	1.103E+07	0.0058	0.0106	0.0178	0.0106
WP	71.45	1.160E+04	4.054E+06	4.624E+01	4.066E+06	0.0054	0.0125	0.0139	0.0125
	76.45	7.228E+03	3.798E+05	2.439E+01	3.871E+05	0.0059	0.0197	0.0177	0.0193
	81.45	4.307E+03	3.551E+04	1.527E+01	3.983E+04	0.0061	0.0220	0.0246	0.0196
Transporter	122.50	3.716E+03	2.328E+04	1.496E+01	2.701E+04	0.0067	0.0216	0.0275	0.0186
	123.00	3.614E+03	1.955E+04	1.468E+01	2.318E+04	0.0065	0.0222	0.0208	0.0188
	128.08	2.499E+03	2.439E+03	9.972E+00	4.948E+03	0.0066	0.0276	0.0218	0.0140
	133.16	1.594E+03	3.129E+02	9.087E+00	1.916E+03	0.0067	0.0367	0.0246	0.0082
	138.24	8.070E+02	4.460E+01	1.921E+01	8.708E+02	0.0065	0.0393	0.0240	0.0064
	140.78	2.141E+02	3.966E+01	2.079E+01	2.746E+02	0.0083	0.0403	0.0180	0.0088
	143.32	6.607E+01	3.522E+01	1.725E+01	1.185E+02	0.0107	0.0412	0.0173	0.0138
	145.86	2.188E+01	2.988E+01	1.332E+01	6.508E+01	0.0137	0.0372	0.0176	0.0181
	148.40	9.289E+00	2.455E+01	1.011E+01	4.395E+01	0.0192	0.0386	0.0189	0.0224
	148.90	8.302E+00	1.791E+01	6.781E+00	3.299E+01	0.0204	0.0338	0.0211	0.0195
Air Space	250.00	6.024E+00	1.083E+01	3.633E+00	2.049E+01	0.0225	0.0460	0.0206	0.0255
Drift Wall	361.00	5.412E+00	8.305E+00	2.789E+00	1.651E+01	0.0234	0.0433	0.0205	0.0234

Numerical Value for

Fig. 2.

Content of this page is shown in the Insert for Fig.3 (next page).

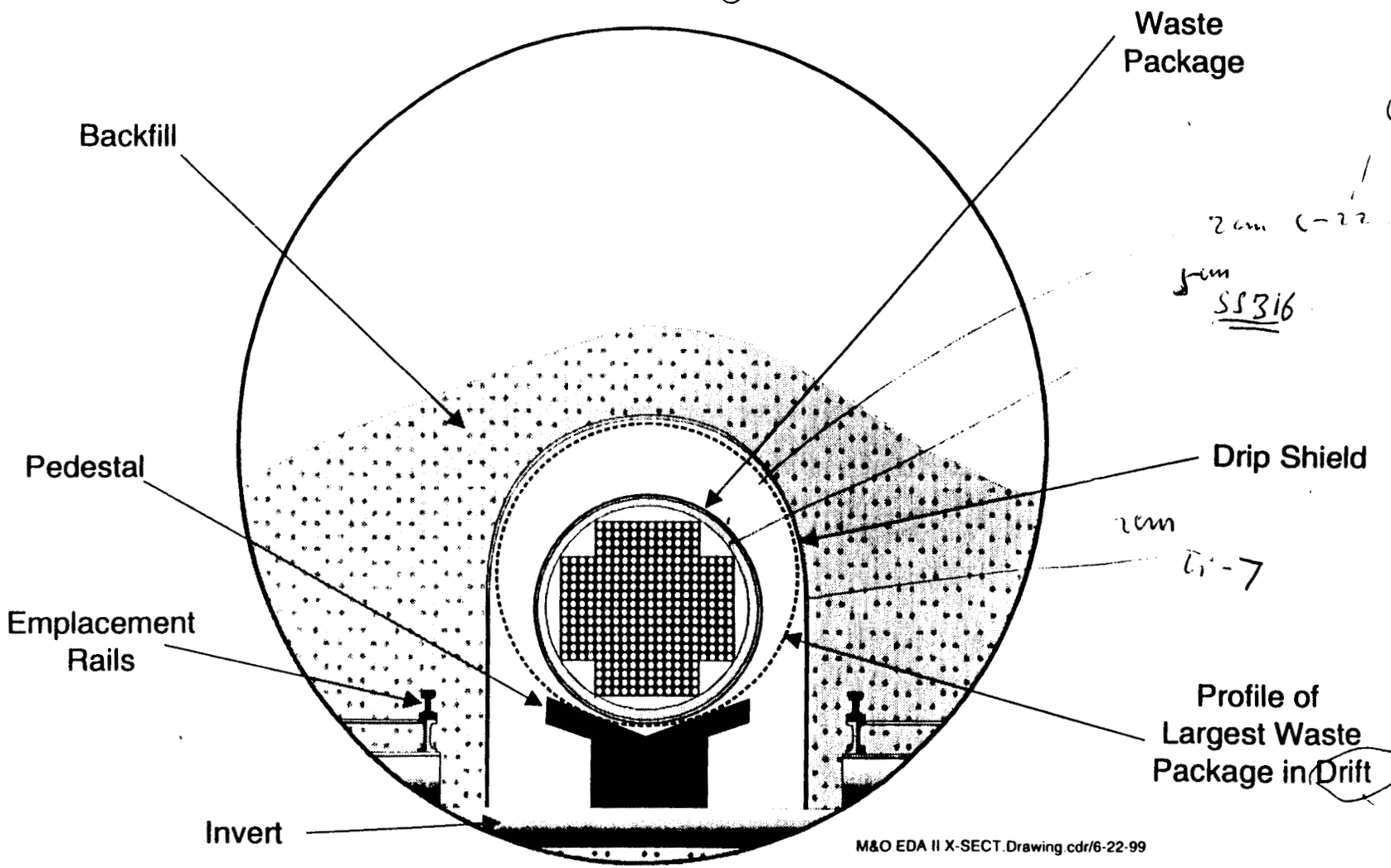
L. Yang.

Figure 3 EDA II Design

Engineered Barrier System of EDA II After Closure

Liner ?

Insert For Fig. 3



Composition ?

2cm C-22

5cm SS316

2cm Ti-7

L.Y.

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Shielding Properties of elements

Properites of elements#

Element	Z	Density	Gamma Mass Absorption, cm^2/g) 0.5 MeV	1MeV	0.6MeV*	Gamma Linear Abspt, cm^2/g) 0.5 MeV	1MeV	0.6MeV	den(g/cm^3)
Fe	26	7.85	0.084	0.0598	0.08158	0.6594	0.46943	0.640403	
Cr	24	6.92	0.0827	0.0589	0.08032	0.572284	0.407588	0.555814	
Ni	28	8.9	0.0866	0.0613	0.08407	0.77074	0.54557	0.748223	
Mo	42	10.2	0.0879	0.0581	0.08492	0.89658	0.59262	0.866184	
Cu	29	8.89	0.0834	0.0588	0.08094	0.741426	0.522732	0.719557	
Mn	25	7.2	0.0817	0.0583	0.07936	0.58824	0.41976	0.571392	
Co	27	8.71	0.0828	0.0598	0.0805	0.721188	0.520858	0.701155	
W**		19.3	0.125	0.064	0.1189	2.4125	1.2352	2.29477	
									Total
Ti	22	4.5	0.0818	0.0588	0.0795	0.3681	0.2646	0.35775	
Lead	82	11.347	0.152	0.0703	0.14383	1.724744	0.797694	1.632039	

Rockwell III, 1956, Pp..462-465
*interpolated from 0.5 to 1 MeV , 0.6 is the main source

** Etherington, 1958, P 762

Shielding Properties of Alloys

Composition*** (wt%) Alloy 825	A22****	SS316B6 A	SS316L	A516 C-Steel		Gamma mass & linear absorption coefficient Alloy 825	A22****	SS316B6 A	SS316L	A516 C-Steel
8.14	8.69	7.745	7.95	7.83		8.14	8.69	7.745	7.95	7.83
28.6	4	60.6	65.5	98.5		0.023784	0.003263	0.050653	0.053975	0.08158
21.5	21	19	17			0.017603	0.016867	0.015636	0.013792	0
42	56	13.5	12			0.035993	0.047079	0.011629	0.01019	0
3	13	2.5	2.5			0.002597	0.01104	0.002175	0.002144	0
2						0.00165	0	0	0	0
1	0.5	2	2	0		0.000809	0.000397	0.001626	0.001603	0
	2.5					0	0.002013	0	0	0
	3					0	0.003567	0	0	0
98.1	100	97.6	99	98.5	Mass=	0.082436	0.084226	0.081719	0.081705	0.08158
					Linear =	0.671032	0.73192	0.632915	0.649554	0.638771

*** Su et al (1997), page 20-22

**** Cragnolino et al, 1999 p. 2-3

Figure 4 Shielding properties of the materials used in the WP designs

Referes to Figure 1, the thickness from r=69.45 cm to 69.45+5+2 cm was 2 cm A825 alloy and 5 cm carbon steel, which will be replaced by 5 cm SS316 L and 2 cm A22 alloy in the EDA II design. For this thickness, the mean attrenuation cofficient for the VA design is

$$\mu = (0.082436) * 8.14 * 2 + 0.08158 * 7.83 * 5)/7$$
$$= 4.53468/7$$
$$= 0.6478$$

The first term in the above equation is for alloy 825 and the second term is for Carbon steel(the data is from Figure 4).

Similarly, for the thickness from the thickness from r=69.45 cm to 69.45+5+2 cm, the mean attrenuation cofficient for the EDA II design is

$$\mu = (0.081705) * 7.95 * 5 + (0.084226) * 8.69 * 2)/7$$
$$= 4.7116/7$$
$$= 0.6731$$

The first term in the above equation is for SS316L and the second term is for alloy A22(the data is from Figure 4).

The ratio is

$$0.6478/0.6731 = 0.9624$$

Figure 5 is the enlarged view of Figure 2 for the wall thickness from 60 to 85 cm. The solid line is the Gamma dose rate for the VA design and the dashed line is for the EDA II design. The value for the EDA II design is derived based the VA value with a correction factor of 0.962.

The radiation dose value at the outside surface of the EDA II design is 360 rem/hr. Or 260 Rad/hour for Gamma (3.6 Gy/hr).

According to Figure 2, at 76 cm, the Gamma dose is 380 and the Neutron dose rate is 7.2 rem/hr. Therefore, the contribution to the total dose from neutron is less than 2% (for VA design). Hence the neutron dose is neglected in the present analysis.

