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SAVANNAH RIVER NATIONAL LABORATORY
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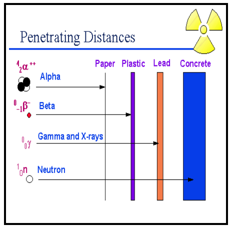
Enabling Technologies for Spent Fuel Reprocessing:

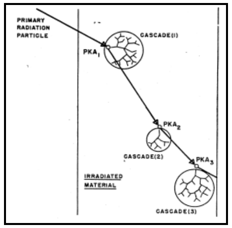
Nuclear Radiation & Radiation Damage to Materials

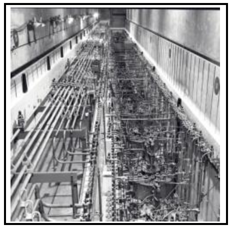
Robert L. Sindelar

Kristine E. Zeigler

July 21, 2011







Introduction to Nuclear Chemistry and Fuel Cycle Separations

Consortium for Risk Evaluation with Stakeholder Participation

EM Office of Environmental Management
safety ❖ performance ❖ cleanup ❖ closure

Outline

- **Radioisotopes in Spent Fuel**
- **Shielding**
  - Concepts
  - Evaluation Methodologies
- **Radiolysis**
  - Concepts
  - Radiolysis Effects in Separations Process Solutions/Materials
- **Radiation Effects on Materials**
  - Concepts
  - Radiation Effects on Seal and Gasket Materials
  - Radiation Effects on Structural Materials

Effects of Radiation Must be Considered in Facility Design (Shielding and Materials of Construction) and Chemical Processes (Radiolysis)

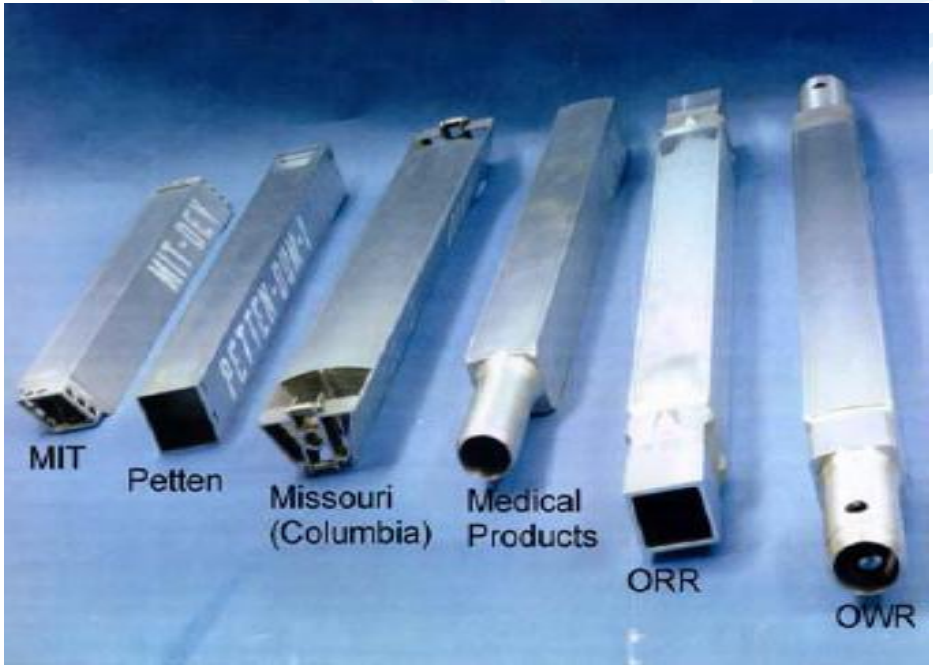
SRS Canyon Photograph Pre-Operation (circa 1955)

Overview of Radiation Effects on Materials and Systems Relevant to Nuclear Fuel Cycle Separations is Presented

Radioisotopes in Spent Nuclear Fuel

Example of Research Reactor Spent Nuclear Fuel –

- **Radioisotopes include**
  - Alpha Emitters*
  - Beta Emitters*
  - Gamma Emitters
  - Spontaneous Neutron Emitters
  - Secondary Reactions (e.g. (α, n))
- **Fuel Isotope Content Dependent on Irradiation & Decay Times**

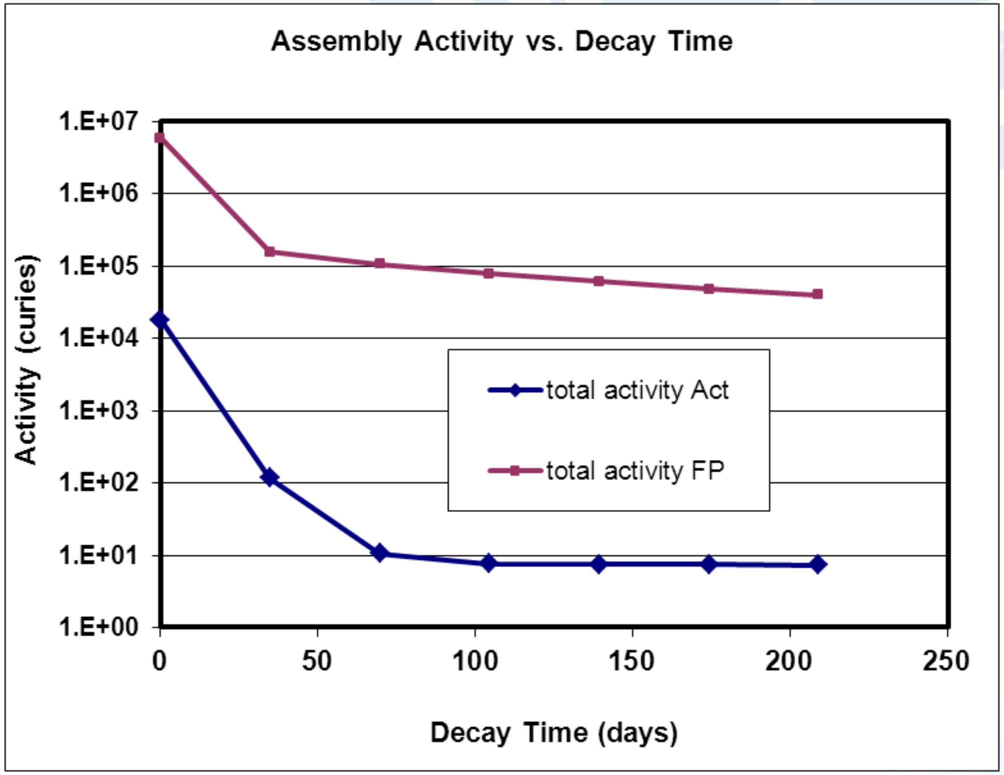


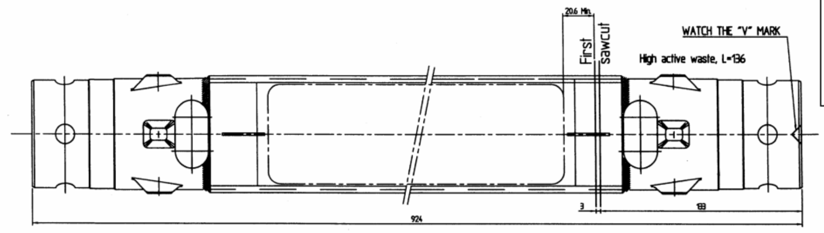
*There are few pure Alpha or Beta emitters, Gamma emission is concomitant

Radioisotopes in Spent Nuclear Fuel, CONT'D

Example of Research Reactor Spent Nuclear Fuel –

- **Materials Test Reactor Design Assembly**
- **HFR Petten Assembly #F1369**
  - 93% Enriched
  - 484 gm total U initial
- **158 Day Irradiation in 50 MW Reactor with 211 MWD/assembly, 58% Burn-up**





