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SALTSTONE VAULT #2 INTERIOR LINING REVIEW (U)**T. E. Skidmore, K. D. Billings**

SAVANNAH RIVER NATIONAL LABORATORY

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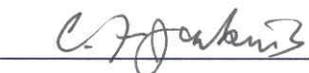
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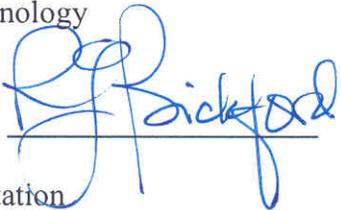
Saltstone Vault #2 Interior Lining Review (U)

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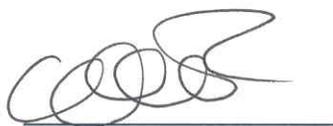
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LIST OF ACRONYMS, ABBREVIATIONS, AND UNITS

ADC	Authorized Derivative Classifier
ARP/MCU	Actinide Removal Process/Modular CSSX Unit
ASTM	American Society of Testing and Materials
CSSX	Caustic Side Solvent Extraction
CSR	Compression Stress Relaxation
DBA	Design Basis Accident
DDA	Deliquification, Dissolution, and Adjustment
DGEBA	Diglycidal ether of bisphenol A (epoxy)
DLO	Diffusion Limited Oxidation
E _a	activation energy
EPA	Environmental Protection Agency
EPDM	Ethylene-propylene diene monomer
EPRI	Electric Power Research Institute
ESCR	Environmental Stress Crack Resistance
ETF	Effluent Treatment Facility
EVA	Ethylene Vinyl Acetate
FML	Flexible Membrane Liner
FRP	Fiber-reinforced plastic (or polymer)
G value	The number of molecules, radicals, crosslinks, etc., of a specified type formed or consumed per 100 electron volts (eV) of energy absorbed.
Gray (Gy)	International unit of radiation absorbed dose, 1 Gy = 100 rad = 1E+04 ergs/gram
HDPE	high density polyethylene
HP-OIT	high pressure - oxidative induction time
LCS	low curie salt solution
LDPE	low-density polyethylene
MCU	Modular CSSX Unit
MDPE	medium density polyethylene
mils	unit of thickness, typical for coatings/linings (1 mil = 0.001 inch)
MS&T	Materials Science & Technology
NRC	Nuclear Regulatory Commission
OIT	oxidative induction time
PA	Performance Assessment
PVC	Polyvinyl chloride
QF	quality factor
R	universal gas constant
rad	radiation absorbed dose, 1 rad = 100 ergs/gram
SDF	Saltstone Disposal Facility
SWPF	Salt Waste Processing Facility
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
USEPA	United States Environmental Protection Agency
UV	ultraviolet
WSRC	Washington Savannah River Company

1.0 EXECUTIVE SUMMARY

SRNL/Materials Science & Technology was requested to evaluate lining options for the new Saltstone Vault #2 design. To improve the probability of the new design to meet the 10,000-year Performance Assessment (PA), SRNL/Environmental Restoration Technology previously recommended that a “long-term” coating or lining be used to protect the concrete from sulfate attack and other degradation mechanisms. The service life desired for the coating is 100 years.

Given specific design requirements, many coating types were reviewed. Manufacturers of organic coatings and linings typically used for commercial nuclear power plant containments, tank linings and secondary containments were consulted. Due to higher installed cost of metallic linings and concerns regarding the use of unbonded membrane liners, the focus of this review was on liquid-applied lining systems. Bonded membranes such as Marseal[®] 8000 were also considered but cannot be recommended at this time.

For the service conditions anticipated, mat-reinforced epoxy-novolac thermosetting linings are recommended. Flexible or elastomeric coatings such as flexible epoxies, polyureas and polyurethanes cannot be recommended at this time, primarily due to concern over chemical degradation at peak temperatures as well as lower radiation resistance. However, these may be options for future vaults with lower radioactivity levels or thermal conditions, or if more flexible systems are required.

Service life prediction of organic materials is complex. There are no known case histories of polymeric linings or coatings beyond 50-75 years. Such linings are typically used in facilities with a limited design life (20-60 years) and are often accessible for inspection and maintenance. Coatings used for protection of underground or offshore structures are less accessible but are not generally intended for 50+ years of service, though 100-year service life requirements are becoming more common. Accelerated-aging data for thermosetting linings are also limited.

Under the anticipated conditions, mat-reinforced thermosetting polymer linings are expected to maintain high integrity during initial vault operations and for the first 50-100 years of service. This is based on several assumptions including: limited oxidation, gradual temperature decline, tolerable radiation dose with minimal dose rate effects, minimal differential settlement and proper installation. As with HDPE geomembranes, such linings will likely remain physically intact and act as a diffusion barrier for much longer periods, though time to actual failure is difficult to predict.

From radiation exposure alone, reinforced thermosetting linings are expected to resist degradation for at least 300-400 years (10 Mrad total) with no significant dose rate effects. The dose at 3000-4000 years (50 Mrad) is also expected to be tolerable. The 10,000-year total dose (123 Mrad) is still far lower than the qualification dose for nuclear power plant coatings (1000 Mrad). However, as the long-term aging performance of thermosetting linings at relevant conditions has not been widely studied, a test program is recommended to study lining performance in a simulated Saltstone environment.

2.0 BACKGROUND

The mission of the Saltstone Facility in Z-Area at the Savannah River Site is to process and dispose of radioactive salt solution from the Liquid Waste Disposition tank farm facilities. The Saltstone Facility immobilizes the low radioactivity salt solution waste by mixing it with a dry material mixture of flyash, slag, and cement to produce a non-hazardous grout (Saltstone). This grout is then poured into large concrete vaults for permanent disposal.

The Saltstone Vault 2 Project is specifying the design of prestressed cylindrical concrete tanks (Cells 2A and 2B) to meet future facility disposal capacity and throughput requirements. As part of the Performance Assessment (PA) for the Vault#2 design, SRNL/Environmental Restoration Technology previously recommended that a “long-term” coating barrier be installed on the vault interior floor and wall surfaces to protect the concrete from sulfate attack and other degradation mechanisms [1]. Sulfate attack has been identified as the degradation mechanism of concern, though several mechanisms can occur. C_3A ($3CaOAl_2O_3$) in the presence of sulfates leads to the formation of ettringite within the concrete, which leads to expansion of the concrete and subsequent cracking.

ASTM C150 covers eight types of portland cement [2]. Type I portland cement is a general-purpose cement. Type II portland cement generates less heat at a slower rate and has a moderate resistance to sulfate attack. Type III cements with less than 5% C_3A are stated as being highly sulfate resistant, though Type III cements typically have C_3A contents of 10%. Type V portland cement is used only in concrete structures that will be exposed to severe sulfate action, principally where concrete is exposed to soil and groundwater with a high sulfate content. The Vault #2, Class 3 sulfate resistant concrete formulation therefore consists of Type V cement with various additions of blast slag, silica fume, Class F fly ash, water, natural sand and granite gravel [1].

Early PA simulations showed that the probability of the vault design meeting the 10,000-year requirement was improved with the use of an interior lining [1]. With no coating, the probability of failure before 10,000 years was estimated at 44%, with a median time to failure of 11,800 years. With a “short-term” coating (effective only during active operations), the probability was 39% with a median time to failure of 13,500 years. With a long-term coating barrier, defined as having integrity for 100 years with gradual degradation over the next 900 years, the probability of failure was reduced to 23%, with a median time to failure of 19,000 years. Increasing concrete thickness from 8 to 12 inches in combination with a “short-term” coating reduced the failure probability to 15%. The acceptable probability value has not been defined.