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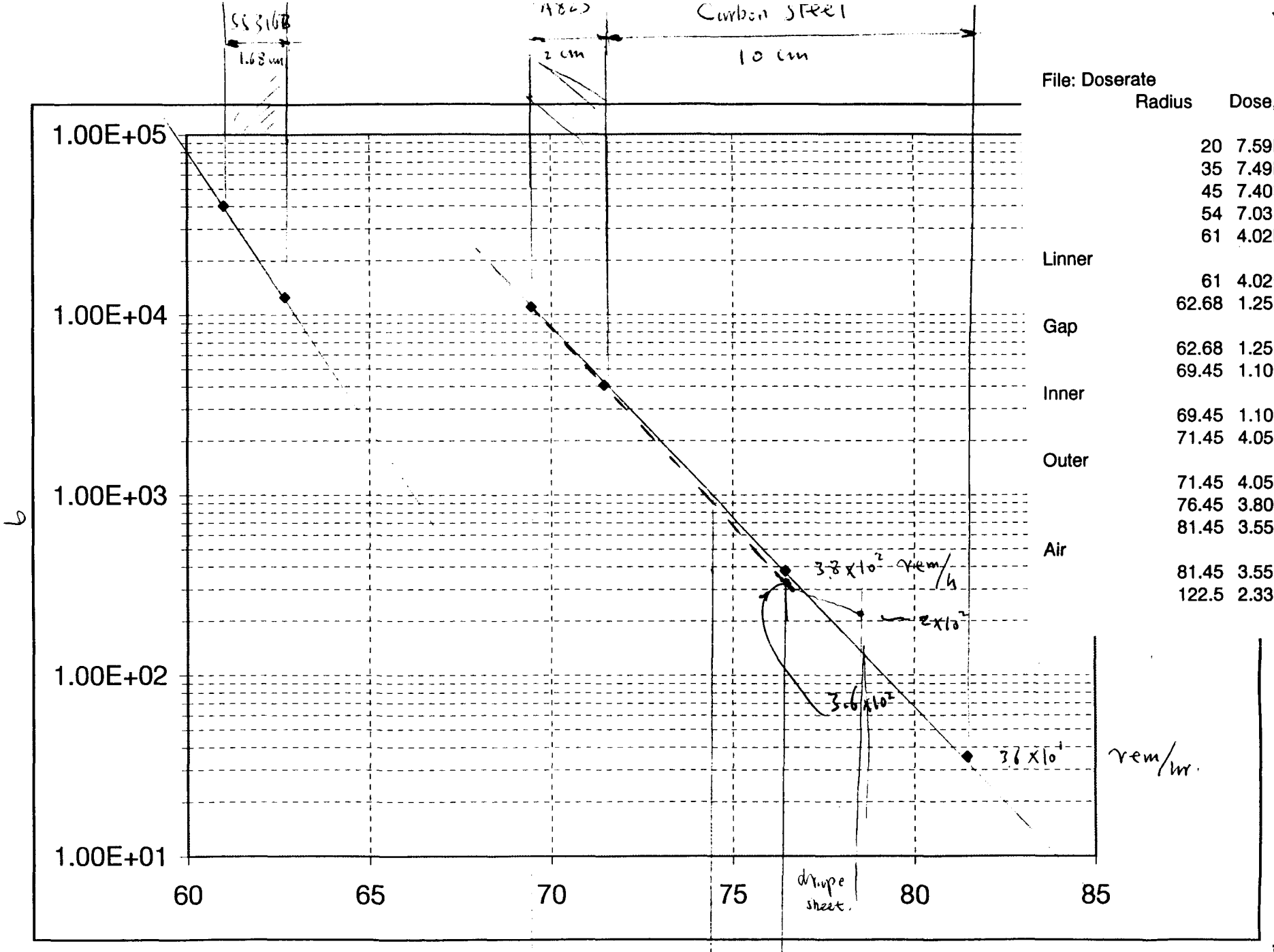
Figure 5 Gamma Dose rate for VA and EDA II Designs. Solid line for VA design and dashed Line for EDA II Design



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	Radius	Dose, Rad/hr
	20	7.59E+04
	35	7.49E+04
	45	7.40E+04
	54	7.03E+04
	61	4.02E+04
Linner		
	61	4.02E+04
	62.68	1.25E+04
Gap		
	62.68	1.25E+04
	69.45	1.10E+04
Inner		
	69.45	1.10E+04
	71.45	4.05E+03
Outer		
	71.45	4.05E+03
	76.45	3.80E+02
	81.45	3.55E+01
Air		
	81.45	3.55E+01
	122.5	2.33E+01

New EDA II → SS316L 5 cm | A22 2 cm

Insert For Fig. 5

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Entries into Scientific Notebook No 373E for period Oct. 28/99 to Jan. 7/00 have been made by

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No original text entered into this Scientific Notebook has been removed

L. Yang / 08/15/00

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July 10, 2000 (Second Printing Period)
(From Jan. 14, 2000 to July 10, 2000)

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1. INITIAL ENTRIES

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Project Title: Radiation Effect on the Chemistry of Near field Environment
Project Number: 20-1402-561

Project Staff: Lietai Yang / N. Sridhar

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1.1. Objectives

The objective of this study is to make bounding calculations for the radiolysis effect of the chemistry in the Nearfield Environment (NFE) of the proposed high-level waste repository at Yucca Mountain, Nevada. The calculation will be conducted on the basis of the EDA II (Enhanced Design Alternative II) Waste Package for typical Waste Form, 21 Fuel Assembly PWR Fuel.

[October 28, 1999]

January 14, 2000

Wilder's Report (1993) (Reference Enfe-93-04-Reed[1]) give the following information:

{
Composition of emplacement gas phase: Water-vapour-saturated with up to 0.13 mol% CO_2.
R. Humidity: 3.9 to 35 for the central pannels during the firdt 300 yrs.
Water mass fraction in the WP vicinity is 100% as long as boiling occurs.
Boiling point (Tb=96 at the altitude, P=640 Torr)
For such locations, the relative humidity would remain close to 100% through out the repository history.

Radiation at the container surface has effective half-life of approximately 30 years.

Certain loading scenarios, T at WP edge may never exceed Tb.

5.3 Radiolytic Yields in an Air-Water-Vapor System

Key products:

Nitrogen fixation products: nitrogen acids, nitrogen oxides, and ammonia
Hydrogenous species: Atomic and molecular hydrogen
Oxygen-containing oxidizing species: oxy-radicals ozone, and hydrogen peroxide.

5.3.1Primary Yields of Bulk Components

-Bulk Components: O_2 N_2 Ar, CO_2, H_2O vapor

5.3.2 Radiolytic Yield of Nitrogen Oxides and Acids

Nitric Acid can be absorbed onto the surface of the WP depending on relative humidity of the system

?? Question: What is the relationship with water contents–LY??

---

[1]Chapter 5 by D.T. Reed et al, in "Preliminary Near-Field Environment Report" Vol. II: by D.G. Wilder 1993.

Nitrogen Oxides and Acids -Nitrogen fixation products

acids OH+NO = HONO
OH+NO2=HONO2

in moisture air. Once formed may decompose because he decomposed products has lower energy (compared with NO or NO2 the acid has lower energy though).

So nitrogen oxides generated are rapidly converted to acids by OH

G(OH)=4.25 to as high as --8.2 mole/100 eV which is high (in irradiated air-water-vapor system)

In low humid systems, (water vapor to air ratio < 0.1)The yield of Nitric acid is equal to the yield of NO2 in the analogous dry air system.

In high humid systems, (water vapor to air ratio > 0.1)The yield of NO2 not well characterized. The yield of Nox was 0.5 to 2.5 for RH=5 to 90 at 28 to 87 oC.

Cross Check: G(HNO3) =1.9 suggested by W.G. Burns et al ,1982. (Nature or J. N. Materials both)

Their tests were 0.01 to 0.4 (10,000 Rad to 400,000 Rad/h , see Reference ENFE-91-09[2])

N2O. Figure 5 shows similar yield as NO2 in low humidity air at 87 to 150 oC.

Table 5-1, G(N2O)=0.06 100RH air
=0.5 to 0.8 at low RH or dry.
At high relative H, G(N2O) lowered because rapid rmoval of NO2 (dioxide) by OH generated from Water vapour (ENFE-91-04REV0).

N2O is from the reduction of NO2 and it is relatively stable. It will reform N2, O2, and NO2 at high concentrations (Reference: ENFE-91-09[2] Table 2) .

---

[2] DE92004722" Process in Assessing the Effect of Ionization Radiation on the Anticipated Waste Package Environment at the Yucca Mountain Potential Repository Site" Argonne National Lab., IL, 1991.

NH3 formation, some metal ammonia cracking

at low O2, 0.1 mole%, in N2-H2O system, G(NH3) = 0.03, very low.

Small amount of NH3 also found in Air-Water vapor mixtures. Oxygen does not preclude NH3 formation in small amount.

Atomic Hydrogen:

Primary yield from water vapor is 0.45 to 0.51 for H2 and 4.2 to 7.2 for H.

In air containing systems, H rapidly converted to HO2. .

Best overall yield for hydrogen in just the primay hydrogen.

In air-water vapour, Hydrogen is observed but no build up with dose.

Ozone, Hydrogen Peroxide, Oxy-radicals

Ozone can be produced by irradiating O2, however, the build up is small, effect minor compared with the other products

H2O2, generated as a secondary reaction:

OH +HO2 = H2O2. Yields are also low. And concentration does not build up with dose.

(Swallow Book, Page 122. Excitation of water leads to formation of H, OH, H2, and O.
When water vapor contains O2, the H will be scavenged not to form H2, G(H2) reduced to 0.5, the primary yield.)

(In "Radiation Chemistry book, Farhataziz Ed, Page: 315 for water vapor

2HO2=H2O2 +O k= 3.6x10^-12 cm^3 Molecule s^-1

2OH +H2O =H2O2 +H2O k= 1x10^-31 cm^6 Molecule
H+H2O2 = H2O + OH k= 1x10^-13 cm^3..... (not much because H very low in air)

OH +H2O2 = H2O +HO2 k= 2x10^-12 cm^3) (Likely)

G Values Page 315

G(e-) = 3.3
G(H3O+ .nH2O+= 3.3

OH 6.2
H 4.1
O 1.08
H2 0.51
)

(In Spinks' book, P245 for water vapor Primary processes are

H2O–> H , OH H2, O, H2O+ e-

In closed systems, back reaction takes place as soon as there is some concentration build up:

2OH + M = H2O2
H+H2O2 = H2O +OH
O + H2O +M = H2O2 +M

)

(Question: ?? I have not seen a G(H2O2) given for the water vapor system–LY)

(F.A. Cotton, "Advanced Inorganic Chemistry, 1962" P281, H2O2 has a strong oxidizing nature and ready decomposition, even in the presence of traces of many heavy metal irons according to
2H2O2 = 2H2O + O2)

In dilute solution, it is more acidic than water:

H2O2 = H+ +HO$^-_2$ K20oC) =1.5x10^-12

)

,

Yield of OH is high, 4.25 to 8.2 (earlier) mainly contributed to Nitric Acid production and to Lowering pH.

G(NOx all) is about 3.2 at 25 and lower at 90, 150 200oC

(Though, Reference Enfe 87-12, Page 10, G(Nitrogen Oxide) =6)

(Observation: So there must be extra OH??)

DOSE RATE ESTIMATIONS

Cs 0.662 MeV
30.2 y half-life

The Dose rate should be expressed as

$$D=Do_1 \exp(-a_1t) + Do_2 \exp(-a_2t) + Do_3 \exp(-a_1t) + Do_4 \exp(-a_4t) + \ldots\ldots$$

According to MGDS Subsurface Radiation Shielding Analysis, (1997), Page 96
D(Gamma Regression) = 34.4 exp(-0.0971t) (0 to 10 years) [T(1/2)=7.15] 34.44

(1) D(Gamma Regression) = 15.34 exp(-0.0314t) (0 to 160 years) [T(1/2)=22.08]
(2) D(Gamma Regression) =7.88 exp(-0.0251t) (30 to 160 years) [T(1/2)=27.6]
(3) D(Gamma Regression) = 6.35 exp(-0.0233t) (90 to 160 years) [T(½)=29.75]
(4) D(Gamma Regression) = 6.12 exp(-0.02303t) (120 to 160 years) [T(1/2)=30.11]

(1)' D(Neutron Regression) = 2.792 exp(-0.0368t) (0 to 10 years) [T(1/2)=18.83]
(1) D(Nutron Regression) = 2.031 exp(-0.0248t) (0 to 160 years) [T(½)=27.94]

(2) D(Nutron Regression) =1.33 exp(-0.0208t) (30 to 160 years) [T(1/2)=33.3]
(3) D(Nutron Regression) = 0.45 exp(-0.0119t) (90 to 160 years) [T(1/2)=58.25]
(4) D(Nutron Regression) = 0.266 exp(-0.0081t) (120 to 160 years) [T(1/2)=85.57]

We should use (4) to predict the dose beyond 160 years. However as the real data decays slower than even (4). The prediction based on (4) is not bounding!!

Background level :

0.004 mrem/h (from James Weldy's Presentation at CNWRA) and 0.01 mrem/h measured at CNER, the research facility I used to work at)

Does rate at the outside surface at time zero (emplacement Time):

From Note book 1, there should be
380 rem/hr gamma.

Based on the following Table, the EDA II design should have and 7.22 rem/h neutron at the outside surface (Although Page 96 gives 2.793 rem/hr).