Radioisotopes in Spent Nuclear Fuel, CONT'D

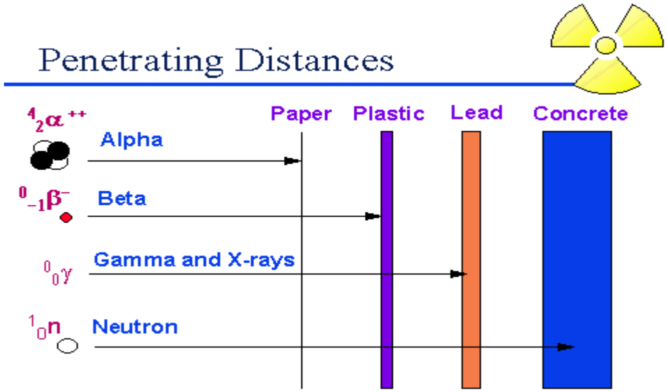
Spent Nuclear Fuel, High Activity Radioisotopes –

- **HFR Petten Assembly #F1369**
- **ORIGEN-S Code for Isotopic Analysis**
- **209 Days Cool**
- **Radioisotope Content**
  - Actinides with > 10^{-4} Ci
  - Fission Products with > 10^{2} Ci
- **Note: Lists Do Not Include the Very Long-Lived Isotopes Important for Sequestration in a Waste Form (e.g. Tc-99, Zr-93, I-129)**

Actinide	**Curies**
Th231	3.95E-04
Pa233	6.34E-04
U235	3.95E-04
U236	2.69E-03
U237	1.34E-04
Np237	6.34E-04
Np239	1.06E-04
Pu236	1.36E-04
Pu238	1.57E+00
Pu239	3.25E-02
Pu240	3.49E-02
Pu241	5.54E+00
Am241	7.32E-03
Am243	1.06E-04
Cm242	1.42E-01
Cm244	2.80E-03
Total	**7.34E+00**

Fission Product	**Curies**
Sr89	1.21E+03
Sr90	6.84E+02
Y90	6.84E+02
Y91	2.25E+03
Zr95	3.09E+03
Nb95	6.28E+03
Ru103	3.33E+02
Rh103m	3.33E+02
Ru106	6.81E+02
Rh106	6.81E+02
Cs134	3.35E+02
Cs137	6.91E+02
Ba137m	6.53E+02
Ce141	2.86E+02
Ce144	9.59E+03
Pr144	9.59E+03
Pr144m	1.34E+02
Pm147	1.83E+03
Total	**3.96E+04**

Shielding – Concepts



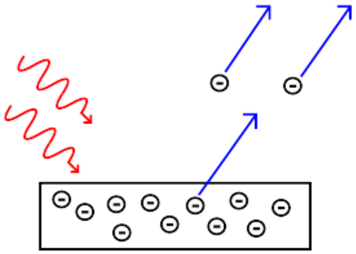
Type of Ionizing Radiation	Characteristics	Range in Air	Shield	Hazards	Source
Alpha	Large mass, +2 charge	Very short, 1- 2 inches	Paper, skin	Internal	Pu, U
Beta	Small mass, -1 charge	Short, 10 feet	Plastic, glass, metal	Internal, external skin & eyes	Fission & activation products
Gamma/x-ray	No mass or charge, photon	Several 100 feet	Lead, steel, concrete	Whole Body internal or external	Fission & activation products
Neutron	Mass, no charge	Several 100 feet	Water, concrete, plastic	Whole Body internal or external	Cf, neutron sources

Shielding – Concepts, CONT'D

Gamma Ray Interaction with Matter (principal interactions)

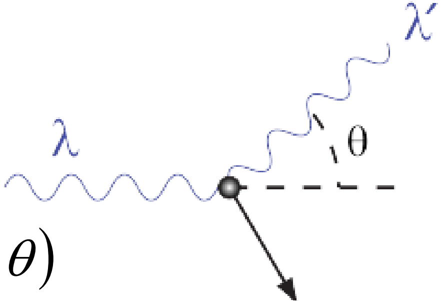
Photoelectric Effect

$$hf = \phi + E_{k_{\max}}$$



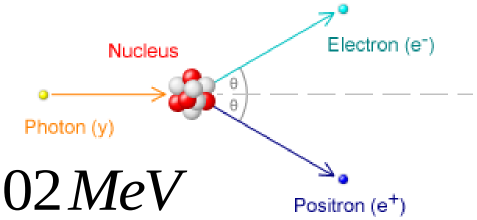
Compton Effect

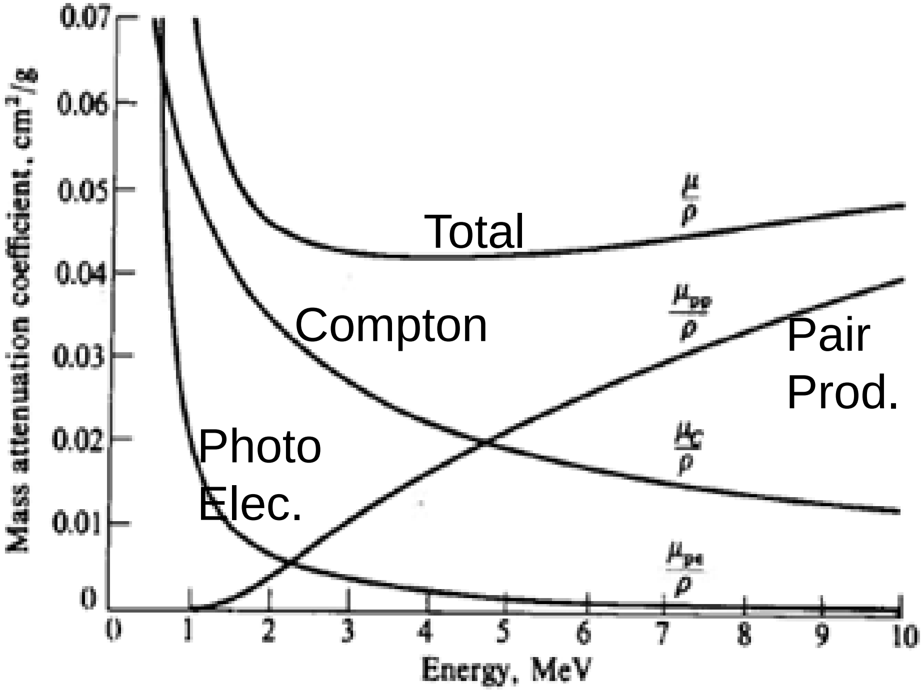
$$\lambda' - \lambda = \frac{h}{m_e c}(1 - \cos\theta)$$



Pair Production

$$hf \geq 2m_e c^2 = 1.02\,MeV$$





Mass attenuation coefficients of lead as a function of γ-ray energy

Ref: J.R. Lamarsh, Introduction to Nuclear Engineering, Addison-Wesley,

Shielding – Evaluation Methodologies

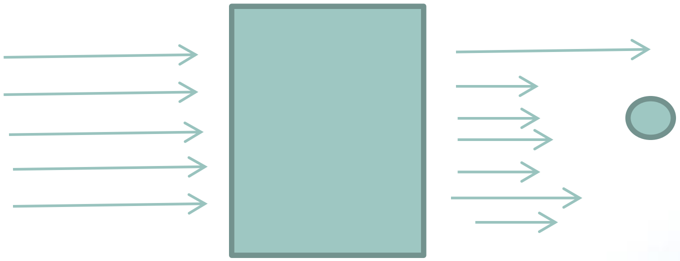
Gamma Radiation – Exposure Rate for Flux at Initial Energy E_0

- Exposure Rate With No Shield:

$$X_0 = 0.0659 E_0 (\mu_a / \rho)_{\text{air}} \phi_0 \quad \text{(mR/hr)}$$

- Exposure Rate With Shield:

$$X = 0.0659 E_0 (\mu_a / \rho)_{\text{air}} \phi_b \quad \text{(mR/hr)}$$



- With Mass Absorption Coefficient, $(\mu_a/\rho)_{\text{air}}$

See NIST **NISTIR 5632** for database of attenuation and absorption coefficients for materials