High-density polyethylene (HDPE) was extensively reviewed by SRNL/Environmental Restoration Technology for use as a geomembrane barrier on the vault exterior [3]. HDPE is commonly used in landfill and geomembrane barrier systems alone or as part of a multiple barrier system [4-11]. Reference 3 found that HDPE could be used on the vault exterior to prevent soil-side degradation of the concrete and minimize outward diffusion of pore fluid, and would remain as a functional barrier for the 10,000 year period based on review of various studies. Reference 3 also indicated that HDPE should be limited to a radiation dose of 2.6 Mrad over the 10,000 year period to minimize oxidation and dose rate effects.

SRNL/Materials Science & Technology was requested to evaluate potential coating and lining options for the Saltstone Vault #2 interior. The primary purpose of the lining is to protect the concrete vault from sulfate attack induced by Saltstone pore fluid. The use of an interior lining is also considered prudent for overall containment of low-level radiological wastes.

The vaults are permitted in accordance with the South Carolina Department of Health and Environmental Control (SCDHEC) Regulations R.61-107.16, Solid Waste Management: Industrial Solid Waste Landfills. Due to the nitrate concentration of the waste stream, the vaults are classified as a Class 3 Industrial Solid Waste Landfill (ISWLF). The design criteria are found in R.61-107.16.42. There is no regulatory requirement for secondary containment or to be RCRA compliant.

3.0 VAULT LINING REQUIREMENTS

Per Reference 12, the following lining requirements were identified:

- The coating/lining will be applied to all walls and floor only. A two foot clean grout cap over the saltstone reduces the concentrations of sulfate that will diffuse to the roof.
- The coating/lining will be applied to the bottom 2 feet of any cell interior support structures.
- The coating/lining should mitigate sulfate attack from short-term Saltstone bleedwater (10,900 mg/L) penetration through surface cracks and by capillary suction, and diffusion of sulfate from the pore fluid of the cured Saltstone.
- The coating/lining should be radiation resistant.
- The coating/lining should be chemical resistant. Resistance to sulfates, nitrates and hydroxides (6.93E+03 to 4.84E+04 mg/L) are of particular concern. The pH of the pore fluid (13.7) is primarily driven by the hydroxide concentration, which is assumed comparable to a 5-10 wt% NaOH solution.
- The coating/lining should resist peak grout temperature (68 °C) for 1000 hours.
- Based on differential settlement calculations, the coating/lining should exhibit a minimum elongation value of 2%.
- The coating/lining should provide a long-term diffusion barrier. Initial SRNL PA modeling assumed the lining to maintain integrity for the first 100 years with gradual degradation over the next 900 years.
- The coating/lining material should be easily applied to joints, penetrations, and attachments for a large horizontal (18,000 square feet per cell) and vertical (10,000 square ft per cell) surface area.
- The coating/lining should allow for the installation of an internal drainwater collection system that may include sheet drain attachments on the wall and piping for fluid collection attached to the floor.
- Flammable gas generation rates should be identified to support development of a safety strategy.

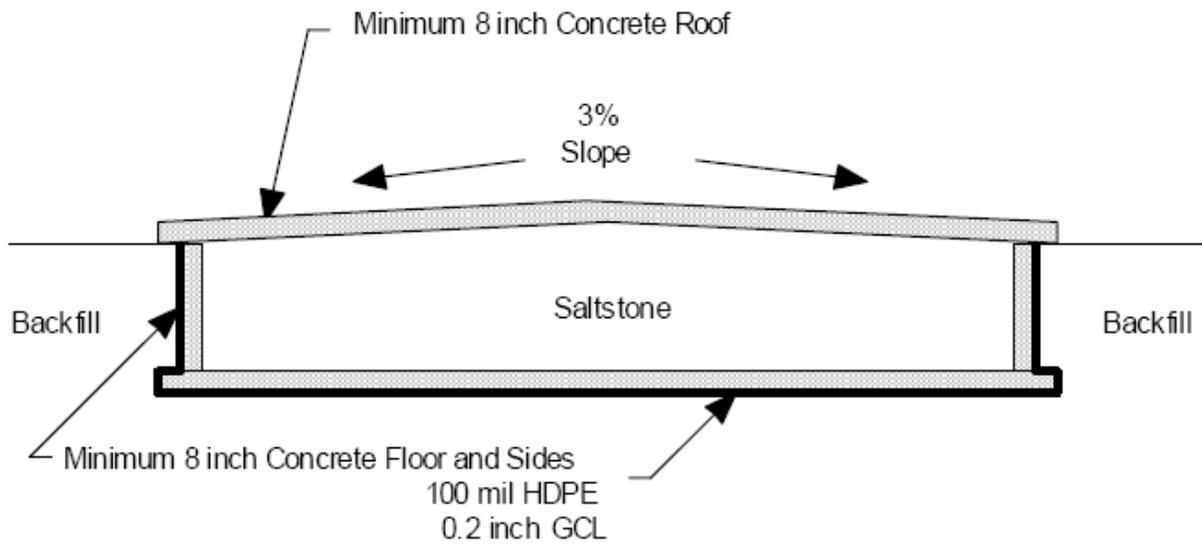


Figure 1. Preliminary Vault #2 Configuration with HDPE exterior barrier (150 feet in diameter (75 ft radius) and 22 feet high)

4.0 SALTSTONE CHARACTERISTICS

4.1 Saltstone Overview

A general description of Saltstone characteristics is provided, most of which comes from Reference 3. Saltstone is a dense, micro-porous, monolithic, low-level radioactive waste form produced by mixing low-level radioactive salt solution (~47 wt%) with blast furnace slag (~25 wt%), flyash (~25 wt%), and cement or lime (~3 wt%) to form a grout that is pumped into vaults and subsequently solidifies. The low-level radioactive salt solutions to be received in the Vault#2 design (Saltstone Processing Facility or SPF) will originate from the following processes:

- Effluent Treatment Facility (ETF)
- Deliquification, Dissolution, and Adjustment (DDA) process (Low Curie Salt (LCS) solution)
- Actinide Removal Process (ARP)/Modular CSSX (Caustic Side Solvent Extraction) Unit (MCU)
- Salt Waste Processing Facility (SWPF)

These salt solutions are expected to contain 15-32 wt% soluble salts, with an expected average of about 28 wt%. The specific gravity of the solution is expected to range from 1.1 to 1.28, with an expected average of about 1.25. The salt solutions have an average pH of 13+.

4.2 Physical Characteristics

Saltstone grout has a porosity of approximately 0.42, an effective diffusion coefficient (D_m/t) of approximately $0.16 \text{ cm}^2/\text{yr}$, and an initial saturated hydraulic conductivity of approximately $1.0\text{E}-11 \text{ cm/s}$ (Reference 13). It is assumed that the saturated hydraulic conductivity will increase over time to $1.0\text{E}-09 \text{ cm/s}$ after 10,000 years. After burial, the Saltstone is assumed to remain essentially saturated due to high capillary suction. The specific gravity (SG) of Saltstone ranges from 1.6 to 1.8, with an expected average of about 1.7 (density of 1.76 g/ml). Drainwater has a SG of 1.3. More recent data indicate that Saltstone has the following physical properties: saturated hydraulic conductivity = $1.0\text{E}-08$ to $1.0\text{E}-09 \text{ cm/s}$; porosity = 61 to 62%; particle density (specific gravity) = 1.75 to 1.79 g/cm^3 , and a bulk density $\sim 1.0 \text{ g/cm}^3$.