Because it has 5+2 cm thickness compared with 2+10 =12 cm thickness. Omit the difference in materials

MGDS Subsurface Radiation Shielding Analysis, (1997), Page 79				
File: Doserate		Sheet: VA-Design		
		Gamma		Neutron
	Radius	Dose, Rad/hr		
			log (dose)	
	20	7.59E+04	4.880127	
	35	7.49E+04	4.874482	
	45	7.40E+04	4.869173	
	54	7.03E+04	4.84677	
	61	4.02E+04	4.604118	
Linner				
	61	4.02E+04	4.604118	
	62.68	1.25E+04	4.097257	
Gap				

	62.68	1.25E+04	4.097257	
	69.45	1.10E+04	4.042182	14
Inner				
	69.45	1.10E+04	4.042182	14
	71.45	4.05E+03	3.607884	11.6
Outer				
	71.45	4.05E+03	3.607884	11.6
(Outside EDAII)	76.45	3.80E+02	2.579555	7.228
Outside WP(VA)	81.45	3.55E+01	1.550351	4.307
Air				
	81.45	3.55E+01	1.550351	4.307
	122.5	2.33E+01	1.366983	

Based on the data between 120 to 160 years to extrapolate the dose rate for gamma:

D(Gamma Regression) = 380/36 {6.12 exp(-0.02303t) } (120 to 160 years) [T(½)=30.11]

and Neutron:

D(Nutron Regression) = 7.22/2.792 { 0.266 exp(-0.0081t)} (120 to 160 years) [T(1/2)=85.57]

The data between 120 to 160 is the best suitable data to extrapolate into several thousands years (However may not be conservative enough because as the data shift away from the origin, the half time is getting longer.)

Table Estimation of Gamma and Neutron based on the regression equations

	Gamma					Neutron				
t0=	0	0	30	90	120	0	0	30	90	120
		(1)	(2)	(3)	(4)		(1)	(2)	(3)	(4)
D0	363.111	161.922	83.1778	67.0278	64.6	7.22518	5.25585	3.44179	1.16452	0.68836
a1	-0.097	-0.0314	-0.0251	-0.0233	-0.023	-0.0368	-0.0248	-0.0208	-0.0119	-0.0081
	Multiplied by					Miltiplied by				
	380/36					7.22/2.792				
t										

[8] LY 2.LY 4/15/01

0	363.111	161.922				7.22518	5.25585			
10	137.649	118.287				5.00067	4.10145			
20		86.4111					3.20061			
30		63.125	39.1727				2.49763	1.8441		
40		46.114	30.4772				1.94905	1.49779		
50		33.6871	23.712				1.52096	1.21652		
60		24.6091	18.4484				1.1869	0.98806		
70		17.9774	14.3533				0.92621	0.80251		
80		13.1328	11.1672				0.72277	0.65181		
90		9.59379	8.68833	8.23264			0.56402	0.5294	0.39904	
100		7.00845	6.75971	6.52152			0.44014	0.42998	0.35427	
110		5.1198	5.25921	5.16604			0.34347	0.34924	0.31452	
120		3.74011	4.09178	4.0923	4.07885		0.26803	0.28365	0.27924	0.26042
130		2.73222	3.1835	3.24173	3.24013		0.20916	0.23038	0.24791	0.24016
140		1.99594	2.47683	2.56795	2.57388		0.16322	0.18712	0.2201	0.22147
150		1.45807	1.92703	2.03421	2.04463		0.12737	0.15198	0.1954	0.20424
160		1.06515	1.49927	1.61141	1.6242		0.09939	0.12344	0.17348	0.18835
170		0.77811	1.16647	1.27648	1.29022		0.07756	0.10026	0.15402	0.1737
180		0.56843	0.90754	1.01117	1.02492		0.06053	0.08143	0.13674	0.16018
190		0.41525	0.70608	0.801	0.81417		0.04723	0.06614	0.1214	0.14772
200		0.30335	0.54935	0.63452	0.64676		0.03686	0.05372	0.10778	0.13623
210		0.2216	0.42741	0.50263	0.51377		0.02876	0.04363	0.09568	0.12563
220		0.16188	0.33253	0.39816	0.40812		0.02245	0.03544	0.08495	0.11585
230		0.11826	0.25872	0.31541	0.3242		0.01752	0.02878	0.07542	0.10684
240		0.08639	0.20129	0.24985	0.25754		0.01367	0.02338	0.06696	0.09852
250		0.06311	0.15661	0.19792	0.20458		0.01067	0.01899	0.05945	0.09086
260		0.0461	0.12184	0.15678	0.16251		0.00832	0.01542	0.05278	0.08379
300		0.01313	0.04464	0.06174	0.06471		0.00309	0.00671	0.03279	0.0606
350		0.00273	0.01273	0.01926	0.02047		0.00089	0.00237	0.01808	0.04042
400		0.00057	0.00363	0.00601	0.00648		0.00026	0.00084	0.00997	0.02696
450		0.00012	0.00103	0.00187	0.00205		7.5E-05	0.0003	0.0055	0.01798
500		2.5E-05	0.00029	0.00058	0.00065		2.2E-05	0.0001	0.00303	0.01199
550		5.1E-06	8.4E-05	0.00018	0.0002		6.3E-06	3.7E-05	0.00167	0.008
600		1.1E-06	2.4E-05	5.7E-05	6.5E-05		1.8E-06	1.3E-05	0.00092	0.00534
650		2.2E-07	6.8E-06	1.8E-05	2.1E-05		5.2E-07	4.6E-06	0.00051	0.00356
700		4.6E-08	1.9E-06	5.5E-06	6.5E-06		1.5E-07	1.6E-06	0.00028	0.00237
750		9.6E-09	5.6E-07	1.7E-06	2.1E-06		4.4E-08	5.8E-07	0.00015	0.00158

800		2E-09	1.6E-07	5.4E-07	6.5E-07		1.3E-08	2E-07	8.5E-05	0.00106
Bacground level at CNER										
		0.1 uSv/h	0.01 m rem/h							
Background Presentation:		James	0.004	mrem/h						
			4.00E-06							

Integrated Dose Calculations

Table 7.7-4 (MGDS Subsurface Radiation Shielding Analysis, (1997), Page 99) shows the integrated dose as a function of time. Figure 1 shows the log (Dose) vs time plot. The slope in Figure 1 becomes smaller as the time increases. If we take the last 7 data points (from year 90 to year 150) to extrapolated, we have

Table in the reference Pages 99 and 100 give the following data.

MGDS Subsurface Radiation Shielding Analysis, (1997), Page 99					
	Integrated Dose (rem)		lg(Dose / rem)		
Year	Neutron	Gamma	Neutron	Gamma	
0	0	0	#NUM!	#NUM!	
5	1.12E+05	1.19E+06	5.048442	6.074085	
10	2.05E+05	1.91E+06	5.31133	6.281488	
20	3.47E+05	2.77E+06	5.540329	6.44295	
30	4.47E+05	3.26E+06	5.649821	6.513351	
40	5.17E+05	3.58E+06	5.713407	6.55364	
50	5.67E+05	3.80E+06	5.753813	6.579898	
60	6.00E+05	3.97E+06	5.778441	6.598462	
70	6.32E+05	4.09E+06	5.800923	6.612148	
80	6.54E+05	4.19E+06	5.815312	6.622525	
90	6.70E+05	4.27E+06	5.826075	6.63053	
100	6.83E+05	4.33E+06	5.834548	6.636688	
110	6.94E+05	4.38E+06	5.841485	6.641474	
120	7.04E+05	4.42E+06	5.847449	6.645226	
130	7.12E+05	4.45E+06	5.852663	6.648262	
140	7.20E+05	4.47E+06	5.857332	6.650599	
150	7.27E+05	4.49E+06	5.861654	6.65244	

after emplacement

L.Y. 11/20/00

~~[10]~~ 17. 8.00 4/18/01

Log (Gamma/rem) = 6.6006 +0.000358 t(year)

Log (Neutron/rem) = 5.776 +0.000584 t(year)

Note, the extrapolation beyond 150 year based on the above linear regressions over estimates the dose because Figure 1 shows that slope becomes lower as time increases. The extrapolations are shown in Figure 2.

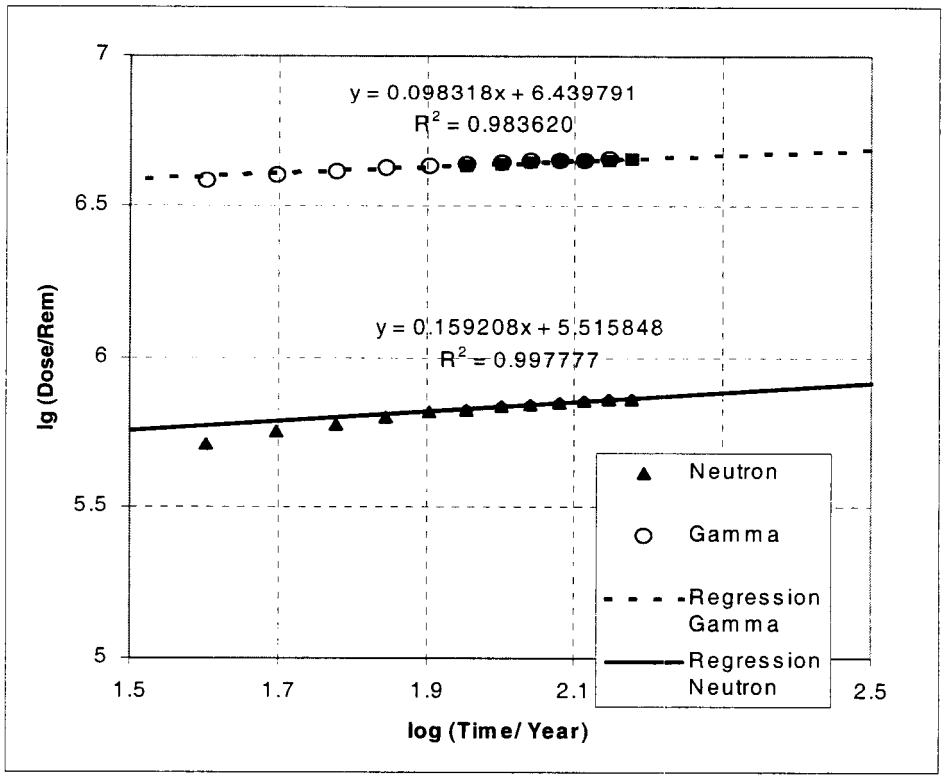


Figure 1 Integrated dose and regression for time period from 90 to 150 years using log scale for time VA Design

According to Figure 2, the integrated dose from year 50 to year 2000 can be calculated as in Table 2

Table 2

Dose calculation from 50 to 2000 years						
Year	Cofficients of regression	Log (Dose/rem)		Dose/rem		
		Neutron	Gamma	Neutron	Gamma	total
	A	5.7758	6.6006			
	B	0.000584	0.000358			
50		5.805	6.6185	6.3826E+05	4.1543E+06	4.7926E+06
2000		6.9438	7.3166	8.7862E+06	2.0730E+07	2.9516E+07
Difference						2.4724E+07

The integrated dose from year 50 to 2000 would be 2.47×10^7 rem.

It seems using the above approximation would give too much over estimation. The following paragraph tries to use log(dose) vs log (time) relationship to extrapolate. Figures 3 and 4 shows the regression with the x on log scale. The regression still over estimate the dose as the dose tends to level as time increases. Since the x is on log scale the increase of dose is much slower than in the Figure 2.