Shielding – Evaluation Methodologies, CONT'D

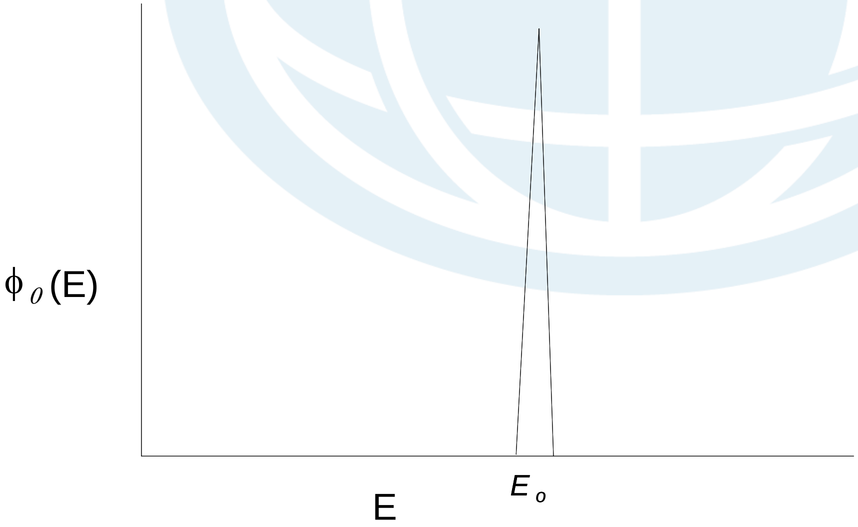
Gamma Radiation – Buildup Flux

- Scattered Radiation is Built-Up at Lower Energies from Compton-Scattered Radiation and Bremsstrahlung (deceleration of electrons from Compton, Photoelectric, and Pair-Production)
- Buildup Flux:
  - *For Point Source at Distance R :*

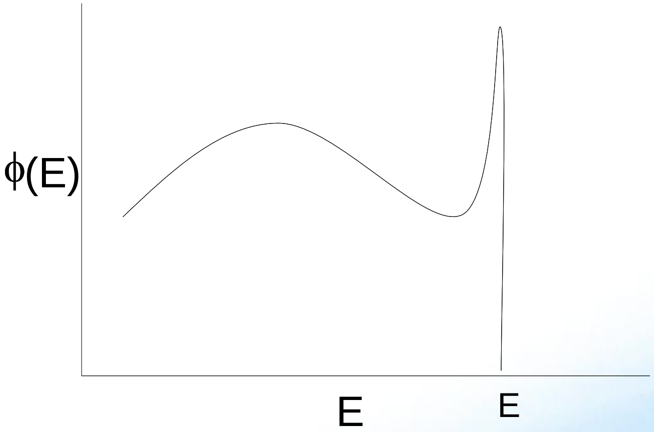
$$\phi_b = \phi_0 \times Buildup = \frac{S e^{-\mu R} B_p(\mu R)}{4\pi R^2}$$

- Buildup Factor:
  - *Point Source Factor (Taylor Form):*

$$B_p(\mu r) = A e^{-\alpha_1 \mu r} + (1 - A) e^{-\alpha_2 \mu r}$$



Energy spectrum of incident γ-ray beam



Energy spectrum of emergent γ-rays

Shielding – Evaluation Methodologies, CONT'D

Considerations in Neutron Shielding

- Similar Concepts as for Gamma Shielding except Interactions Occur with Atoms (not electrons)
- Significant Contribution to Dose from Secondary Photons from Inelastic Neutron Scattering and from Neutron Capture
- Isotopic (Rather than Elemental) Composition of Medium
- Challenges with Shine or Indirect Streaming

Shielding – Evaluation Methodologies, CONT'D

Deterministic Transport Theory

- **Linear Boltzmann Equation is Solved Numerically**
- **Discrete-ordinate Methods**
  - Multigroup Form of Transport Equation Integrated over Each Spatial and Directional Cell of Mesh of Geometry
  - Problems with Irregular Shapes and Boundaries where Simplified Techniques such as Point Kernels with Buildup Cannot be Used
  - Can Treat Very Deep Penetration Problems

Monte Carlo Methods

- **Simulation Made of Stochastic Particle Migration through the Geometry**
  - Probability Relationships of Radiation Interacts with the Medium
  - No Use of Transport Equations
  - Complex Geometry Simulations
  - Computationally Very Expensive, Especially for Deep Penetration
  - PRIMARY TOOL OF SHIELDING ANALYSIS IS MCNP CODE

Shielding – Radioactivity Units

Units to Characterize Amount of Radioactivity

- **Curies (Ci)**
  - 1 Ci = 3.7×10^{10} decays/sec
  - Total or Radionuclide-Specific
- **Becquerel (Bq)**
  - 1 Bq = 1 decay/sec
  - Total or Radionuclide-Specific
- **Decays per Minute per milliliter (dpm/ml)**
  - Used to Characterize Activity of Solutions
  - Total or Radionuclide-Specific

Shielding – Exposure/Dose Units

Radiation Unit	Measures	Effect On	Type of Radiation	Relates to	Conversion
Roentgen (R) C/kg	Exposure	Air	Gamma and x-ray		1 R = 1000 milliroentgen (mR) 1 C/kg = 3,876 R
rad (Radiation Absorbed Dose); Gray (Gy)	Dose	Any Material	All Types		1 Gy = 100 rad =1 J/kg 10 μGy = 1 mrad 1 Wh/l ≅ 360,000 rad
rem (Roentgen Equivalent Man); Sievert (Sv)	Dose Equivalence (Dose Equivalence = Dose x Quality Factor)	Man	All Types	Accounts for Difference in Dose and Damage	1 Sv = 100 rem 10 μGy = 1 mrad

Radiolysis – Concepts

- **G-values**
  - G = # Molecules Produced per 100 eV absorbed energy
  - Dependent on Incident Radiation Type
- **Forward (Radiolytic) vs. Back Reactions**
  - Forward:

$$H_2O \xrightarrow{\text{incident radiation}} H_2O^+_{aq},\ OH,\ e^-_{aq},\ H,\ H_2O_2,\ H_2$$

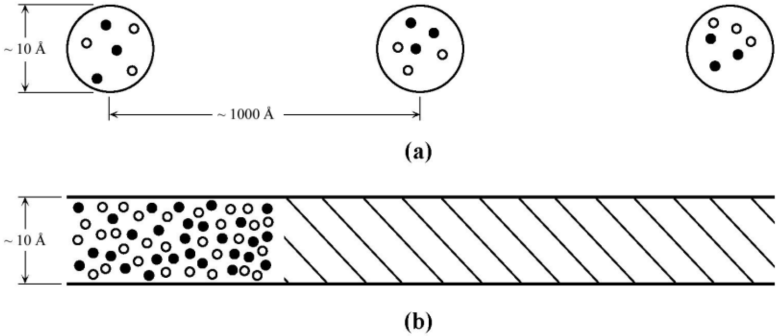
  - Back:

$$H + H_2O_2 \rightarrow OH + H_2O$$

$$OH + H_2 \rightarrow H + H_2O$$

$$H_2 + H_2O_2 \rightarrow 2H_2O$$

Linear Energy Transfer Concept



Schematic depicting the formation of H and OH radicals in the track of a 1-MeV electron (a) and alpha particle (b)