4.3 Chemical Composition

The solid components of Saltstone (i.e. blast furnace slag, flyash, and cement or lime) make up ~53% by weight, and consist primarily of the following in descending order: silicon dioxide, aluminum oxide, calcium oxide, magnesium oxide, and iron (III) oxide. The blast furnace slag contains sulfides which produces reducing conditions within the Saltstone. The primary soluble salts present within the salt solution (~47 wt% of the Saltstone) include in descending order: sodium nitrate, sodium hydroxide, sodium nitrite, sodium aluminum hydroxide ($\text{NaAl}(\text{OH})_4$), sodium carbonate, and sodium sulfate. Saltstone results from the mixture of the solid components with the salt solution and the subsequent hydration and other chemical reactions between the two.

Saltstone is described as an alkaline, reducing, microporous, cementitious matrix (grout), consisting of solids such as calcium aluminosilicate and containing a solution of salts within its

pore structure (pore fluid). The pore fluid consists predominately of sodium, nitrate, and nitrite ions, with hydroxides estimated at $6.93\text{E}+03$ to $4.84\text{E}+04$ mg/L and 74,234 mg/L nitrate/nitrite. The pH of the pore fluid is 13.7, comparable to a dilute NaOH solution.

Saltstone contains many metals, most of which are contained within the cementitious matrix or are insoluble under the alkaline, reducing conditions. The salt solution may contain relatively low concentrations of organics such as benzene, butanol, isobutanol, isopropanol, methanol, phenoltetraphenylborate, toluene, tributylphosphate, and EDTA. Organics from inhibitors used in tank farm processing or added at Saltstone (antifoaming additives, etc.) may also be present. Since many of the organics are volatile, it is likely that the Saltstone will contain significantly less organics than the salt solution due to the elevated temperatures resulting from the heat of hydration and radioactive decay. Estimates of organic concentrations in the pore fluid or bleedwater were not provided, but certain compounds are known to cause degradation in polymeric linings.

4.4 Thermal Characteristics

The Vault #2 design will have a cylindrical configuration. A trapezoidal vault model was used to estimate the temperature over time from Saltstone produced from salt solution containing 0.2 Ci/gallon of Cs-137 [14]. Elevated temperatures result from both heat of hydration and radioactive decay. The temperature of the Saltstone mass is maintained <95 °C since the grout product quality degrades above this temperature. For thermal modeling purposes, a ten degree conservative pad was subtracted from the temperature limit, so the target in the analysis is 85 °C. The use of a low solar absorptivity coating on the vault roof reducing the solar absorptivity of the roof concrete from 0.65 to 0.2, which drops the peak saltstone temperature by approximately 7 °C.

In the model described, the ground below a vault to a depth of 25.0 meters serves as a heat sink for the curing saltstone. The bottom boundary at 25.0 meters is adiabatic. The initial temperature distribution in the ground varies with the time of year that pouring commences. The temperature of the top six meters varies on an annual basis, and the temperature below is constant at approximately 16.5 °C. The steady-state temperature of the earth below six meters was determined by running the model with no pouring for 1000 years.

In Figures 2-3, temperatures are shown for three locations: the vault bottom, the mid plane of the two ft. thick concrete vault base, and the interface between the concrete base and the soil. Figure 2 shows temperatures for the initial five years with Figure 3 showing the temperatures for the first 200 years. The vault bottom will reach a peak temperature of ~ 68 °C in the first month as a consequence of the heat of hydration of the curing saltstone. The foundation thereafter will cool slowly. The influence of the seasonal changes in the environmental temperature on the foundation is evident from the superimposed sinusoidal variation in the foundation temperatures. The decay of radionuclides in the saltstone will slow the cooling of the foundation. Within 5 years, the temperatures at these locations are below 30 °C. Wall temperatures were not specifically modeled but are not anticipated to exceed 68°C.

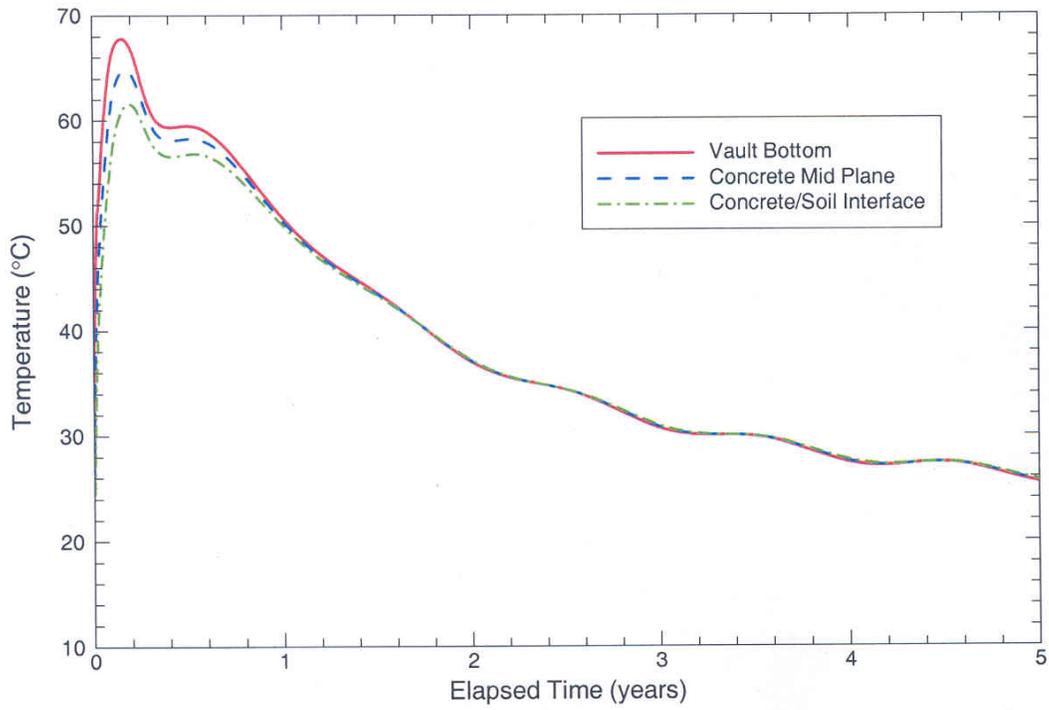


Figure 2. Thermal Behavior of Saltstone During Initial Curing [14].

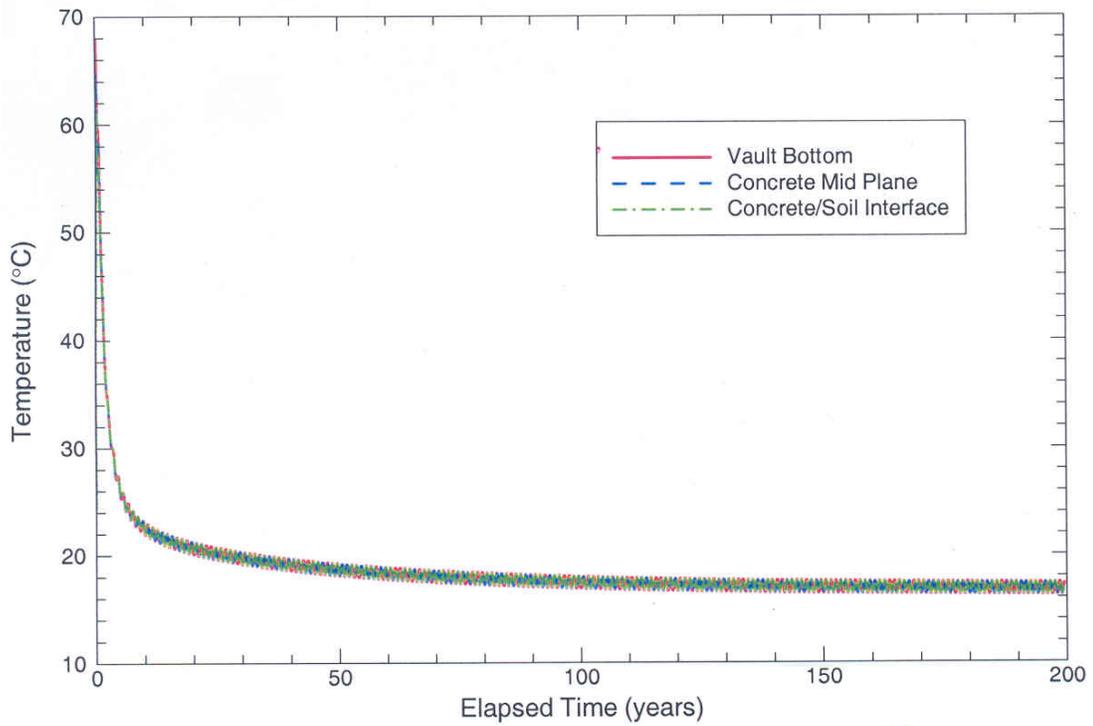


Figure 3. Thermal Behavior of Saltstone during first 200 years [14].