Estimation based on LOG term extrapolation

The regression equations are:

`log (D/rem) = 0.09832 log(t/year)` +6.44 for Gamma

`log (D/rem) = 0.1592 log(t/year)` +5.516 for neutron

Table 3

Dose calculation from 50 to 2000 years							
			Log (Dose/rem)		Dose/rem		
			Neutron	Gamma	Neutron	Gamma	total
Year	log year	A	5.516	6.44			
		B	0.1592	0.09832			
50	1.69897		5.786476	6.60704273	6.1161E+05	4.0462E+06	4.6578E+06

2000	3.30103		6.041524	6.76455727	1.1003E+06	5.8151E+06	6.9154E+06
Difference							2.2577E+06

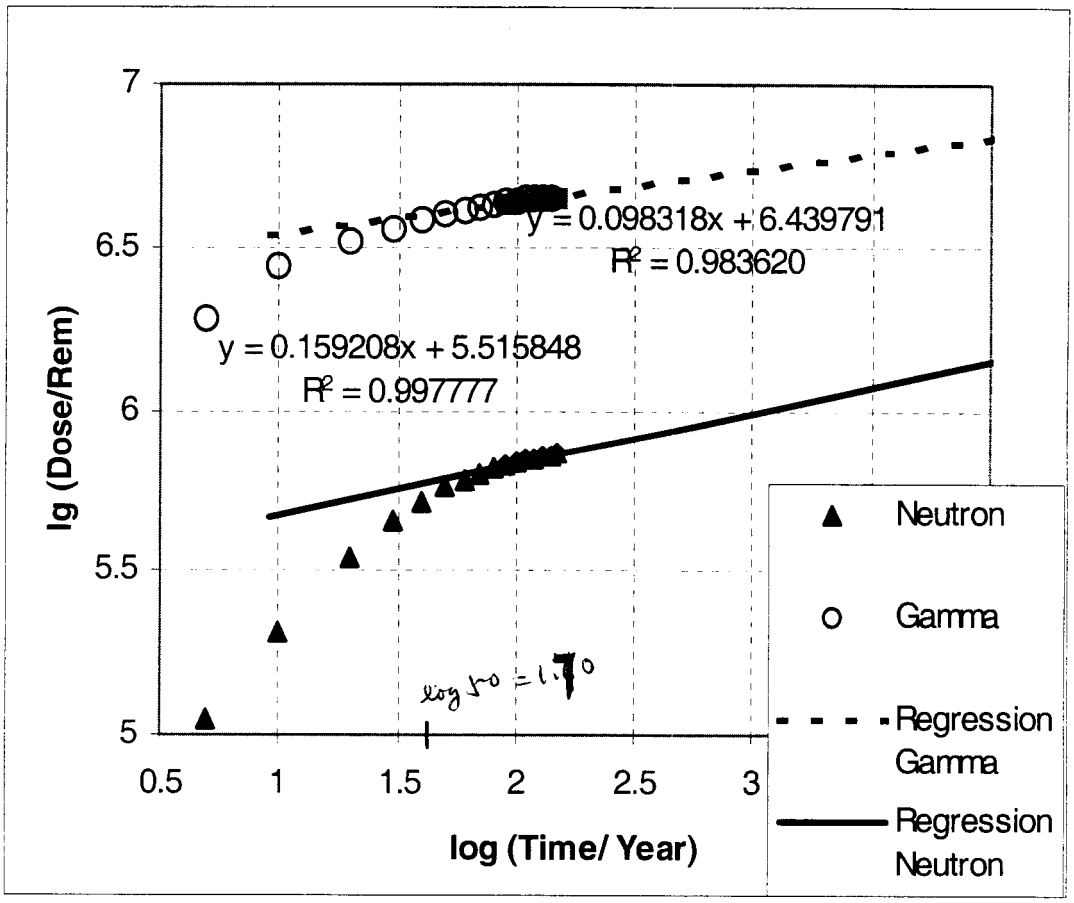


Figure 2 Log D vs log t extrapolation

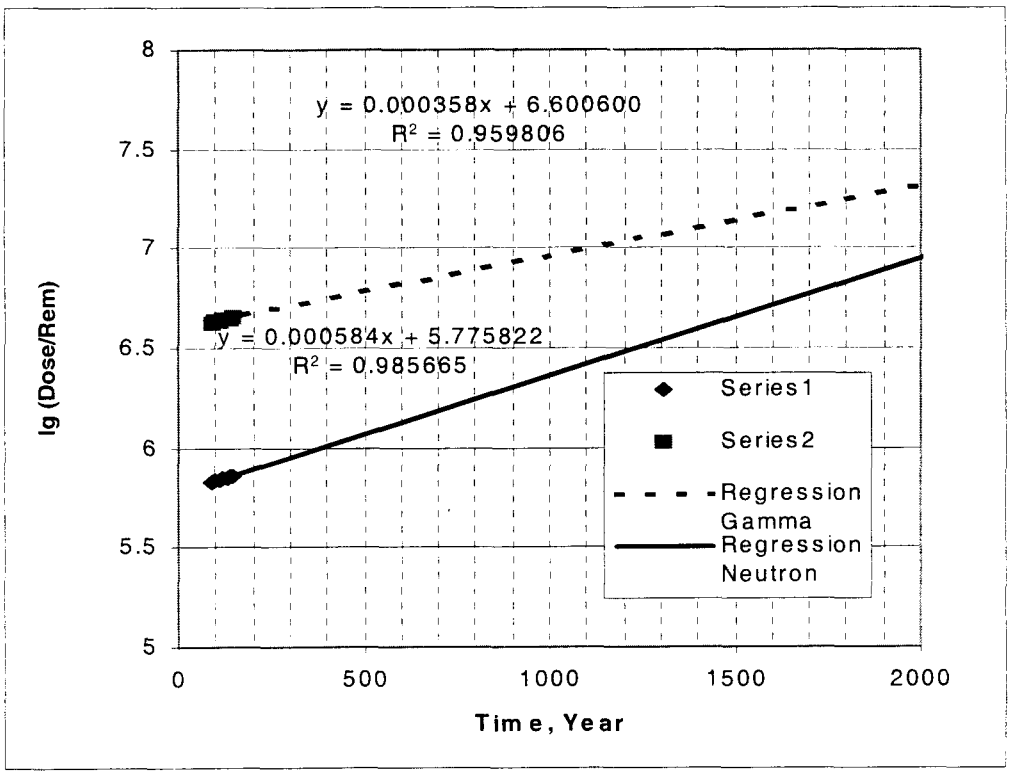


Figure 3 Extrapolation of dose to 2000 years VA Design

According to Figure 3, the dose for the time period from 50 to 2000 years is 2.2577e6 rem (see Table 3) (Compared with 2.47E7 rem from the previous extrapolation).

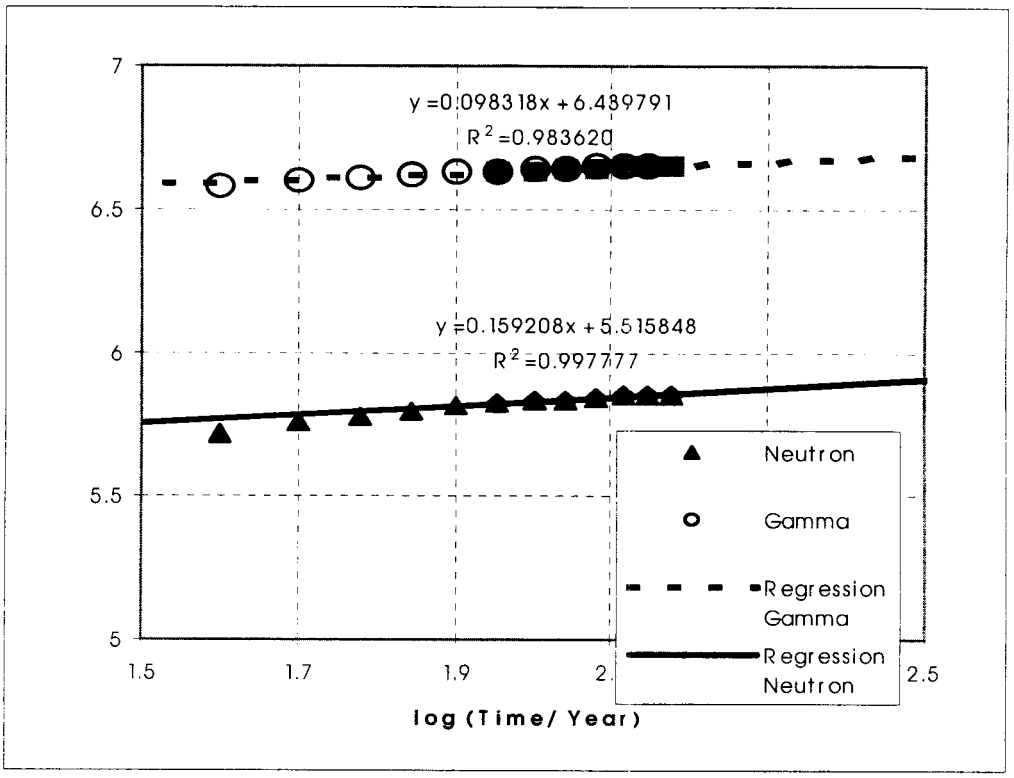


Figure 4 Log D vs log t

Reconsider the Dose Rate Estimations

--Bounding values for the dose rate beyond 150 years.

In the previous section, we have obtained

log (D/rem) = 0.09832 log(t/year) +6.44 for Gamma

log (D/rem) = 0.1592 log(t/year) +5.516 for neutron

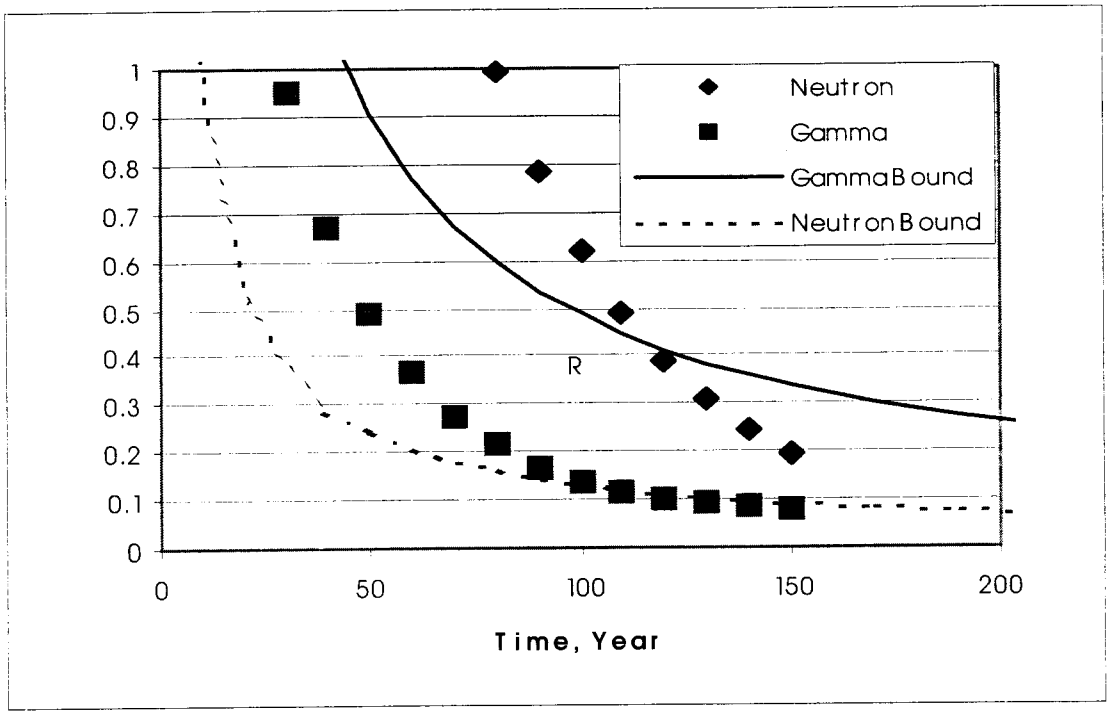


Figure 5 Bounding withing 150 years VA Design

(For T>120 years)

These equations producing bounding values for the dose. They should also providing the bounding values for the dose rate if differentiated

$$D\ (\text{Gamma}) = 10^{6.44}\ 10^{0.09832\log(t)}$$

$$D\ (\text{Neutron}) = 10^{5.516}\ 10^{0.1592\log(t)}$$

for

$$D = 10^{A}\ 10^{B\ \log(t)}$$

$$dD/dt = 10^{A*}\{10^{B\log(t)}\ \ln(10)\}*[B]*\ 1/t*\ 1/\ln(10)$$
$$dD/dt = 10^{A}10^{B\log(t)}[B]\ 1/t$$
$$dD/dt = 10^{A}B\ \{10^{B\log(t)}/t\}$$

So that

$$R(Gamma) = dD(Gamma)/dt = 10^{6.44}0.09832\ \{10^{0.09832\log(t)}/t\} \qquad \text{III.1}$$

$$R(Neutron) = dD(Gamma)/dt = 10^{5.516}0.1592\ \{10^{0.1592\log(t)}/t\} \qquad \text{III.2}$$

Euations III.1 and III.2 along with the experimental data (File Doserate_time) are plotted in Figures 5 and 6. It can be seen from Figures 3 and 4, the bounding values do bound the rates at times beyond 150. Since the bounding equations were derived using the data from 90 to 150 years (see previous section). It is not valid within ~120 years (the mid points between 90 and 150).