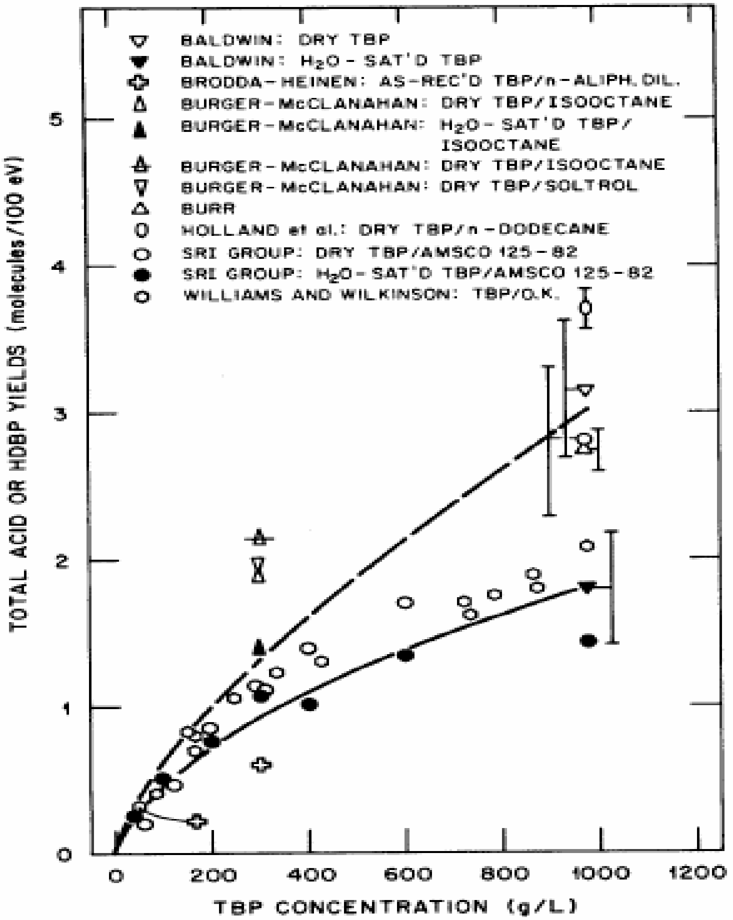
Radiolysis – Effects in Separations Process Solutions

- **Tri-*n*-butyl Phosphate (TBP)**
  - TBP Used in PUREX and HM Processes
  - Chemical (Hydrolytic) and Radiolytic Reactions Decompose TBP
  - Breakdown Sequence: TBP → Dibutyl Phosphoric Acid (HDBP) → Monobutyl Phosphoric Acid (H_2MBP) → Phosphoric Acid (H_3PO_4)
  - Many Hydrocarbons Formed Through Radiolysis of TBP
  - Addition of nitric acid to TBP solutions introduces many thermal reactions
- **Ferrous Sulfamate**
  - Fe(II) Used to Reduce Np(V) to Np(IV) and Pu(IV) to Pu(III) for Subsequent Separation; Protects Reduced Pu and Np from OH^- Radical
  - Sulfamate Added to Prevent NO_3^- Oxidation of Fe(II)
  - Radiolytic Reactions Decompose Fe^{2+} and Sulfamate
- **Radiation Effects on Ion Exchange Materials**
  - Various Resin Systems are Used
  - Radiation Causes Loss of Exchange Capacity
  - Radiation Causes Gas Evolution

Radiolysis – Effects in Separations Process Solutions, CONT'D

Radiolysis of TBP

- Radiolysis of TBP Alone or in Diluents, Anhydrous or Water-Saturated Cause Ionized or Excited TBP
- Radiolysis Product in Greatest Yield is HDBP
- Greater Yield in Anhydrous TBP than Water-Saturated
    - Anhydrous: G = 3 total acid molecules/100 eV
    - Water-Saturated: G = 1.8 total acid molecules/100 eV



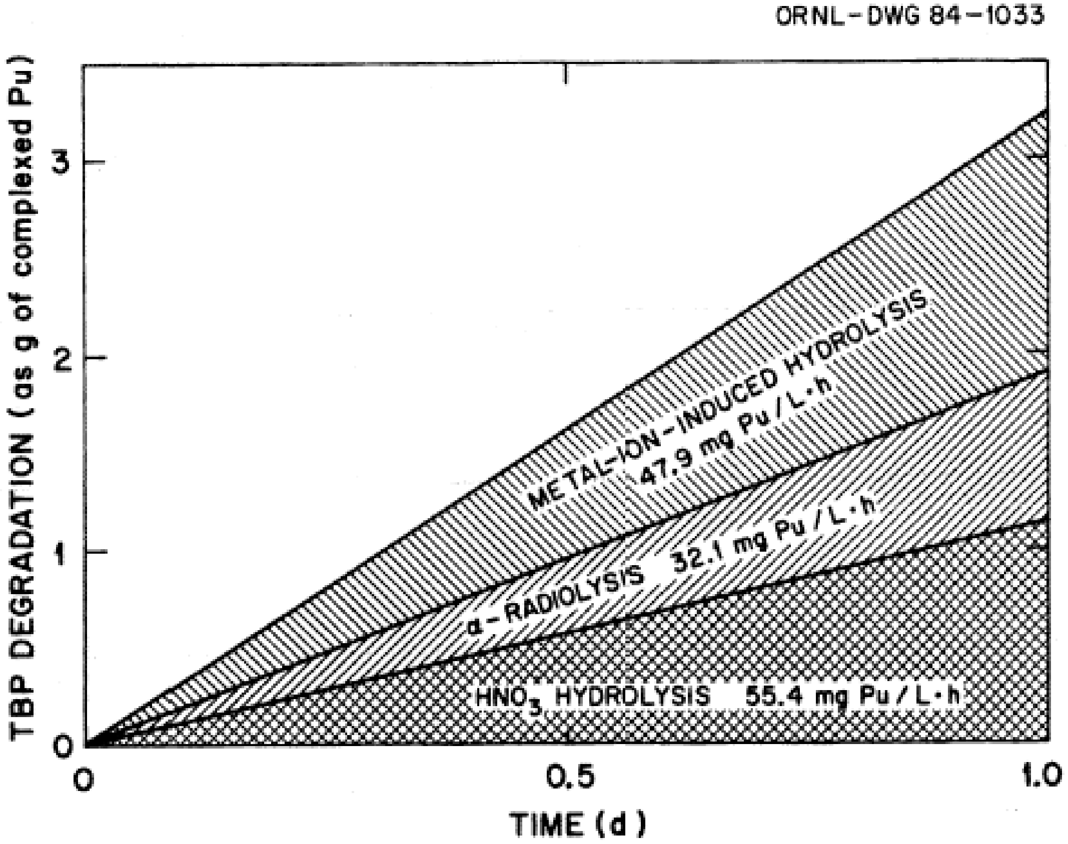
Correlation of published data for yields of total acid and HDBP from TBP-aliphatic diluent solutions

Ref: Chapter 7, "RADIOLYTIC BEHAVIOR," in Science and Technology of Tributyl Phosphate, Volume I, Wallace W. Schulz and James D. Navratil, eds., CRC Press, Inc., 1984

Radiolysis – Effects in Separations Process Solutions, CONT'D

Total Degradation of TBP

- TBP Degradation is Due to Hydrolysis and Radiolysis
- Strong Effect of Temperature on TBP Degradation Rate



TBP degradation rates due to acid hydrolysis, alpha radiolysis, and metal-ion-induced hydrolysis at 80°C

Ref: M.H. Lloyd and R.L. Fellows, "Alpha Radiolysis and Other Factors Affecting Hydrolysis of Tributyl Phosphate," ORNL/TM-9565, June 1985

Radiolysis – Effects in Separations Process Solutions, CONT'D

Radiolysis of Ferrous Sulfamate
$Fe(SA)_2$ or $Fe(II) + (NH_2SO_3^-)_2$

- If Fe^{2+} not Present, Quick Reversion of Np(IV) to Np(V) and Pu(III) to Pu(IV)
- High Dose Rate Process Solution Can Cause Rapid Depletion of Fe^{2+}