4.5 Saltstone Radioactivity

The salt solutions produced from the ARP/MCU and SWPF processes will have significantly lower curie contents than the LCS. Vault #2 will receive Saltstone produced from LCS, whereas future vaults will receive Saltstone produced from the lower curie content salt solutions. Therefore, radiation dose rates to the lining in future vaults may be reduced.

The primary contributor to the dose rate associated with Saltstone made from LCS is Cs-137. Cs-137 has a half-life of 30.07 years, decays by β -decay, and emits predominately gamma rays and beta particles (i.e. electrons). Radiation dose calculations were previously performed for an external HDPE membrane (density of 0.95 g/cm), for which only gamma contributions from Cs-137 were considered [15]. However, for an internal vault lining in direct contact, alpha and beta contributions must also be considered. Dose rate calculations were performed for the interior lining with the following assumptions [16]:

- The Cs-137/Ba-137m concentration is assumed to be 0.1 Ci/gal. The calculation assumed that the Cs-137/Ba-137m will be blended down or processed out of the waste solution to achieve radioactive concentrations to < 0.1 Ci/gal.
- Vault 2 is 150 feet in diameter (75 ft radius) and 22 feet tall; for the purpose of this calculation the diameter was reduced to 30 feet to optimize the mesh size. The dose rate from a 150 feet diameter vault is the same as a 60 feet diameter vault and the nuclide concentrations are maintained.
- For the integrated alpha and beta dose, only the isotopes that contribute more than 95% of the dose were included in the calculation.
- The grout density was assumed at 1.7 g/cc and the composition is the same as given in references 1 and 6 of the calculation. This grout concentration is slightly conservative than the concentration of 1.76 Ci/gram, provided in reference 1 of the calculation.
- The calculation determined the dose rate in Rem/hr in tissue by using the ANSI/ANS-1977 flux to dose conversion factors (table S1.4.8, calc reference 4). The type of liner was not specified at the time of the calculation. Therefore, the calculation assumes that one rem is equal to one rad in tissue, which results in slightly conservative dose rates. The gamma and neutron absorbed dose in most polymers is generally comparable to the dose absorbed in tissue.
- The calculation assumes that the alpha and beta radiation deposits all its energy in the liner. This assumption yields conservative absorbed alpha dose estimates, because the range of an alpha particle is small compared to the anticipated liner thickness (~100 mil).
- The calculation assumed a liner density of 1.7 g/cc for a glass-fiber reinforced epoxy lining system. A density of 0.95 g/cc is representative of an HDPE lining.

The integrated radiation dose to the lining and dose fractions are shown in Figures 4-5. Tabulated dose rates (Table 1) indicate the total absorbed dose to the lining at 10,000 years is $1.23\text{E}+08$ rad (123 Mrad), with only $7.455\text{E}+06$ rad (7.5 Mrad) from gamma contributions. The total dose at 100 years is $6.7\text{E}+06$ (6.7 Mrad), with about half from gamma ($3.4\text{E}+06$ rad or 3.4 Mrad). At the beginning of the grout storage, the beta and alpha dose is lower than the gamma dose. After ~100 years, the dose fractions from alpha/beta and gamma contributions converge and the alpha/beta dose begins to dominate. The neutron dose is negligible.

The majority of the alpha dose comes from Pu-239. However, the entire alpha dose is not deposited in the entire lining thickness (100 mils was assumed for calculation purposes or 0.254 cms). The majority of the alpha dose is deposited within one range of the 5.15 Mev alphas from Pu-239. Assuming the liner to be similar to polyethylene (like water), the range of a 5.15 Mev alpha is 0.00512 cms. Therefore, though alpha particles will not penetrate the bulk liner thickness, alpha energy will be deposited to the inner liner surface 0.00512 cms deep. Variations in liner density will influence this aspect.

For perspective, the 10,000-year total dose (123 Mrad) is much lower than the dose typically used to qualify nuclear coatings (1000 Mrad) [17]. The 10,000-year total dose is more in the range of 50-200 Mrad often used to qualify electric motors and nuclear cables for commercial nuclear service [18-20]. Thermosetting epoxy and polyester resins typically used in electric motors qualified for harsh environments are generally rated to 50 Mrad for initial or threshold damage, with a service limit of 200-500 Mrad. Thermosetting silicone, polyimide and polyamide-imide polymers have initial damage thresholds of 200 Mrad with indeterminate service limits [20].

It is conservatively assumed that the bulk lining will see equal damage through-thickness. Realistically, the alpha and beta contributions are limited to the surface layers. The 10,000-year total dose is 123 Mrad but the bulk gamma dose is much lower (7.5 Mrad). A 50 Mrad total dose is not reached for the lining until 3000-4000 years, at which point the bulk gamma dose is only about 5 Mrad. This dose is only about twice as high as the dose typically used to sterilize medical devices (2.5 Mrad).

It must be emphasized that NPP (nuclear power plant) coatings and components are typically qualified for service through exposure to target radiation doses at very high dose rates. This approach provides a pedigree and protocol for comparing materials exposed at similar conditions, but many studies have shown that such methods are not necessarily useful for service life prediction. This is primarily due to diffusion-limited oxidation and variation in the degradation mechanism at varying dose rates. This behavior is discussed in more detail later in this report.

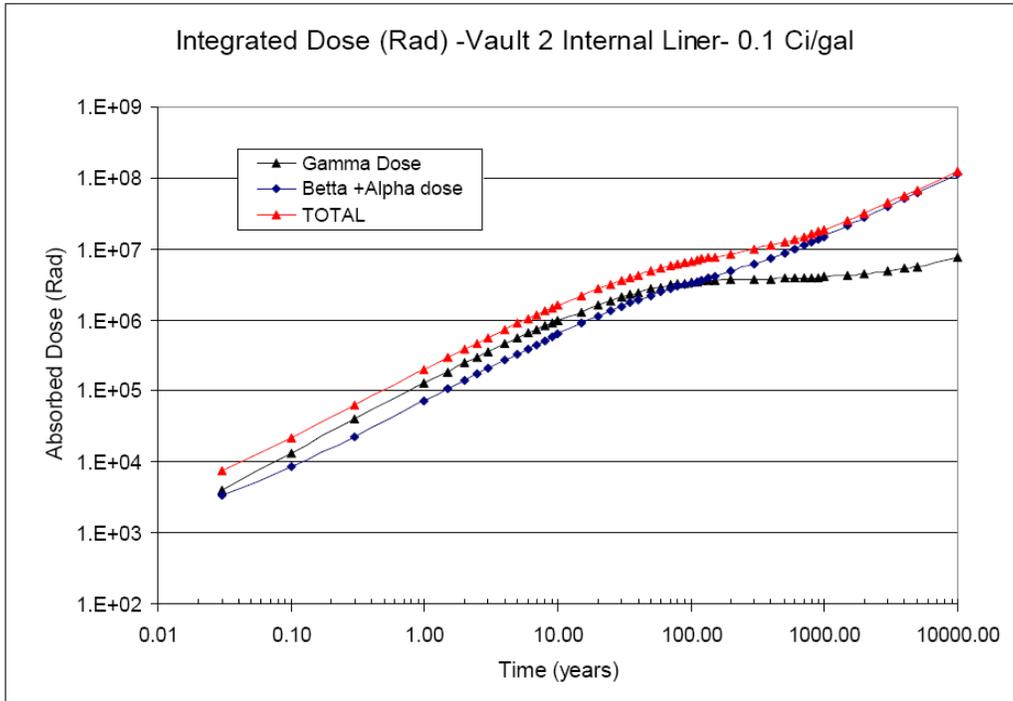


Figure 4. Integrated Radiation Dose for Vault #2 Lining [16]