Bounding Values for Dose and Dose Rates with EDA II Designs

The only difference between the VA and EDA II designs are the initial dose rate is higher in the EDA II design by factors of

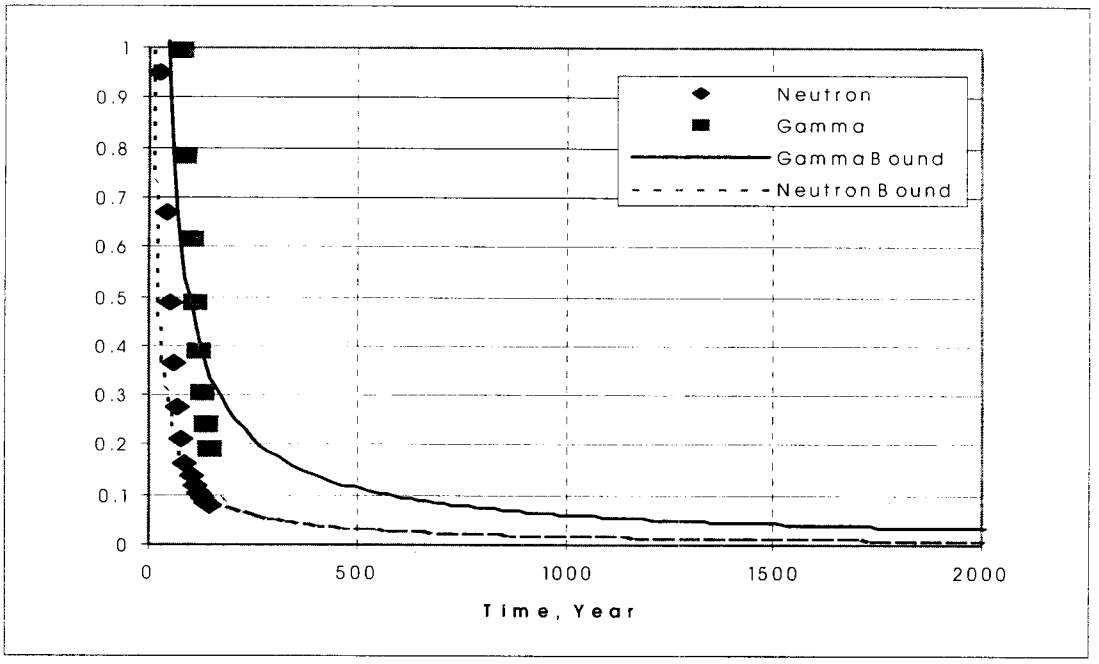


Figure 6 Bounding Rate extrapolation VA Design

4/15/01

380/36 = 10.56 for Gamma

and

7.22/2.79 = 2.59 for Neutron.

Therefore, the dose or dose rate for bounding values should be the values for VA design multiplied by the corresponding factors. That is for t > 120 years

$$D\ (\text{Gamma}) = 10.56 * 10^{6.44}\ 10^{0.09832\log(t)}$$
$$D\ (\text{Gamma}) = 2.91\text{x}10^{7}\ 10^{0.09832\log(t)} \qquad \text{III.1}$$

$$D\ (\text{Neutron}) = 2.59\text{x}10^{5.516}\ 10^{0.1592\log(t)}$$
$$D\ (\text{Neutron}) = 8.498\text{x}10^{5}\ 10^{0.1592\log(t)} \qquad \text{III.2}$$

$$D\ (\text{total}) = 2.91\text{x}10^{7}\ 10^{0.09832\log(t)} + 8.498\text{x}10^{5}\ 10^{0.1592\log(t)} \qquad \text{III.3.}$$

Equation III.1, III.2 and III.3 are shown in Figure 7, along with the data given in Ref. ??

L.Y. 11/20/00

Similarly the dose rates are

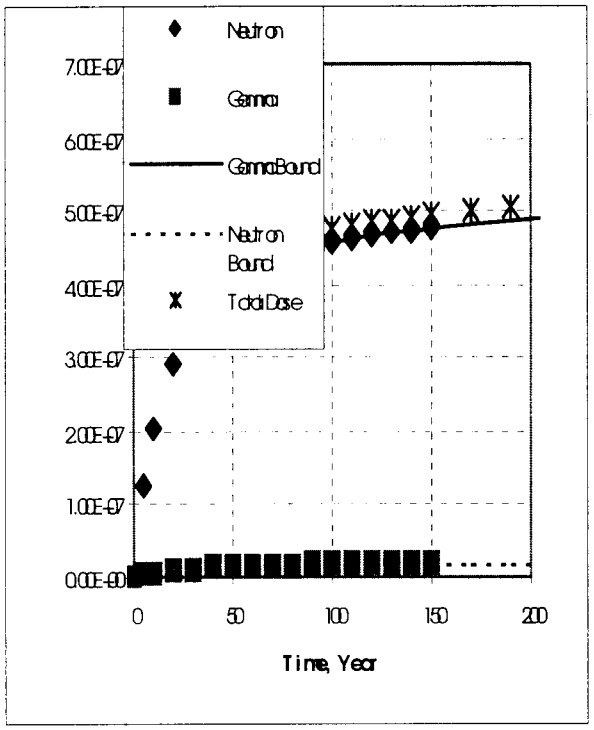
$$R(\text{Gamma}) = 10.56 * 10^{6.44} 0.09832\ \{10^{0.09832\log(t)}/t\}$$
$$= 2.86\text{x}10^{6}\ \{10^{0.09832\log(t)}/t\} \qquad \text{III.4}$$

[Rem/year]

$$R(\text{Neutron}) = 2.59 * 10^{5.516} 0.1592\ \{10^{0.1592\log(t)}/t\}$$
$$= 1.35\text{x}10^{5}\ \{10^{0.1592\log(t)}/t\} \qquad \text{III.5}$$

$$R(\text{Total}) = 2.86\text{x}10^{6}\ \{10^{0.09832\log(t)}/t\} + 1.35\text{x}10^{5}\ \{10^{0.1592\log(t)}/t\} \qquad \text{III6}$$

Equation III.4, III.5 and III.6 are shown in Figure 8, along with the data given in Ref. ??



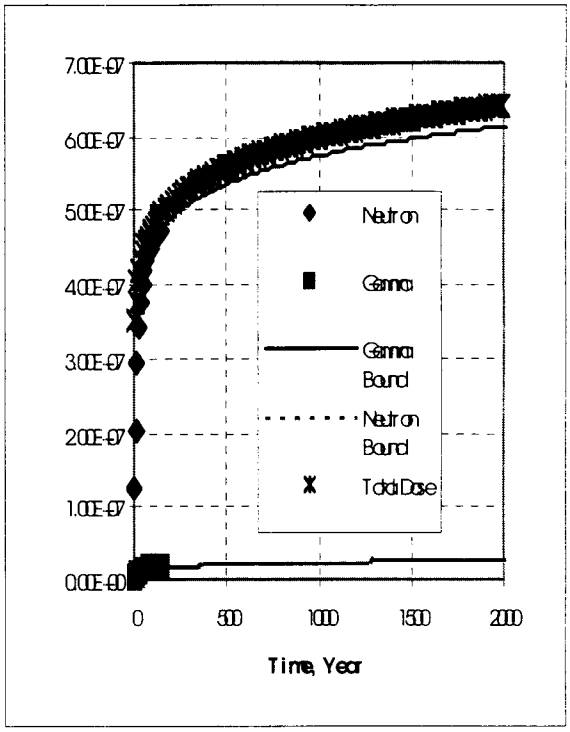
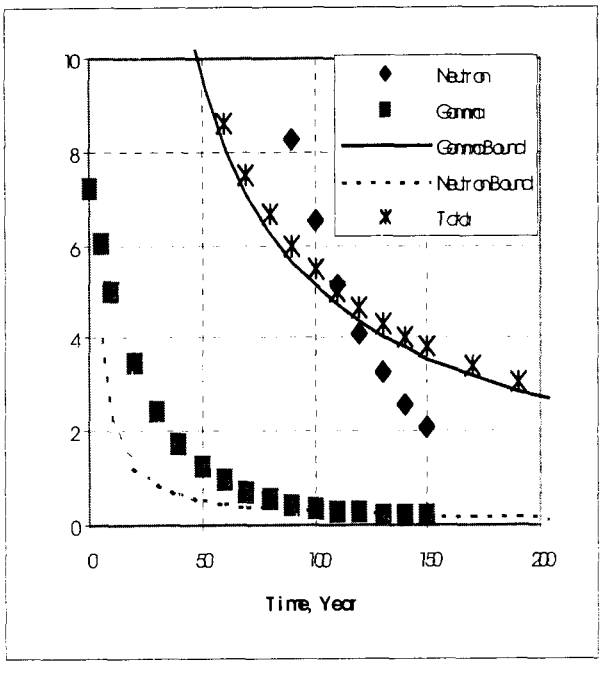


Figure 7 Bounding Dose for EDA II Design



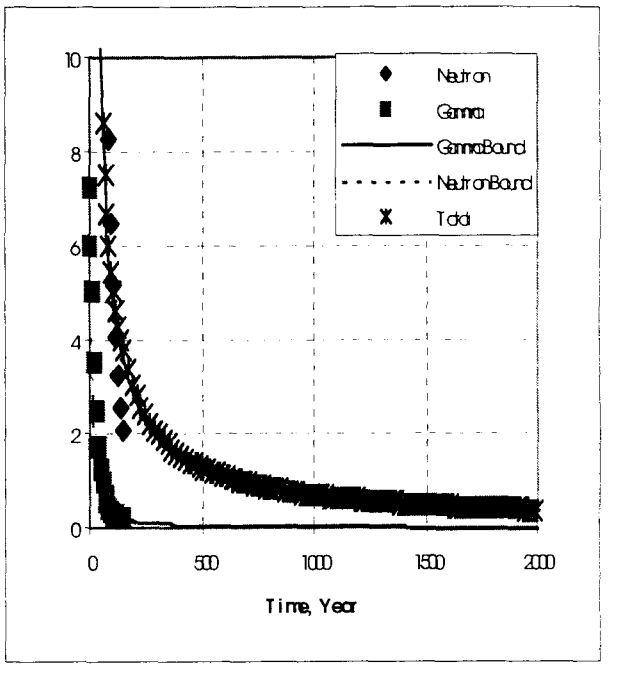


Figure 8 Bounding Dose Rate for EDA II design

Production of Radiolytic products in the WP environment:

The WP environment can be divided into 3 stages. One is the pre-closure vantilation stage. This is assumed to be 50 years. In this stage, there will be forced vantilation through the drift. There should be no radiolysis build up. In addition, during this stage, the drift is dry and there will be no noticeable corrosion on the WP outside surface.

Entries into Scientific Notebook No 373E for pages 1 to 20 have been made by

Lietai Yang / L. Yang / 08/15/00

NITROGEN OXIDES PRODUCTION IN THE AIR SPACE BETWEEN THE WP AND THE DRIP SHIELD

The average temperature in the air space is assumed at 75oC see Excel File From Osvado). Assuming the Volume of the Air Space is 5.96 m^3 (see detailed assumptions in the Excel File, the NO_x Production is shown in Figure 9 for per 1 m length of the Drift. Note, the space between the Wps is 10 cm for the EDAII design.