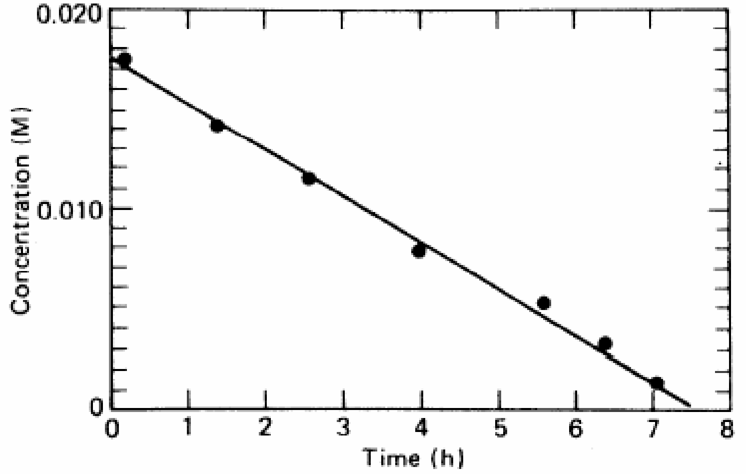


Fig. 2. Depletion of Fe(II) from radiolysis by dissolved fission products of ^{235}U in actual process solution. Dose rate = 1.5×10^5 rad/h, T = ~25°C.

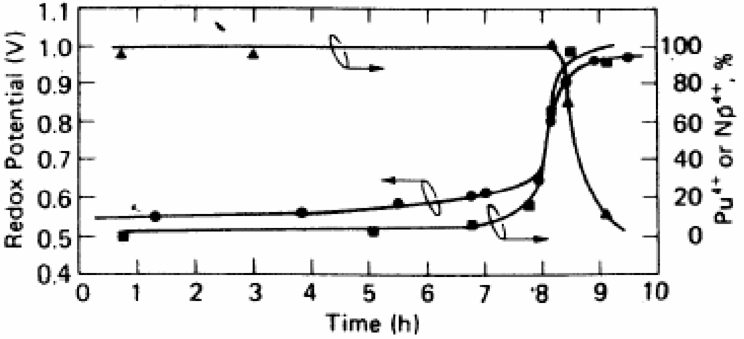


Fig. 3. Dependence of the redox potential and fraction of ^{237}Np or ^{238}Pu in the 4+ state on radiolysis by dissolved fission products of ^{235}U in an actual process solution. Dose rate = 1.5×10^5 rad/h, T = ~25°C, ● = redox potential, ■ = percent Pu(IV), and ▲ = percent Np(IV).

Ref: N.E. Bibler, "Radiolytic Instability of Ferrous Sulfamate in Nuclear Process Solutions," Nuclear Technology, Volume 34, August 1977

Radiolysis – Effects in Separations Process Solutions, CONT'D

Radiolysis of Ferrous Sulfamate

- Co-60 Gamma Irradiator Used to Investigate Radiolysis Effects in Process Solutions
- Both Fe^{2+} and Sulfamate are Depleted

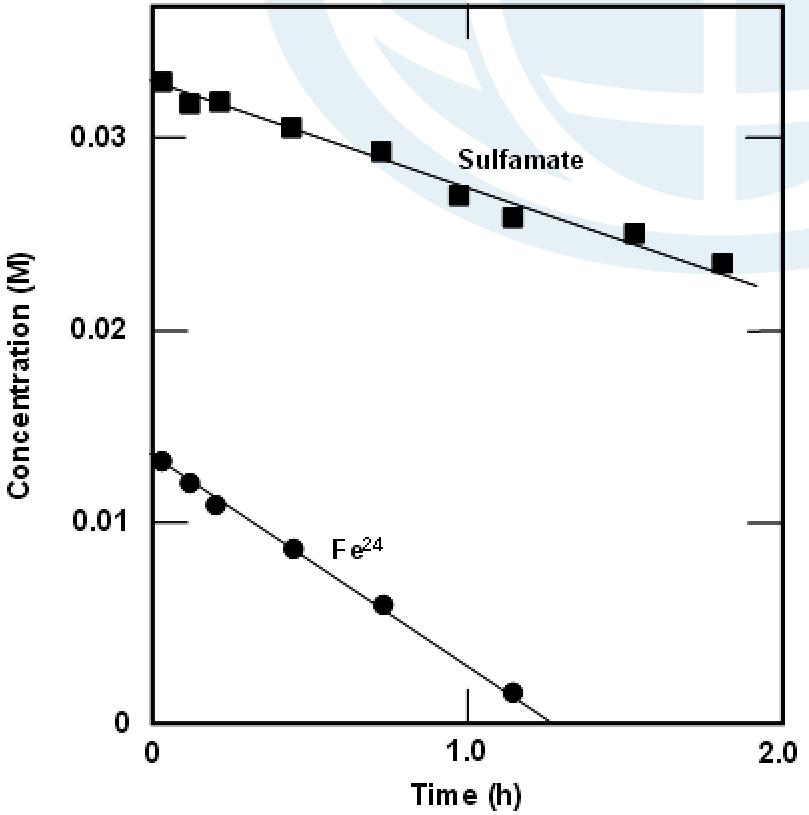


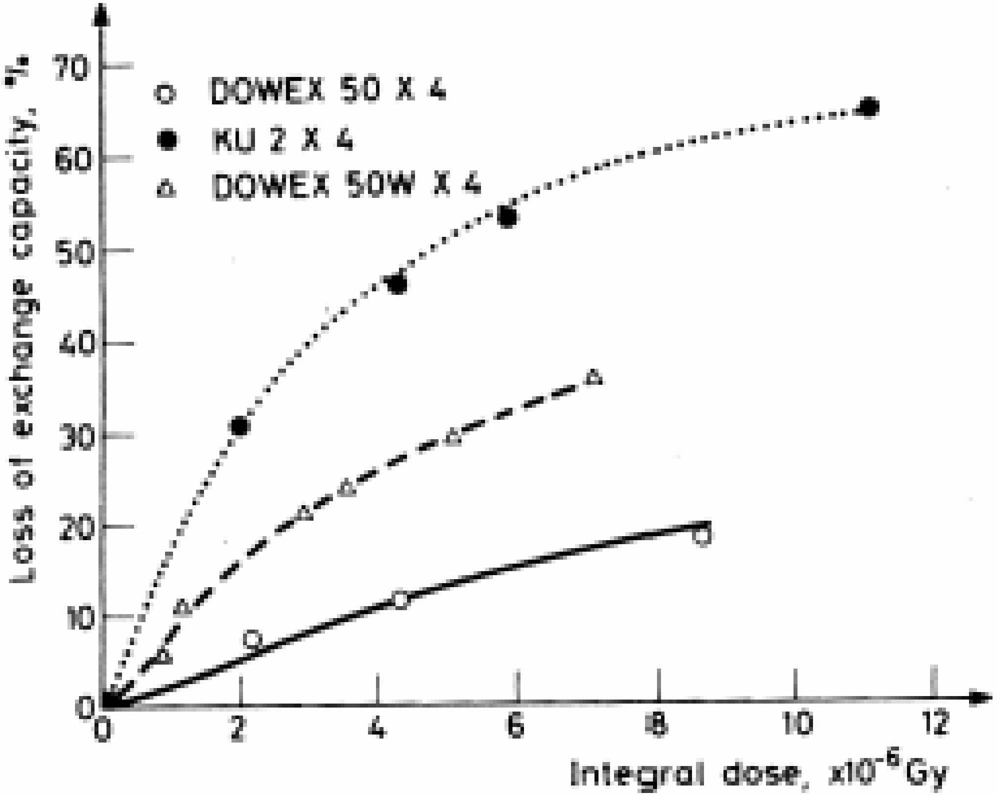
Fig. 1. Depletion of Fe(II) and sulfamate from ^{60}Co gamma radiolysis of simulated process solutions. Dose rate = 6.09 X 10^5 rad/h T = 30 to 37°C, ● = Fe(II), and ■ = sulfamate.