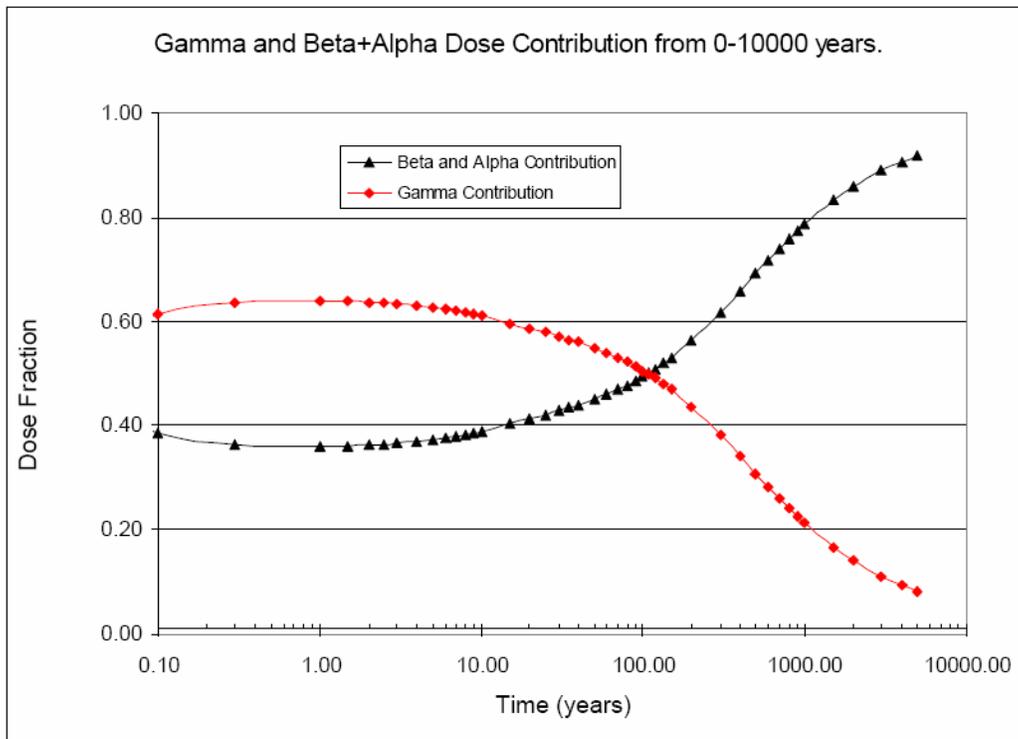


Figure 5. Dose Fraction from Gamma and Alpha/Beta Contributions [16]

Table 1. Tabulated Absorbed Dose Values for Vault #2 Interior Lining [16]

Years	Delta Time (years)	Gamma and Neutron Dose Rate (Rad/hr)	Integrated Gamma dose (Rad)	Gamma Cumulative Dose (Rad)	Beta+ Alpha (Rad)	TOTAL (Rad)
0.001	0.001	1.532E+01	1.342E+02	1.342E+02	1.931E+02	3.273E+02
0.003	0.002	1.532E+01	2.684E+02	4.026E+02	5.470E+02	9.496E+02
0.010	0.007	1.530E+01	9.382E+02	1.341E+03	1.535E+03	2.876E+03
0.030	0.020	1.527E+01	2.675E+03	4.016E+03	3.393E+03	7.409E+03
0.100	0.07	1.516E+01	9.296E+03	1.331E+04	8.404E+03	2.172E+04
0.300	0.2	1.490E+01	2.610E+04	3.942E+04	2.244E+04	6.185E+04
1.000	0.7	1.409E+01	8.640E+04	1.258E+05	7.083E+04	1.967E+05
1.500	0.5	1.359E+01	5.952E+04	1.853E+05	1.048E+05	2.901E+05
2.000	0.5	1.313E+01	5.751E+04	2.429E+05	1.382E+05	3.811E+05
2.500	0.5	1.271E+01	5.567E+04	2.985E+05	1.712E+05	4.697E+05
3	0.5	1.233E+01	5.401E+04	3.525E+05	2.037E+05	5.562E+05
4	1	1.166E+01	1.021E+05	4.547E+05	2.674E+05	7.221E+05
5	1	1.107E+01	9.697E+04	5.516E+05	3.296E+05	8.812E+05
6	1	1.055E+01	9.242E+04	6.441E+05	3.903E+05	1.034E+06
7	1	1.009E+01	8.839E+04	7.324E+05	4.496E+05	1.182E+06
8	1	9.672E+00	8.473E+04	8.172E+05	5.077E+05	1.325E+06
9	1	9.293E+00	8.141E+04	8.986E+05	5.645E+05	1.463E+06
10	1	8.945E+00	7.836E+04	9.769E+05	6.201E+05	1.597E+06
15	5	7.534E+00	3.300E+05	1.307E+06	8.821E+05	2.189E+06
20	5	6.477E+00	2.837E+05	1.591E+06	1.120E+06	2.711E+06
25	5	5.636E+00	2.469E+05	1.837E+06	1.338E+06	3.176E+06
30	5	4.941E+00	2.164E+05	2.054E+06	1.538E+06	3.592E+06
35	5	4.355E+00	1.907E+05	2.245E+06	1.723E+06	3.967E+06
40	5	3.851E+00	1.687E+05	2.413E+06	1.893E+06	4.307E+06
50	10	3.034E+00	2.658E+05	2.679E+06	2.200E+06	4.879E+06
60	10	2.403E+00	2.105E+05	2.890E+06	2.468E+06	5.358E+06
70	10	1.910E+00	1.673E+05	3.057E+06	2.706E+06	5.763E+06
80	10	1.523E+00	1.334E+05	3.190E+06	2.921E+06	6.111E+06
90	10	1.216E+00	1.065E+05	3.297E+06	3.117E+06	6.414E+06
100	10	9.741E-01	8.533E+04	3.382E+06	3.299E+06	6.681E+06
110	10	7.822E-01	6.852E+04	3.451E+06	3.469E+06	6.919E+06
120	10	6.301E-01	5.520E+04	3.506E+06	3.630E+06	7.135E+06
135	15	4.589E-01	6.030E+04	3.566E+06	3.858E+06	7.424E+06
150	15	3.380E-01	4.441E+04	3.611E+06	4.074E+06	7.685E+06
200	50	1.383E-01	6.058E+04	3.671E+06	4.751E+06	8.422E+06
300	100	5.583E-02	4.891E+04	3.720E+06	6.031E+06	9.751E+06
400	100	4.763E-02	4.172E+04	3.762E+06	7.292E+06	1.105E+07
500	100	4.676E-02	4.096E+04	3.803E+06	8.548E+06	1.235E+07
600	100	4.662E-02	4.084E+04	3.844E+06	9.801E+06	1.364E+07