7

Film thickness:

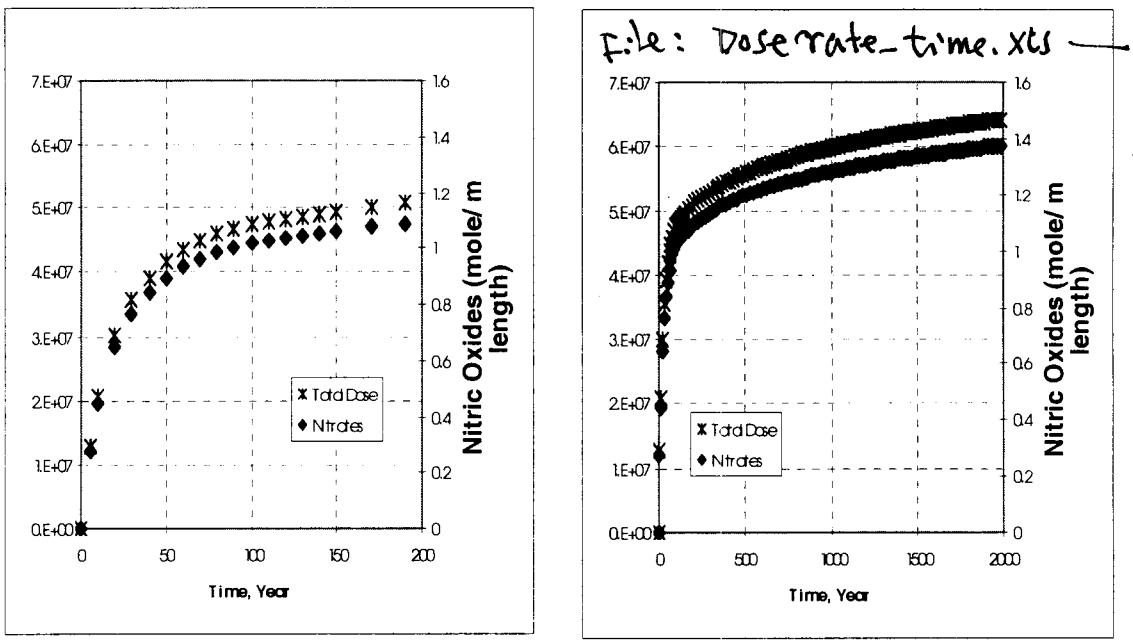


Figure 9 Total Doses and Production of Nitrogen Oxides

Assumptions: G=4.0 Molecule/100eV, T=75 oC (through out) P=640 Torr, Drip Shirld Volume 5.96 m^3 per 1 m length of drift.

according to Osvado, the thickness is 1 to 3 mm.

Assuming 2 mm then

Analysis on Tae's Calculation (Mail received December, 1999)

Field at WP , Rem/hr, Su et al 1997	
Year 10 Gamma	35.2
Year 160 Gamma	0.194
Ratio	0.005511
Source, Phonton/s/MTU, Su et al 1997	
Year 10 total	1.12E+16
Year 160 total	4.07E+14
Ratio	3.62E-02
Raio of the two ratios	6.572
Gamma Souce at 22 years and 5000 years	
Tae's Correspondence with McCoy, 1997	
Year 22 Gamma total	6.459e15
Year 5000 Gamma total	5.400e12
ratio	0.0008361
Ratio of the Two Ratios	Must be even smaller

Based on the ratio of the gamma source to predict the dose rate after 5000 years is a very conservative practice.

Because the Gamma energy shifted to lower end. This means two things. First, the conversion factor from source (Pho/s /cm^2 to rem/hr) is only 2.58E-7 for 0.07 MeV photon and 1.98-6 for 1 MeV (Note, 3.96e-6 for 0.01 MeV so 2.58E-7 for 0.07 MeV is not the lowest, Su, 1997, page 24).

Fuel Cladding:

According to VA design , 1998, page 5-3 Vol 2:

Fuel Assemblies, 6 to 17 ft overall length. Fuel rods: 0.25 to 0.5 inches in diameter. 99% are made of zircalloy. Wall thickness 0.7 mm. Assume o.1 breached for reactor safety analysis.

(Need to know: spacer, baskets, fuel rods numbers in a assembly. Absorber rods, how many?).

(Need to know (experimentally) :

1) Relationship between the Humidity and the film thickness (for C22, Ti-7 WP outside and Zircaloy, carbon steel basket and supporting materials, SS316)
2) What is the minimum thickness corrosion starts at very high acidity

One Point: If the film is very thin, the reaction can't go long to reach equilibrium if there is a reaction).

Waste Package for PWR 21 Fuel Assemblies (Drawing 5-2, Page 57, VA Volume 2).

Lenth: ?
Side Guide (Carb Steel A 516)
Interlocking Plates (S.S. Boron)
Corner Stiffener (A 516)

CRWMS M&O 1997as. Design Basis Cladding Analysis., BBA000000-01717-0200-00054 Rev. 1., Las Vegas, Nevada: CRWMS M&O. MIL. 19980325.0102.
CNWRA Lib. Has

Charactristics of WP

Internal diameter: 1423.4 mm (Ref 5.29), But Su et al 1997 used 1.22 m.
Width of basket side guide assembly : 733 mm (Ref 5.37)

Capacity :21 (Ref 5.38)
Number of Columns of assemblies: 5 (ref 5.38)

From: R. B. Stout and H. R. Leider, Waste Form Charactistics Report Rev1 LL Nat. Lab. (1997) Version 1.2, Page 2.1.2.2-2

Westinghouse 17x17 fuel assembly

Tranverse Dimention (in) 8.426
Assembly weight(lb): 1450
Overall assembly length: 161.3 in

Number of rod per Assembly: 264
Rod pitch 0.496 in
Rod length 151.6 in
Fuel length 143.7 in
Rod OD 0.374 in
Cladding thickness 0.0225 in

Fuel Pellet Diam 0.3225 in

Guide Tubes number 24
Guide Tube Upper OD 0.480

Instrument Tubes number 1
Instrument tube Upper OD 0.480

Spacer number 8

17x17 =289

264 + 24 +1 289 ok

ly. 08/14/00

Surface Area of the WE 17x17 fuel Assembly Temp Worksheet File: Enfe\WPdimention (in 00_01 – 00_08\Enfe of zip disk)

	Number	OD		length	Individual Surf A	Individual Volume	Total Surf A	Total Volume
		incm			cm^2	cm^3	m^2	m^3
Fuel Rod	264	0.374	0.950	151.600	452.433	107.448	11.944	0.028

[~~24~~] 31 ly 08/15/00

Guide Tube	24	0.480	1.219	151.600	580.662	176.986	1.394	0.004
Instrument1 tube		0.480	1.219	151.600	580.662	176.986	0.058	0.000
					sum		13.396	0.033
Assumblyes in WP				21.0000			281.3135	0.6886
WP Inside Diam (Su et al 1997)		1.2200					15.7630	4.6617
~~Length~~ 157 in= (m) assumed		3.9878						

Total surface area in WP 281.3 + 15.76 = 297.07 m^2 (neglecting the baskets and other things)

if deposition of 4 um film of water
then the volume could be 297.07*4e-6= 0.001188 m^3 = 1.188 L

Void space in WP (neglecting the baskets)

4.6617-0.6886 = 3.97 m^3

Ratio of air volume to water film volume= 3.97/0.001188 = 3343

Dose Rate Estimation at the Fuel Surface after 5000 years

L.Y. 08/14/00

File: Dose_rate_estimation_5000_years ; c:\work\ENFE\ (00_1-00_08\ Enfe\ after Zipped)

According to
Oak Ridge National Laboratory 1992, "haracteristics of Potential Repository Wastes, Oak Ridge, TN: Oak Ridge National Laboratory.
Total Photon (Photon/sec/MTIHM) from PWR spent fuel as a function of decay time
Burnup = 50 000 MWd/MTIHM 4.26 enrichment

	1	10	15	100	1000	5000	10000	100000
	-9	0.1	5	90	990	4990	9990	99990
						estimated		
photon	9.35E+16	1.17E+16		1.29E+15	3.62E+13	8.50E+12	4.49E+12	8.48E+11
		1.00E+00		1.11E-01	3.10E-03	7.27E-04	3.84E-04	7.25E-05

according to
S.Su and M.N. Haas, MGDS Subsurface Radiation Shielding Analysis (BCAE00000-01717-0200-00001 Rev 00, OCRWM (Office of Civilian Radioactive Waste Management) Report (1997). Note: MGDS stands for ""Mined Geologic Disposal System""

photon		1.12E+16	9.04E+15	1.25E+15		same trend as the Oak Ridge number		
		1.00E+00	8.04E-01	1.11E-01				
gamma doserate rem/hr	Fuel	7.40E+04						
extimated		7.40E+04	0.00E+00	8.18E+03	2.29E+02	5.38E+01	2.84E+01	5.37E+00
	out	3.52E-02	2.03E-02	7.85E-04				
		1.00E+00	5.76E-01	2.23E-02				

L.Y. 4/12/02

for 4.2% enrichment, 48086 burnup, PWR

From Plot, the estimate of 5000 photon would be 8.5e12
The estimate for gamma only at 5000 years is about 53.8 rad/hour
which is close to Tae's estimation

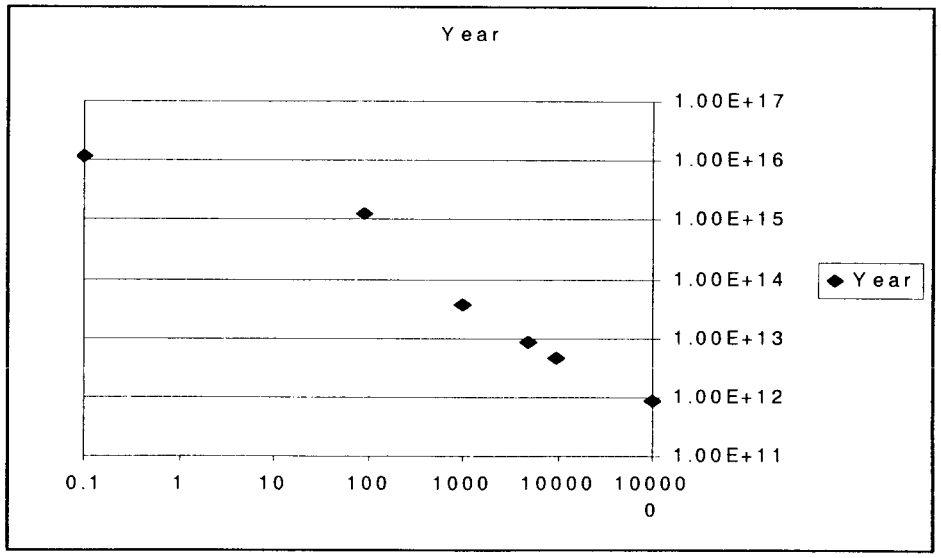


Figure 10 Estimation of Gamma Dose Rate after 5000 years

Note the above estimation does not account the fact that the energy bands shifted to lower level as time increases. The above extrapolation based on the photon rate may be a conservative way to predict the dose rate. Also note that the above analysis is only for gamma. Alpha and Belta radiation has been neglected.

Entries into Scientific Notebook No #373E for pages 21 to 28 have been made by

Lietai Yang / L. Yang / 08/15/00

Water Film Corrosion

Objective for this topic

Calculation to support the study of the effect of radiolytically produced acids in the water film on the WP outside and the titanium drip shield.

{
Table 2 presents the approximate number of monolayers at 25oC and steady state conditions, which had been experimentally determined by quartz crystal microbalance method on a variety of materials [28,29] (C. Leygraf in "Corrosion Mechnisms and Theory and Practice", ed by P. Marcus and J. Oudar, Chapter 12, "Atmospheric Corrosion, page 427)

Approximate Number of Water Monolayers on Diffferent Metals versus Relative Humidity

RH%	Number of Water Monolayers
20	1
40	1.5-2
60	2.-5
80	5-10

Referenced to [28, 29]

[28] Phipps, P.B.P., and D.W.Rice, "The role of water in atmospheric corrosion Chemistry, ACS Symp. Ser. 89 (G.R. Brubaker and P.B.P. Phipp eds.), American Chemical Society, Washington DC, 1979, P. 235.

[29] Mikhailovsky, Y.N., "Theoretical and Engineering principles of atmospheric corrosion of metals, Atmospheric Corrosion (W.H. Ailor, ed.), Wiley, New York, 1982., p.85.
}

{

Mattsson, E., "The Atmospheric Corrosion properties of some common structureal metals- A comprehenssive Study", Plenary Lecture, Corrosion/82, March, 1982, Houston, Texas.

"It has not been clariffied hoever what the minimum thickness of the electrolyte film rerquired for the operation of the corrosion cell is. The metal surface maybe wetted if hydroscopic salts absorb water from the atmosphere. Such absorption occurs above a certain relative humidity, called critical relative humidity. Its value depends on the metal surface contaminants. Estimation by Barton et al (?? To ask Tae) are:

Conditions	Amount of water G/cm^2	Thickness um	Monolayer*
Critical RH	0.001	0.01	32
100% RH	1	1	
Covered by Dew	10	10	
Wet from rain	100	100	

Assuming 0.31 nm for one monolayer (see next)
}

{most recently,
Eichhorn, K.-J., and W. Forker, "The Properties of Oxide and Water films formed during the atmospheric exposure of iron and low alloy steels", Corrosion Science, Vol. 28, No. 8, pp.745-758, 1988.