Ref: N.E. Bibler, "Radiolytic Instability of Ferrous Sulfamate in Nuclear Process Solutions," Nuclear Technology, Volume 34, August 1977

Radiolysis – Effects in Separations Process Solutions, CONT'D

Radiolysis of Ion Exchange Media

- Doses of 10^5 to 10^6 Gy Significant to Synthetic Organic Ion Exchangers
- Polycondensation Type Resistant to Radiation Damage, but Overall Initial Properties Poor
- Gas Evolution During Radiolysis



A comparison of the change in total exchange capacity of 4% cross-linked stytrene DVB sulfonic acid resins

Ref: K.K.S. Pillay, "A Review of the Radiation Stability of Ion Exchange Materials," Journal of Radioanalytical and Nuclear Chemisry, Articles, Vol. 102, No. 1 (1986) 247-268.

Radiation Effects on Materials – Concepts for Polymers

Effects on Polymers

- Irradiation Effects
  - Loss of Elasticity and Sealing Ability; Gas Evolution; Leaching
- Important Factors
  - Total Dose (rad); Dose Rate
  - Presence of O_2
- Degradation Mechanisms – One Mechanism Frequently Predominates
  - Scission: Molecular Bonds Ruptured - Reduces the Molecular Weight and Strength; Gas Evolution
  - Cross-Linking: Polymer Molecules Linked to Form Large 3D Molecular Networks – Causes Hardening and Embrittlement
  - Enhanced Oxidation

Radiation Effects on Materials – Concepts for Polymers, CONT'D

Effects on Polymers, CONT'D

- **Radiation Effects Difficult to Predict**
  - For Carbon-Carbon Chains (Backbones), Cross-Linking will Occur if H attached to C; Scission will Occur at Tetra-Substituted Carbon
  - Polymers with Aromatic Molecules More Resistant than Aliphatic
    - Polystyrenes (aliphatic)
    - Polyamides (aromatic)
- **Loss of Mechanical Properties Important**

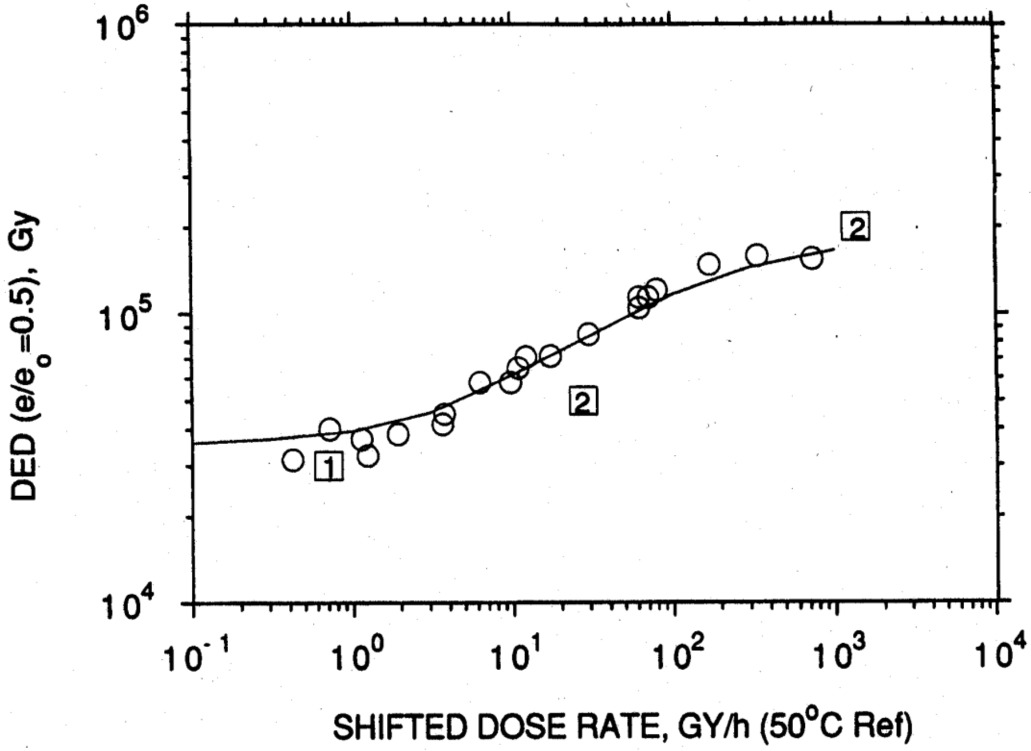
Material	Radiation Stability	Comments
Polystyrene	Excellent	
Polyethylene, various densities	Good/Excellent	High-density grades not as stable as medium- or low-density grades.
Polyamides (nylon)	Good	Nylons 10, 11, 12, 6-6 are more stable than 6. Film and fiber are less resistant.
Polyimides	Excellent	
Polysulfone	Excellent	Natural Material is yellow.
Polyphenylene sulfide	Excellent	
Polyvinyl chloride (PVC)	Good	Yellows. Antioxidants and stabilizers prevent yellowing. High-molecular-weight organotin stabilizers improve radiation stability; color-corrected radiation formulations are available.
Polyvinyl chloride/Polyvinyl acetate	Good	Less resistant than PVC.
Polyvinylidene dichloride (Saran)	Good	Less resistant than PVC.
Styrene/acylonitrile (SAN)	Good/Excellent	
Polycarbonate	Good/Excellent	Yellows. Mechanical properties not greatly affected; color-corrected radiation formulations are available.
Polypropylene, natural Polypropylene, stabilized	Poor/Fair	Physical properties greatly reduced when irradiated. Radiation-stabilized grades, utilizing high molecular weights and copolymerized and alloyed with polyethylene, should be used in most radiation applications. High-dose-rate E-beam processing may reduce oxidative degradation.
Fluoropolymers:		When irradiated, PTFE and PEA are significantly damaged. The others show better stability. Some are excellent.
Polytetrafluoroethylene (PTFE)	Poor	
Perfluoro alkoxy (PEA)	Poor	
Polychlorotrifluoroethylene (PCTFE)	Good/Excellent	
Polyinyl fluoride (PVF)	Good/Excellent	
Polyvinyllidene fluoride (PVDF)	Good/Excellent	
Ethylene-tetrafluoroethylene (ETFE)	Good	
Fluorinated ethylene propylene (FEP)	Fair	
Cellulosicsc		Esters degrade less than cellulose does.
Esters	Fair	
Cellulose acetate propionate	Fair	
Cellulose acetate butyrate	Fair/Good	
Cellulose, paper, cardboard	Fair/Good	
Polyacetals	Poor	Irradiation causes embrittlement. Color changes have been noted (yellow to green).
ABS	Good	High-impact grades are not as radiation resistant as standard-impact grades.
Acrylics (PMMA)	Fair/Good	
Polyurethane	Good/Excellent	Aromatic discolors, polyesters more stable than esters. Retains physical properties.
Liquid crystal polymer (LCP)	Excellent	Commercial LCPs excellent; natural LCPs not stable.
Polyesters	Good/Excellent	PBT not as radiation stable as PET.
Thermosets:		
Phenolics	Excellent	Includes the addition of mineral fillers.
Epoxies	Excellent	All curing systems.
Polyesters	Excellent	Includes the addition of mineral or glass fibers.
Allyl diglycol carbonate (polyester)	Excellent	Maintains excellent optical properties after irradiation.
Polyurethanes:		
Aliphatic	Excellent	
Aromatic	Good/Excellent	Darkening can occur. Possible breakdown products could be derived.
Elastomers:		
Urethane	Excellent	
EPDM	Excellent	
Natural rubber	Good/Excellent	
Nitrile	Good/Excellent	Discolors.
Polychloroprene (neoprene)	Good	Discolors. The addition of aromatic plasticizers renders the material more stable to irradiation.
Silicone	Good	Phenyl-methyl silicones are more stable than are methyl silicones. Platinum cure is superior to peroxide cure; full cure during manufacture can eliminate most postirradiation effects.
Styrene-butadiene	Good	
Polyacrylic	Poor	
Chlorosulfonated polyethylene	Poor	
Butyl	Poor	Friable, sheds particulates.