Years	Delta Time (years)	Gamma and Neutron Dose Rate (Rad/hr)	Integrated Gamma dose (Rad)	Gamma Cumulative Dose (Rad)	Beta+ Alpha (Rad)	TOTAL (Rad)
700	100	4.655E-02	4.078E+04	3.884E+06	1.105E+07	1.494E+07
800	100	4.649E-02	4.073E+04	3.925E+06	1.230E+07	1.622E+07
900	100	4.643E-02	4.067E+04	3.966E+06	1.354E+07	1.751E+07
1000	100	4.637E-02	4.062E+04	4.006E+06	1.478E+07	1.879E+07
1500	500	4.611E-02	2.020E+05	4.208E+06	2.095E+07	2.516E+07
2000	500	4.586E-02	2.009E+05	4.409E+06	2.704E+07	3.145E+07
3000	1000	4.540E-02	3.977E+05	4.807E+06	3.900E+07	4.381E+07
4000	1000	4.496E-02	3.938E+05	5.201E+06	5.069E+07	5.589E+07
5000	1000	4.453E-02	3.901E+05	5.591E+06	6.210E+07	6.769E+07
10000	5000	4.257E-02	1.865E+06	7.455E+06	1.153E+08	1.228E+08

Table 1 (continued) [16]

5.0 LINING MATERIALS

5.1 SERVICE CONDITIONS

From previous sections, the service conditions or requirements identified for the Vault #2 lining are summarized below:

Chemistry: Bleedwater/leachate, saturated Saltstone, pH 13.7 pore fluid, comparable to a dilute 5-10 wt% NaOH solution (w/sulfates, nitrates, nitrites, low levels of organics)

Temperature: Peak temperature of 68 °C for 1000 hours; average temperatures of 61-64 °C over the first year. Gradual decline to 30 °C over 100 years.

Radiation: Lining integrity is desired for 100 years. At 10,000 years, the total dose is 123 Mrad (7.5 Mrad gamma). At 100 years, the total dose is 6.7 Mrad (3.4 Mrad gamma). For conservatism, the total dose is assumed for the bulk lining.

Elongation: 2% minimum

These were the primary inputs considered for lining review. This review was limited to liquid-applied polymer linings such as typically used for secondary containments, tank linings, wastewater systems, interior/exterior waterproofing and nuclear power plant containment coatings. This was mainly due to concerns raised by SRNL/Environmental Restoration (References 1 and 3) regarding the use of an unbonded liner such as HDPE that could allow pore fluid to reach the concrete in the event of a leak.

Therefore, membrane linings such as HDPE, ethylene-propylene diene monomer (EPDM), butyl rubber, neoprene and plasticized PVC as well as metallic linings such as stainless steel were not extensively considered. With proper installation and inspection, the risk of using an unbonded lining is reduced though certainly not eliminated. An adhesively-bonded lining such as Marseal[®] 8000 (similar to EPDM) could minimize gap concerns and bridge cracks that may form in the concrete substrate.

EPDM linings are particularly resistant to alkaline solutions at elevated temperature. Such a system would certainly provide more flexibility and crack-bridging capability than a thermosetting lining. However, as with HDPE, there are some concerns over oxidative/radiation degradation of EPDM as well as possible effects of trace organics. This can be reviewed at a later time for future vaults if needed. Butyl rubber is more sensitive to ionizing radiation than many other polymers. Plasticized PVC is reasonably resistant to the alkaline chemistry at temperature, but there are concerns regarding HCl gas generation due to radiolysis and possible effects of organics.

The safe radiation dose limit of 2.6 Mrad established in Reference 3 for HDPE on the vault exterior over 10,000 years would be reached within 40-50 years (gamma) or 15-20 years (total dose) if used on the vault interior. Oxidation effects within these shorter periods are likely more limited, but linings with higher radiation tolerance are desired. Therefore, focus was given to

lining systems based on thermosetting polymers that are known or anticipated to have high radiation resistance, in combination with high chemical and thermal stability.

5.2 COATING AND LINING MATERIALS

A summary of thermosetting protective coatings and linings is provided. Specific formulations and lining systems offer a wide range of properties and performance. Lining systems sometimes need to be custom-tailored for the specific application. Thermosetting, chemical-resistant linings primarily consist of epoxy, epoxy-novolac, epoxy-phenolic, phenolic, polyester and vinyl ester resins. Other co-reactive types of coatings such as polyurethanes and polyureas are widely used in wastewater and waterproofing applications, though are less commonly used in aggressive chemical service. Fluoropolymer linings were not reviewed due to higher cost, limited radiation resistance and lack of need for their extreme chemical resistance. Cementitious or crystalline waterproofing linings were also not considered due to limited resistance to high pH solutions.

5.2.1 Epoxies

Epoxy coatings are the most common types used for secondary containment and tank lining applications [21, 22]. Epoxies are generally resistant to dilute acids, alkaline solutions, salt solutions, water, solvents, oils, petroleum-based products, heat, radiation, etc. Epoxy coatings are typically based on epoxy resins that are most commonly reactant products of bisphenol A and epichlorohydrin to form diglycidial ether or DGEBA epoxy (Figure 6). The uncatalyzed resin is carried in a solvent or mixture of solvents. A second component (hardener or curing agent) is then mixed in the correct proportion to initiate the reaction (cross-linking), which can be quite exothermic. Bisphenol F and other resins can be used to improve chemical and heat resistance.

Epoxy coatings of different formulations can vary significantly in terms of flexibility, chemical resistance, heat resistance, wt% solids, immersion resistance, viscosity, cure times, etc. Polyamide-cured epoxies are generally tougher, more flexible, and more weathering resistant, whereas amine-cured epoxies tend to have higher chemical/solvent resistance but are harder and more brittle. Both types may be suitable for immersion/secondary containment applications.

All epoxies tend to chalk and/or yellow when exposed to sunlight/UV radiation. This is generally considered surface degradation only and not a serious problem, but epoxies are often topcoated with more weather-resistant coatings such as polyurethanes or acrylics for outdoor applications. Overcoating of epoxies used for outdoor secondary containment is not always required, depending upon conditions. Fortunately, ultraviolet light degradation is not a factor in the Vault #2 lining application.

Coal-tar epoxies are epoxy coatings modified with coal tar emulsion to impart high water impermeability. Coal tar epoxies have historically been used for immersion and below-ground service. Though they offer excellent performance, their high solvent content and carcinogenic nature has significantly reduced their use in recent years. Coal-tar epoxies have been widely used at SRS for corrosion protection of underground steel piping, but are now being replaced with epoxy-phenolic coatings.

Cardonal-based epoxies are generally higher solids, lower viscosity products marketed and well-suited for applications where surface preparation cannot be ideally performed. Epoxy mastics are extremely useful, multi-purpose, surface tolerant products which are often used for above-ground protection of industrial structures. However, epoxy mastics are not always suitable for immersion and/or secondary containment applications as they only have moderate chemical resistance.

Epoxy-phenolic coatings combine the toughness and chemical/alkaline resistance of epoxies with the immersion, heat, and solvent resistance of the phenolics, which otherwise tend to be hard and brittle. Epoxy-phenolics are commonly used as tank linings, nuclear power plant containment coatings and coatings for under thermal insulation.

Epoxies can be made with novolac resins (via acid condensation) to produce epoxy novolacs (EPNs) or novolac epoxies. These coatings are generally more chemical-resistant than straight epoxies due to greater functionality and cross-linking, hence they are often used for tank linings and secondary containment applications to handle chemicals such as concentrated sulfuric acid, strong caustics and many solvents. An example of epoxy-novolac chemistry is given in Figure 7.