Measured with Ellipsommetry rather than the microbalance method by [4,5 to get detailed paper].

In low air humidity: <80%, only one or two layers of water mollecules are formed on the surface of all studied materials (taking 0.31 nm as the diameter of a water molecule). Above a certain critical humidiy $(RH)_{cr.}$ d_{H2O} values increase abruptly and for RH =100%, the most favorable adsorption propteris of primary oxide approach average values which point to 10 -12 layers of water molecules. (RH)cr depends on the initiate state of the primary oxide layers and varies from 80-90%. SO2 increase the thickness.

So

RH < 80%	1-2 layer
Rhcr(=80-90%)	increase abruptly

~100% 10-12

, }

{
L.L. Shreir, Corrosion, Volume 1, Metal/Environment Reactions, Ed by L.L. Shreir and R.A> Jarman and G.T. Burstein, 3rd eddition, 1994 Butterworth -Heinemann Ltd page 2:38

It is estimated that at 55% RH the film on polished iron is about 15 molecule layers thick, increasing to 90 molecular layerss at just below 100% RH [4]. Such films are capable of supporting electrochemical corrosion processes and these have been studied.
[4] Tomashov, N.D., Theory of Corrosion and Protection of Metals, Macmilan, New York(1966).
This probablly too old, the data here is more than 10 to 15 times higher than the latest measured results
}

According to the above reference, we shall use:

at RH =80%, take 5 to 10 mono layers	1.55 to 3.1 nm
at RH=100%, >10	>3.1 nm
at RH=100, covered dew	10 um
at RH=100, rain running	100 um

Rhcr = 80 to 90 somewhere between depends on surface and contaminants in the air.

Entries into Scientific Notebook No 373E for period 01/01/00 to 07/10/00 have been made by

Lietai Yang / L.Yang / 08/15/00

No original text entered into this Scientific Notebook has been removed

L.Yang / 08/15/00

SCIENTIFIC NOTE BOOK # 373E
Radiation Effect on the Chemistry of Near-Field Environment

by

Lietai Yang

Southwest Research Institute
Center for Nuclear Waste Regulatory Analyses
San Antonio, Texas

(From July 10, 2000 to April 11, 2001)

Copied for QA Record 04/11/01.

L. Yang.

1. INITIAL ENTRIES

Scientific Note Book: # 373E

Issued to: Lietai Yang

Issue Date: October 28, 1999

Printing Period:

Project Title: Radiation Effect on the Chemistry of Near field Environment
Project Number: 20-1402-561

Project Staff: Lietai Yang / N. Sridhar

(This layout of computerized Scientific Notebook is designed by A. Ghosh
to address the criteria of CNWRA QAP-001)

1.1. Objectives

The objective of this study is to make bounding calculations for the radiolysis effect of the chemistry in the Nearfield Environment (NFE) of the proposed high-level waste repository at Yucca Mountain, Nevada. The calculation will be conducted on the basis of the EDA II (Enhanced Design Alternative II) Waste Package for typical Waste Form, 21 Fuel Assembly PWR Fuel.

[October 28, 1999]

Sept. 6, 2000

Re-calculation of the production of nitric acid for the Tech Exch Meeting

C:\Work\CLST\Acid-production-on-cladding.xls Sheet1 12/4/00

Acid-production-on-cladding.xls

	Assumed	Calculated
WP Size (notes P.25, #2)		
Diameter, m	1.22	
Length, internal, m	3.99	
WP Internal Volue m^3		4.66189206
WP Inside area (Note #2, P. 25, m^2)	15.79	
Cladding surface area (Note#2 P. 25, m^2)	281	
Total Area surface area in WP m^2		296.79
Water Film thickness m	4.00E-06	
Water Film volume on surfaces (m^3)		0.00118716
Water Film volume on surfaces (L)		1.18716
Temperature oC	25	
Pressure, Atm	0.842105263	
Air MW	29.4	
Air density (kg/m^3)		1.012432168
Air density (Mole/m^3)		34.43646829
~~C of N2 in the air (Mole/m^3)~~		~~0.799821412~~ L.Y. 12/04/00
C of N2 in the air (Mole/m^3)		27.20480995
Air Mass (kg)		4.719849484
Air moles in apace (moles)		160.5390981
N2 mole in the air		126.8258875
G umol/J		
Nitates		0.196916
Dose rate (Rad/hr)	100	
Dose rate (Gy/hr=J/Kg)		1
Dose rate (MRad/hr)		0.0001
NOx production (Mole/hr)		
=D(Gy/hr) x W(of air, kg)*G (umol/J)/(1e6)		9.29414E-07
Hours in a year (hr)		8760
NOx production (Mole/year)		0.008141666
N of NOx production (~~Mole/year~~, mole/L/y)		0.006858103
Use Burn et al formula		
N(mol/L)= 2Co(mol/m^3*R (ratio) [1-exp(-1.45x10^-5 1.9 d (Mrad/h) t (hr)]		0.00515643

L.Y. 12/04/00

Assuming all energy to air is available for NOx production. L.Y. 8/04/02

L.Y. 8/04/02

here (Co is conc, not air!) L.Y. 8/04/02

C:\Work\CLST\ Acid-production-on-cladding.xls Sheet2 12/4/00

C of N2 in the air (Mole/m^3): 27.20481
~~If Initial default 99.9% Ar, only 1% air~~ ~~100~~ L.Y. 9/4/02
C of N2 in the air (Mole/m^3): 27.20481
Dose rate Mrad/h: 0.0001

	Burns Formula From original derived form	Burns Formula If assume C(N2) does not change
N(mol/L)=	2Co(mol/dm^3*R (ratio) [1-exp(-1.45x10^-5 1.9 D (Mrad/h) t (hr)]	2Co(mol/dm^3*R (ratio) *1.45x10^5*1.9 D (Mrad/h) t (hr)

To me I think we should use air concentration not just that of N2 because eneregy absorbed by O2 will also be back to N2, or now I do not wqant to dispute this.

year	hours	mol/L	total mol	mol/L		total mol	pH
1	8735	0.0051	0.0061	0.0051	0	0.0061	2.288892
1.3	11355.5	0.0067	0.0079	0.0067		0.0079	2.17495
1.69	14762.15	0.0087	0.0103	0.0087		0.0103	2.061009
2.197	19190.8	0.0113	0.0134	0.0113		0.0134	1.947068
2.8561	24948.03	0.0147	0.0174	0.0147		0.0174	1.833128
3.71293	32432.44	0.0191	0.0227	0.0191		0.0227	1.719189
4.826809	42162.18	0.0248	0.0295	0.0248		0.0295	1.605252
6.274852	54810.83	0.0323	0.0383	0.0323		0.0383	1.491316
8.157307	71254.08	0.0419	0.0498	0.0419		0.0498	1.377383
10.6045	92630.3	0.0545	0.0647	0.0545		0.0647	1.263452
13.78585	120419.4	0.0709	0.0841	0.0709		0.0842	1.149525
17.9216	156545.2	0.0921	0.1094	0.0921		0.1094	1.035604
23.29809	203508.8	0.1198	0.1422	0.1198		0.1422	0.921688
30.28751	264561.4	0.1557	0.1848	0.1557		0.1849	0.807782
39.37376	343929.8	0.2024	0.2402	0.2025		0.2403	0.693886
51.18589	447108.8	0.2630	0.3123	0.2632		0.3124	0.580004
66.54166	581241.4	0.3419	0.4059	0.3421		0.4062	0.466141
86.50416	755613.8	0.4443	0.5275	0.4448		0.5280	0.352302
112.4554	982298	0.5774	0.6855	0.5782		0.6864	0.238494
146.192	1276987	0.7504	0.8908	0.7517		0.8924	0.124727
190.0496	1660084	0.9750	1.1574	0.9772		1.1601	0.011013
247.0645	2158109	1.2666	1.5036	1.2704		1.5081	-0.102633
321.1839	2805541	1.6451	1.9530	1.6515		1.9605	-0.21619

CO2 in air, %Vol = 0.13

Total mole of air in WP= 160.5391
Total mole of CO2= 0.2087008

L.Y. 12/04/00

This much of CO2 is not enough to counter the acid
HCO3- in J13 water mg/L 139 (see ANL-EBS-MD-000001REV00C)
HCO3- in J13 water mol/L 0.0022787
this is too little compared to 3.86 mol/L of HNO3 after one year

C:\Work\CLST\acid-on-cladding.wpd, December 4, 2000

J.Y. 12/04/00.

Originally Written for Sridhar to be at the T. Ex. Meeting, 09/08/00

Summary of Radiolytic Production of Nitric Acid on Cladding

Our Preliminary Calculations for Nitric Production Rate:

Estimated empty volume in a WP for PWR 17x17 fuel assemblies:	4.7 m^3
Estimated surface area in a WP for PWR 17x17 fuel assemblies:	297 m^2
Estimated water film thickness on the surfaces: (Although some literature mentioned that at critical Relative Humidity the thickness may be as small as 0.01 um)	4 um
Water film on surfaces total volume	1.19 L
G value for N_2 reaction to form nitric oxides	1.9 molecule/100 eV
Dose rate at 5000 years	50 Rad/hr
Dose rate at 0 years	100000 Rad/hr

At time zero, if there is initial default/leak, the production of NOx is

1% of air impurity (99% Ar)	0.063 mol/year -> pH=1.294 in 1 year
In 10 years:	0.54 mol (dose decay ignored)
If all available air converted:	2.53 mol
0.1% of air impurity	0.0060 mol/year -> pH=2.29 in 1 year
In 10 years:	0.0543 mol (Dose decay ignored)
If all available air converted:	0.253 mol

This NOx may be adsorbed on the surfaces of cladding and form acid once the humidity in the drift reaches a certain value (90% for example).

At time 5000, if the WP is filled with air (100% air, D=50 Rad/h), the production of NOx:

Yearly	.0031 mol/year -> pH=2.65 in 1 year
In 10 years:	0.0305 mole
In 100 years:	0.305 mole (Dose decay ignored)

DOE Position:

DOE has considered that the impact from the radiolytically produced nitric acid on pH unlikely based on the following arguments:

1. Nitric acid formation requires introduction of gas phase N2+O2 which, in turn, requires open system. However, accumulation of gas phase NO2 re requires closed system.

C:\Work\CLST\acid-on-cladding.wpd, December 4, 2000

2. In a closed system steel, corrosion and NO2 production deplete O2.

3. In and Open system, gas phase diffusion depletes NO2

4. Bicarbonate and $Fe(OH)_3$ buffer pH; need ~4 moles of HNO_3/L to reach pH=3.

5. Thin films unstable w.r.t. evaporation and heat production.

6. No accumulation of H2O for at least 40,000 years.

Our position:

We consider DOE's argument 4 is valid if it can be demonstrated that the water film on every portion of the cladding surface does contain the predicted amount of Bicarbonate and $Fe(OH)_3$.

However, if the water film on some portion of the cladding is formed by purely condensation from moistured air. This water film may not contain the Bicarbonate and $Fe(OH)_3$ that have been concentrated in the bulk water entering the WP. The total CO_2 in the air is about 0.21 mole inside the WP (based on 0.13% Vol of CO2 in air). Is this CO_2 enough to buffer the acid in a closed system?

Argument 2 is not valid because only a small amount of NO2 (without depleting the O2) is required to cause significant pH .

Argument 3 needs more analysis because if there is water film on the cladding surface, NO2 would tend to go to the water film and form nitric acid which is stable.

Argument 5 requires more analysis because if the surface has salt, water film may be formed at relatively lower humidity.

Argument 6 ?