Ref: K.J. Hemmerich, "RADIATION STERILIZATION, Polymer Materials Selection for Radiation-Sterilized Products," Medical Device & Diagnostic Industry, Feb 2000, p. 78

Radiation Effects on Materials – Concepts for Polymers, CONT’D

Dose Rate Sensitivity

- Polymers are Susceptible to Oxidation, which is Diffusion-Limited
- High Dose Rate Exposures May Not be Indicative of Aging in Low Dose Rate Environments
- Practical Example: Materials “Qualified” for 40-year Service Life May Fail Sooner



Dose to 50% elongation loss in PVC cable insulation
(Data shifted by superposition to a reference temperature of 50°C)

Ref: SAND90-2009, “Predictive Aging Results for Cable materials in Nuclear Power Plants”, K.T. Gillen, R.L. Clough, November 1990, p. 41.

Radiation Effects on Seal/Gasket/Coating Materials in Separations Service

Empirical Knowledge Base – In Vitro Testing and Service Experience

- **Fluoropolymers – needed for chemical resistance**
  - Teflon –initial damage at 1-5E4 rad, severe damage at 1-10 Mrad
  - Jumper Gaskets: Teflon-asbestos (functional to 100-1000 Mrad)
  - Viton® B – FKM fluoroelastomer, older formulations with lead oxide, not suitable for TBP solutions
  - Kalrez® FFKM perfluoroelastomer – expensive, acids at high temp
  - Halar®/ECTFE – low permeability, possible chloride release
  - Tefzel®/ETFE copolymer – used in HLW transfer lines, ball valves
  - Kynar®/PVDF – most resistant fluoropolymer, less resistant to strong nitric acid or NaOH solutions (stress-cracking).

Radiation Effects on Materials – Concepts for Metals

Effects on Metals

- Irradiation Effects
  - Radiation Hardening & Embrittlement at Low Irradiation Temperatures ($T_{irr} < 0.3\ T_{m.p.}$)
- Important Factors in General
  - Total Displacement Damage and Damage Rate
  - Irradiation Temperature
  - Spectral Effects (particle energy distribution)
- Degradation Mechanisms
  - “Black Spot” Damage at Low Irradiation Temperatures

Radiation Effects on Materials – Concepts for Metals, CONT'D

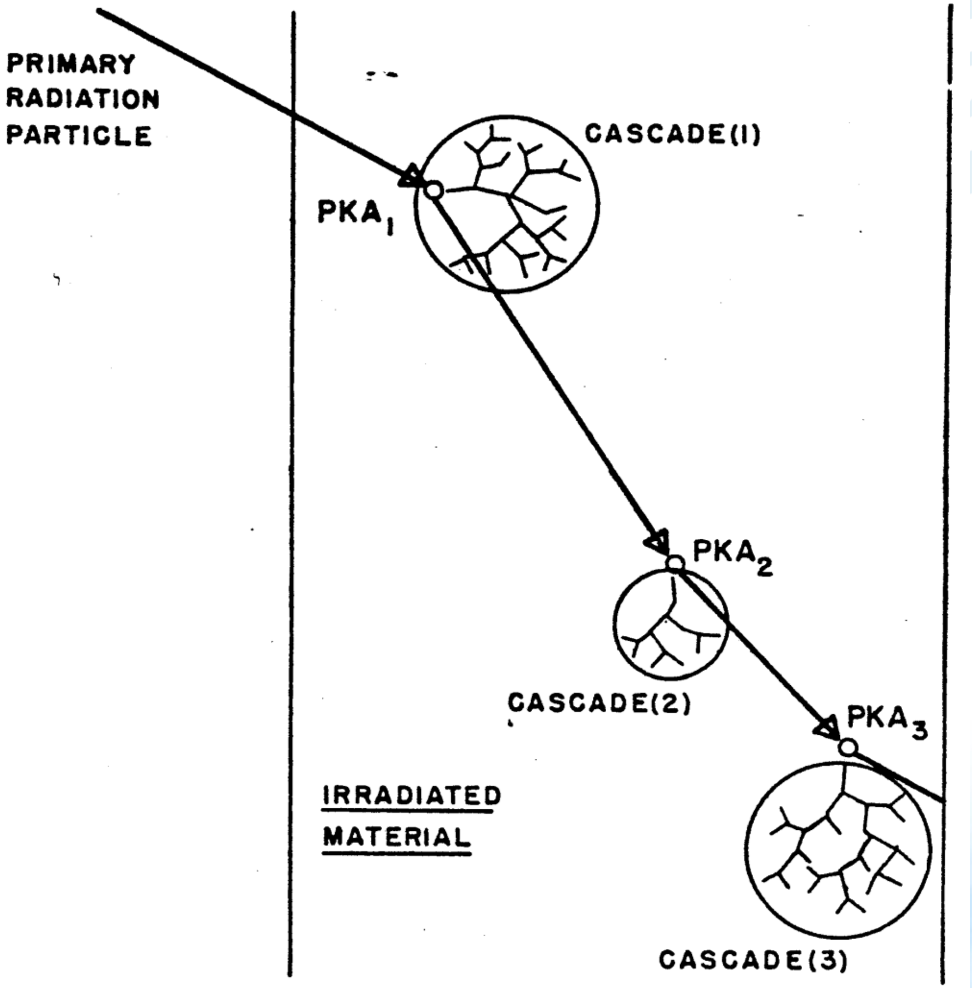
Radiation Damage Phenomena: n-Irradiation of Crystalline Materials

Primary Knock-On Atoms

- Neutron transfers Energy to Lattice atom
- One Neutron Can create Many PKAs

Cascades from PKAs

- Create Free Defects
- Recombination
- Dislocation Loops
- Stacking Fault Tetrahedra



Radiation Effects on Materials – Concepts for Metals, CONT'D

Displacements per Atom Formulation

$\nu(T) = 0$ displacements for $T<E_d$

$\nu(T) = 1$ for $E_d<T<2E_d$

$\nu_{NRT}(T) = 0.8T/(2E_d)$ for $T>2E_d$

E_d = threshold energy to cause a displacement from a crystalline position

$$K\left(\frac{dpa}{sec}\right) = \int_{0}^{E_{max}} \phi(E)dE \int_{E_d}^{\Lambda E} \nu(T)\frac{d\sigma(E,T)}{dT}dT$$