5.2.2 Phenolics

Phenolic coatings (phenol-formaldehyde reaction products) are typically rigid, hard, heat/solvent resistant coatings. In many cases, such coatings must be baked or cured at elevated temperature. Unmodified phenolic coatings are not resistant to alkaline substances and cannot be applied to concrete, therefore are unsuitable for the vault lining. Phenolic coatings are more typically applied to steel as tank linings, machinery finishes, high-heat varnishes, etc. Phenolics are not common in secondary containment systems due to high stiffness and limited acid/base resistance. Phenolic coatings are not suitable for the vault lining.

5.2.3 Polyesters

Polyester linings are often used for chemical exposures, secondary containment linings, tank bottom laminates and other applications. Polyesters are typically resistant to dilute acids and bases, salt solutions, etc., but not to concentrated or strong oxidizing agents such as nitric acid. Resistance to strong caustic solutions at elevated temperature is also limited. Chlorinated polyester coatings can be used for improved acid resistance. Polyesters are typically relatively stiff and rigid coatings, which can sometimes be applied over more flexible substrates and crack-bridging membranes. Glass fiber reinforced or flake-filled systems are not recommended for strong alkaline environments at elevated temperatures or where fluorides are expected, but veil layers or resin-rich topcoats can minimize such concerns. Synthetic veils and carbon-fiber mats can also be used, but at higher cost.

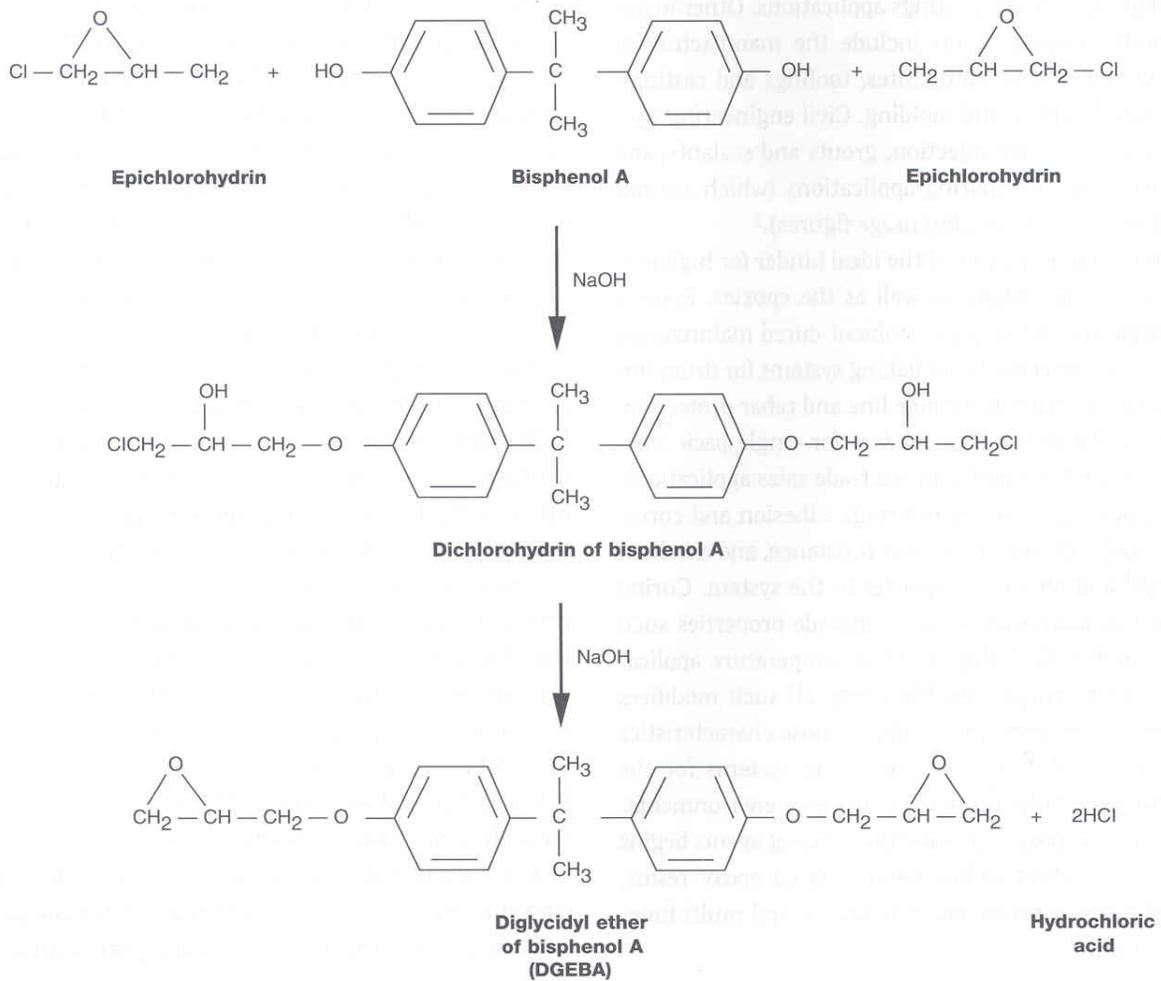


Figure 6. General chemistry of epoxy resins [22].

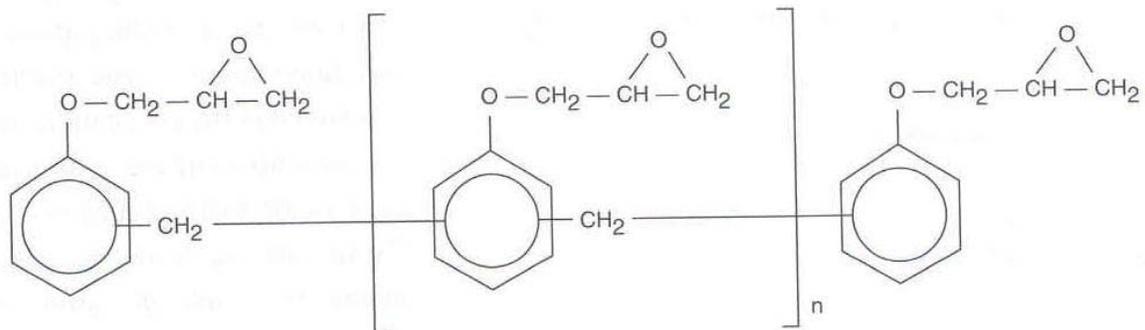


Figure 7. Typical epoxy-novolac (EPN) chemistry [22]

5.2.5 Polyureas

Polyurea coatings are based on polyurea resins initially developed for RIM (reaction-injection molding) applications for the automotive industry. These coatings have become widely popular in recent years. Polyureas are similar to polyurethanes, except that polyureas are reaction products of isocyanates and amines as compared to polyurethanes that are products of isocyanates and polyols. The polyurea reaction occurs very quickly and is hydrophobic in nature, thus allowing polyureas to be applied directly over damp surfaces or even water or ice without affecting the cure. However, film formation and adhesion are two completely different aspects of coating performance. This misconception has led to many early industry failures of polyurea coatings.

The primary advantages of polyureas and related urethane/urea hybrids are rapid cure times, hydrophobicity, low VOC levels and excellent mechanical properties. In contrast to many other organic coatings, polyureas require specialized heated plural component spray equipment in order to properly transport, mix, and apply the coating.

In some cases, reaction times are so fast (seconds), the polyurea can actually cure before it reaches or wet out the substrate. Adhesion to the substrate, particularly concrete and other porous surfaces, can be less than for more fluid, penetrating materials with longer cure times. Therefore, polyurethane or epoxy primers with lower viscosity and longer cure times are generally recommended to penetrate the surface and improve adhesion. Polyurea formulations also contain adhesion promoters to improve adhesion to steel.

The chemical resistance of polyureas is generally comparable to that of polyurethanes with some variations. A comparison of polyurethane and polyurea chemistry is given in Figures 8-9. Polyureas are resistant to salt solutions, dilute acid/bases, certain solvents and fuels. Depending on temperature, stronger concentrations can be tolerated. As with other coatings, the specific chemical, concentration and temperature are important.