L.Y.
12/04/00

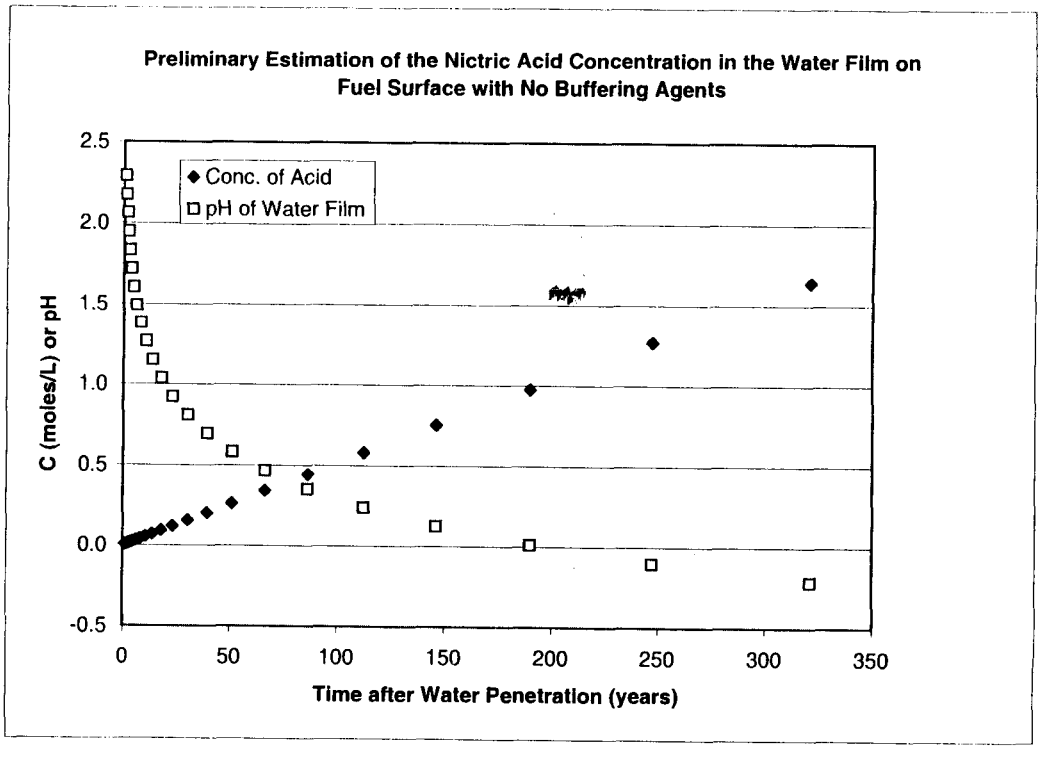
[5] 42 L. Yang 4/13/01

L.Y. 12/04/00

11/20/00 Acid-production-on-cladding_Bobby.xls , c:\work\clst\ sub dir.

Burns Formula
From original derived form

year	mol/L	pH
1	0.0051	2.288892
1.3	0.0067	2.17495
1.69	0.0087	2.061009
2.197	0.0113	1.947068
2.8561	0.0147	1.833128
3.71293	0.0191	1.719189
4.826809	0.0248	1.605252
6.274852	0.0323	1.491316
8.157307	0.0419	1.377383
10.6045	0.0545	1.263452
13.78585	0.0709	1.149525
17.9216	0.0921	1.035604
23.29809	0.1198	0.921688
30.28751	0.1557	0.807782
39.37376	0.2024	0.693886
51.18589	0.2630	0.580004
66.54166	0.3419	0.466141
86.50416	0.4443	0.352302
112.4554	0.5774	0.238494
146.192	0.7504	0.124727
190.0496	0.9750	0.011013
247.0645	1.2666	-0.102633
321.1839	1.6451	-0.21619



Assumptions:
PWR Fuel
The water film thickness: 4 um
Radiation field: 1 Gy/h (100 Rad/h)
(Alfa at 50 k years can be as high as 1 Gy/h)
G Molecu/100 eV
for Nitates 1.9

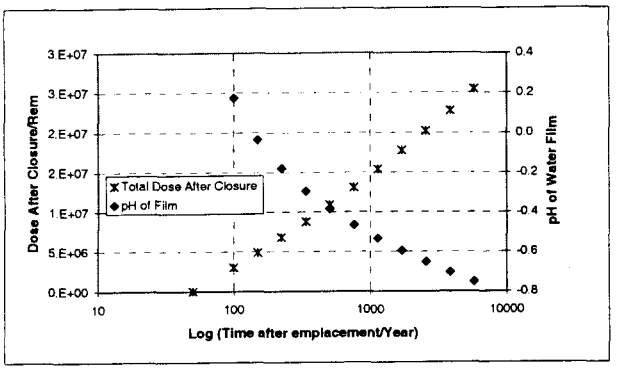
This file was given to R. Papalan.

L.Y. 12/04/00

ite:

11/20/00 Acid-production-on-WP.xls Dose_After_50Y (sheet) L.Y. 12/04/00.

t (year)	Dose* (rem)	Dose after 50Y (rem)	NOX* per 1 m Leng (moles) (Note 1)	NOX in film mol/L (Note 2)	pH
50	4.27E+07	0.00E+00	0	0.00E+00	
100	4.58E+07	3.01E+06	0.043193109	6.71E-01	0.17
150	4.76E+07	4.88E+06	0.069858164	1.08E+00	-0.04
225	4.96E+07	6.81E+06	0.097607703	1.52E+00	-0.18
337.5	5.16E+07	8.83E+06	0.126485833	1.96E+00	-0.29
506.25	5.37E+07	1.09E+07	0.156538455	2.43E+00	-0.39
759.375	5.59E+07	1.31E+07	0.187813335	2.92E+00	-0.46
1139.063	5.81E+07	1.54E+07	0.220360184	3.42E+00	-0.53
1708.594	6.05E+07	1.77E+07	0.254230734	3.95E+00	-0.60
2562.891	6.30E+07	2.02E+07	0.289478819	4.50E+00	-0.65
3844.336	6.55E+07	2.28E+07	0.326160466	5.07E+00	-0.70
5766.504	6.82E+07	2.54E+07	0.364333978	5.66E+00	-0.75



Note 1: NOX(mole) = Dose(Rem)/100*AirMass(kg)*G-Value(umol/J) /1000000
Note 2: Film volume of one side drip shield and WP

Main Assumptions:
1 Produced nitric acids are not reacted or buffered
2 The water film thickness:
4 um
(Note, Some reports mentioned that aqueous corrosion may take place at 2 mono layer)
3 Radiation field
Extrapolated from DOE Report BCAE00000-01717-0200-00001Rev00
4 G (Molecu/100 eV) for Nitrates:
1.9

5. other assumptions, see page 9 (sheet: Assumptions).

L.Y. 12/04/00.

* — see Data-Note-Book sheet (Next page)

* — Accumulated dose after closer (time is zero at 50 years)

L.Y. 12/04/00.

44 L.Y.
4/17/07

11/20/00 Acid-production-on-WP.xls (Data_Note_Book, sheet Name) J.Y. 12/04/00.

Formula from
Note Book Page 18, July 10, 2000.

Note 1: R=2.86x10^6 {10^[0.09832xlog(t)]/t}/365/24
Note 2 D(Gamma) = 2.91x10^7 10^(0.09832(t))

According to MGDS Page 96 and 99

			VA design		VA design *10.56	
					10.56 is the factor for EDII	
	Rem	Rem/hr	Rem	Rem/h	Rem	Rem/h
t (year)	Note 1	Note 2				
50						
50	4.27E+07	9.592563	3.80E+06	2.165	4.01E+07	22.8624
100	4.58E+07	5.134545	4.33E+06	0.616	4.57E+07	6.50496
150	4.76E+07	3.562246	4.49E+06	0.194	4.74E+07	2.04864
225	4.96E+07	2.471417				
337.5	5.16E+07	1.714621				
506.25	5.37E+07	1.18957				
759.375	5.59E+07	0.8253				
1139.063	5.81E+07	0.572577				
1708.594	6.05E+07	0.397243				
2562.891	6.30E+07	0.275599				
3844.336	6.55E+07	0.191205				
5766.504	6.82E+07	0.132655				

J. Yang. 12/04/00

11/20/00 Acid-production-on-WP.xls Assumptions (sheet name)

L.Y. 12/04/00

			Section Area (m)	Volume per m 1	Notes BWR 5.1 m fuel assembly
WP	D (m)	1.8	2.5434	2.5434	
DripShield vs WP dimention	H(main)/D	2			
	H(roof)/D	0.5			
	W/D	1.5			
	H(main, m)	3.6			
DripShield Dimension	H(roof, m)	0.9	10.935	10.935	Neglect line spacing of 10 cm
	W, m	2.7			
Air Space m^3/m			8.3916	8.3916	

Drip Shield Area m^2 per 1 m length (one side)	10.445
WP area m^2 per 1 m length	5.652
Total Area for Film formaion in air space	16.097
Film thickness m	0.000004
Film volume on Drip Shild (m^3)	4.18E-05
Film volume on WP (m^3)	2.26E-05
Film volume on WP and Drip shield (m^3)	6.44E-05
Film volume on Drip Shild (L)	0.04178
Film volume on WP (L)	0.022608
Film volume on WP and Drip shield (L^3)	0.064388

L.Y. 9/24/02

Temperature oC	75
Pressure, Atm	0.842105
Air MW	29.4
Air density (kg/m^3)	0.866968
Air moles in apace (moles/1m)	247.4574
Air Mass (kg)	7.275247
CO2 moles, at 0.13%, Enfe-93-04	0.321695
G Molecu/100 eV	
Nitates	1.9
G umol/J	
Nitates	0.196916

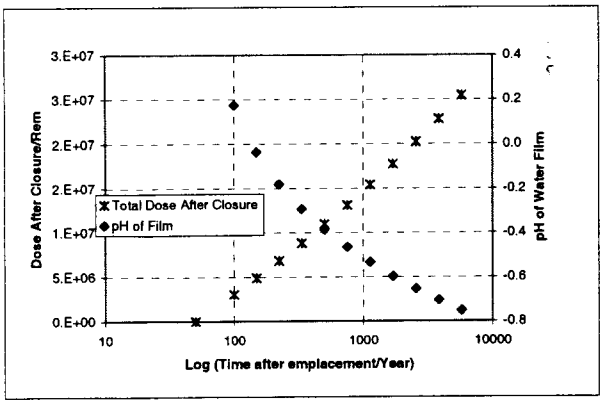
~~[9]~~ 46 L.Y. 4/15/02

11/20/00 Acid-production-on-WP_Bubby.xls

t (year)	Dose (rem)	Dose after (rem)	NOX per 1 m Le (moles) (Note 1)	NOX in film mol/L (Note 2)	pH
50	4.27E+07	0.00E+00	0	0.00E+00	
100	4.58E+07	3.01E+06	0.043193	6.71E-01	0.17
150	4.76E+07	4.88E+06	0.069858	1.08E+00	-0.04
225	4.96E+07	6.81E+06	0.097608	1.52E+00	-0.18
337.5	5.16E+07	8.83E+06	0.126486	1.96E+00	-0.29
506.25	5.37E+07	1.09E+07	0.156538	2.43E+00	-0.39
759.375	5.59E+07	1.31E+07	0.187813	2.92E+00	-0.46
1139.063	5.81E+07	1.54E+07	0.22036	3.42E+00	-0.53
1708.594	6.05E+07	1.77E+07	0.254231	3.95E+00	-0.60
2562.891	6.30E+07	2.02E+07	0.289479	4.50E+00	-0.65
3844.336	6.55E+07	2.28E+07	0.32616	5.07E+00	-0.70
5766.504	6.82E+07	2.54E+07	0.364334	5.66E+00	-0.75

Note 1: NOX(mole) = Dose(Rem)/100*AirMass(kg)*G-Value(umol/J) /1000000
Note 2: Film volume of one side drip shield and WP

Main Assumptions:
1 Produced nitric acids are not reacted or buffered
2 The water film thickness:
4 um
(Note, Some reports mentioned that aqueous corrosion may take place at 2 mono layer)
3 Radiation field:
Extrapolated from DOE Report BCAE00000-01717-0200-00001Rev00
4 G (Molecu/100 eV) for Nitrates:
1.9



This was given to R. Papalan.

L.Y. 12/04/00.

~~[10]~~ 47 L.Y. 4/15/01

No paper or report was published based on the work in the scientific notebook.

4/3/06.

I have reviewed this scientific notebook and find it in compliance with QAP-001. There is sufficient information regarding procedures used for conducting tests, acquiring and analyzing data so that another qualified individual could repeat the activity.

4/11/06

Lietai Yar **SCIENTIFIC NOTEBOOK** 373E INITIALS: L.Y.

Entries into Scientific Notebook No 373E for period 07/10/00 to 04/11/01 have been made by

Lietai Yang / L.Yang /

04/11/01

No original text entered into this Scientific Notebook has been removed

L.Yang 04/11/01

~~[11]~~ 48 L.Yg 4/12/01

ADDITIONAL INFORMATION FOR SCIENTIFIC NOTEBOOK NO. 373E

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