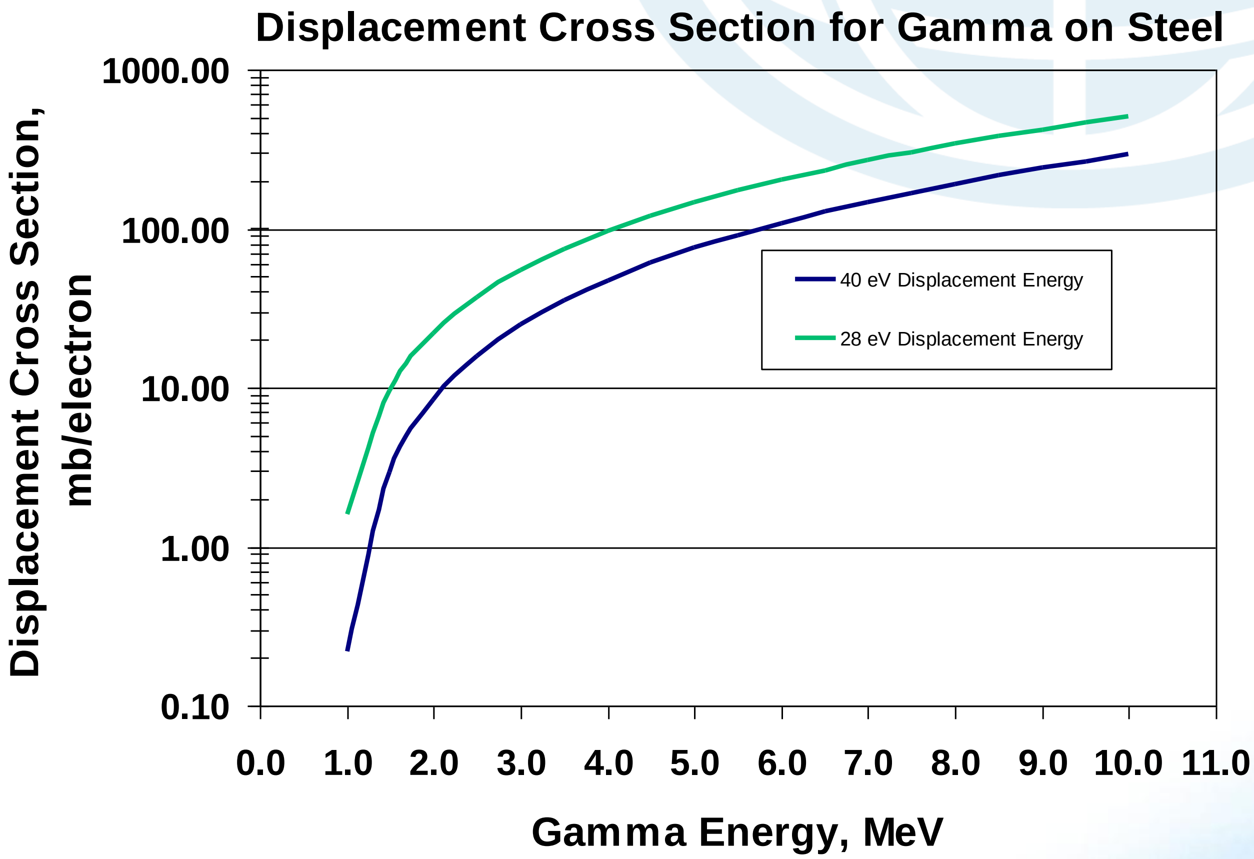
Displacement Rate for Elastic Collision Events

See ASTM E693 for a full discussion including tabulation of $\sigma_d(E)$ that is effectively the integral on the right

Radiation Effects on Metals in Separations Systems

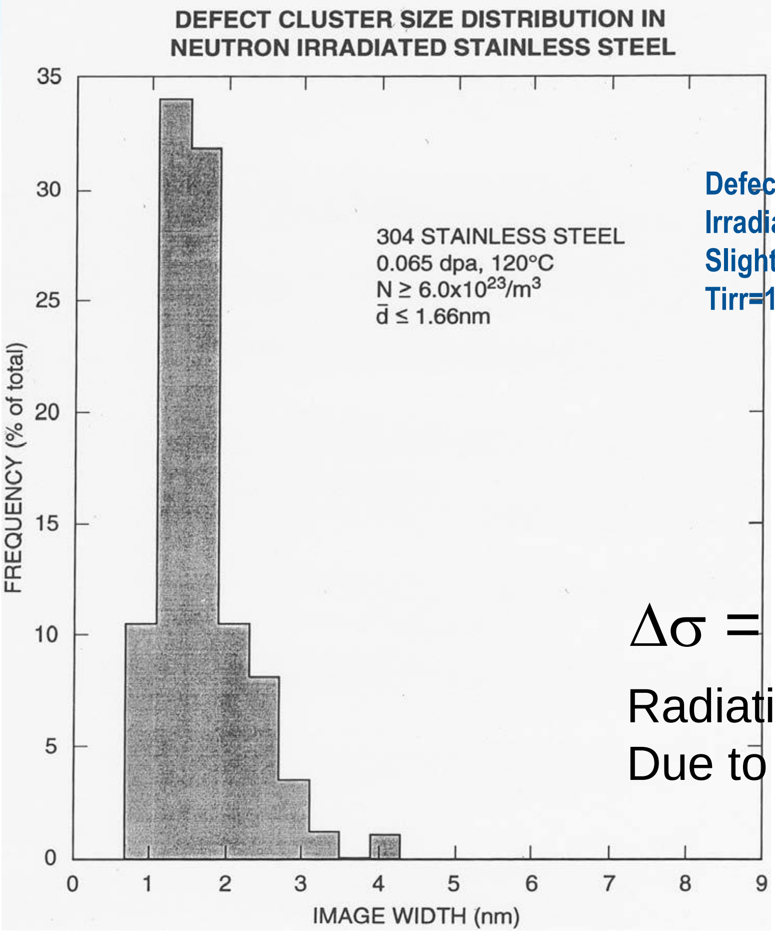
Displacements in metals from:

- Alpha/Beta – Near Surface
- Spontaneous Neutrons – Very Low Dose
- Gamma – Very Low Dose

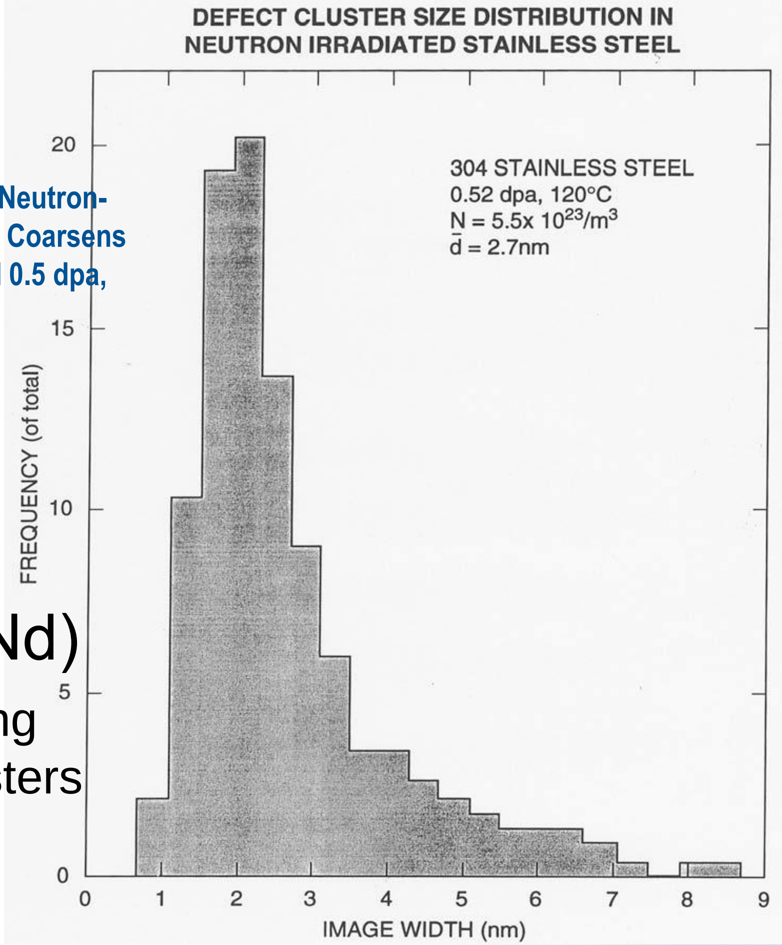


Radiation Effects on Metals in Separations Systems, CONT’D

No Significant Impact to Mechanical Properties Expected for Separations Tanks



Defect Cluster Density in Neutron-Irradiated Stainless Steel Coarsens Slightly Between 0.06 and 0.5 dpa, Tirr=120°C



$$\Delta\sigma = M\alpha\mu b\sqrt{(Nd)}$$

Radiation Hardening
Due to Defect Clusters

Ref: S.J. Zinkle and R.L. Sindelar, "Defect Microstructures in Neutron-Irradiated Copper and Stainless Steel," J. Nucl. Mat. 155-157 (1988) p. 1196

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