One polyurea coating (Envirolastic[®] AR425, manufactured by Sherwin-Williams/General Polymers) was tested and selected for application in secondary containment pits at the Hanford site in order to refurbish the existing lining. The existing coating (Amercoat[®] 33) was an old solution vinyl coating known to contain regulatory levels of lead and/or PCBs, complicating coating removal and surface preparation efforts [23]. The Envirolastic[®] AR425 product was subjected to radiation and decontamination testing per ASTM standards, with good results. Samples exposed to a total gamma radiation dose of 10 Mrad showed no significant change in properties. The basis for testing to only 10 Mrad is unknown. Though far below the dose used for nuclear power plant containment qualification (1000 Mrad), it is higher than the total dose anticipated in 300-400 years for the vault lining and it is bounding for the gamma dose to the lining within 10,000 years.

Upon initial review of the Vault #2 application, polyureas were given much consideration. However, upon consultation with several manufacturers, most if not all expressed some concern about using polyureas in this environment. The primary limitation expressed was resistance to high pH, alkaline solutions at the peak temperatures anticipated. For example, the Envirolastic AR425 product has a dry heat temperature limit of 250 °F, but it is limited to temperatures of 120

°F for immersion. Some softening of the lining may be acceptable during early periods until temperature is reduced, but the degree of softening that will occur or that can be tolerated is unknown. Therefore, polyurea coatings cannot be strongly recommended for the Vault #2 lining application. These types of coatings would be more tolerant of conditions after the first few years of service, with temperatures < 120 °F (49 °C). For future vaults with lower radioactivity or thermal characteristics, such coatings may be suitable.

5.2.6 Polyurethanes

Polyurethanes are similar to polyureas. However, there are some distinct differences, particularly with regard to moisture/humidity tolerance (during application and cure), cure times, and in some cases chemical resistance. Polyurethane coatings are based on reaction between isocyanate compounds and polyols, rather than amines as for polyureas. Urea is actually formed as an intermediate step in the reaction. The reaction product is a carbamide linkage, which may or may not react to full termination (Figure 9).

Polyurethanes may be aromatic or aliphatic in nature, depending upon the specific constituents and prepolymers involved. Aromatic polyurethanes tend to be more resistant to chemicals, heat and solvents, but also tend to discolor upon exposure to UV radiation. Aliphatic polyurethanes are more resistant to UV radiation, and are thus superior in retaining color and gloss, but chemical resistance can be less depending upon the specific environment.

Polyurethanes can vary significantly in flexibility, depending upon specific formulation. Polyurethanes are tough, durable, abrasion-resistant coatings that are most often used for outdoor color/gloss retention, topcoats over epoxies or acrylics, or for specific flooring applications. Elastomeric, 100% solids polyurethane coatings are widely used for exterior waterproofing membrane coatings in bridge decks and other construction applications.

Moisture-curable polyurethanes (MCUs) are a variety that requires moisture to cure. These are typically single component coatings which reduces problems associated with mixing. Though MCU coatings tend to be relatively tolerant of surface condition, they cannot be applied to wet or damp surfaces as the name might imply. Moisture-cure urethanes are often used to overcoat lead-based paint in lieu of complete removal [22].

SRNL/MS&T consulted several manufacturers on the use of 100% solids, elastomeric polyurethanes such as Polibrid[®] 705 (Carboline) for the vault lining application. As with polyureas, the primary limitation is that the “safe” service limit for immersion in alkaline solutions is approximately 120 °F though higher temperatures may be tolerable with some softening. Carboline did not recommend the use of Polibrid[®] coatings for the Vault #2 lining.

5.2.7 Silicones

Silicone coatings are based on polysiloxane polymers with an inorganic backbone (Figure 10). Silicones are naturally inherent to aging and weathering. Silicones are resistant to many hydrocarbon-based fluids, but are not resistant to any significant concentrations of acids or bases. Silicones can be lightly cross-linked (elastomers) or highly cross-linked (thermosetting). Silicone

coatings are generally used for weathering or for high-temperature applications such as under thermal insulation.

One liquid silicone resin (LSR) coating reviewed is EKOR™, a “silicon geopolymer” developed by Russian scientists to encapsulate and stabilize radioactive debris at Chernobyl [24]. This coating has been evaluated for various D&D applications at several DOE sites. The specific composition of EKOR™ (marketed by Eurotech, Ltd, manufactured by NuSil Technology) is proprietary. EKOR™ exhibits many characteristics typical of silicone elastomers, with excellent thermal and UV light stability, with limited mechanical properties and chemical resistance.

The radiation resistance of EKOR™ is reportedly very high, on the order of $1E+10$ rad (1 Grad), without compromising encapsulation properties. Highly thermosetting silicone resins are known to have high radiation resistance. However, the radiation resistance of EKOR™ has not been confirmed and the claim is quite vague. The properties required for encapsulation are not defined. For nuclear applications, silicone elastomers are generally limited to doses of 50-100 Mrad, though higher doses may be tolerated by compositions loaded with inorganic filler and for very static applications. EKOR™ is also quite expensive relative to other coating materials (~\$500.00/gal).

In previous demonstrations at SRS for a specific application, EKOR™ coating exhibited poor adhesion to unprepared stainless steel and concrete substrates compared to other coatings. The coating appeared to tear itself apart upon curing due to either shrinkage stresses or limited tensile strength (Figure 11). Based upon these observations and limited chemical resistance, EKOR™ and other LSR/silicone coatings are not suitable for the Saltstone vault lining. It is also not suitable for any other harsh environment application without close review.

5.2.8 Vinyl esters

Similar to polyesters, vinyl esters are actually esters of acrylic acid (Figure 12). Vinyl esters are hazardous during application due to styrene monomer content and they are very reactive with limited shelf-life. Vinyl esters are used as rigid, medium-build coatings with or without glass flake, and can be used as heavy-duty linings with fiberglass or other types of mat-reinforcement. Graphite additives can be incorporated to provide conductivity and low surface tension. A stainless steel tank at SRS was recently lined with vinyl ester to protect the tank from halide attack (Figure 13). Vinyl ester coatings may be suitable for the Vault #2 lining, but there is some concern over resistance to strong caustics at elevated temperature. Vinyl esters also exhibit relatively high shrinkage and curing stresses. One vinyl ester coating (Sherwin-Williams' Magnalux 304) has been tested for radiation tolerance for an SRS application, exposed to 1000 Mrad at high dose rates with no obvious degradation. However, vinyl esters are not recommended for the vault lining due to styrene monomer hazards, high curing stresses and potential chemical limitations.

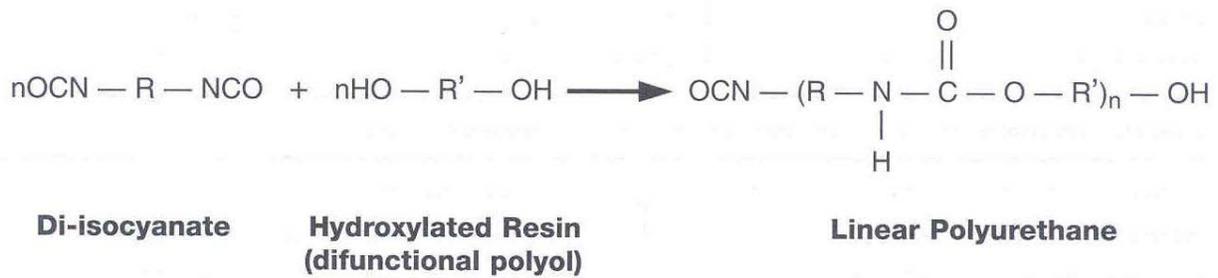
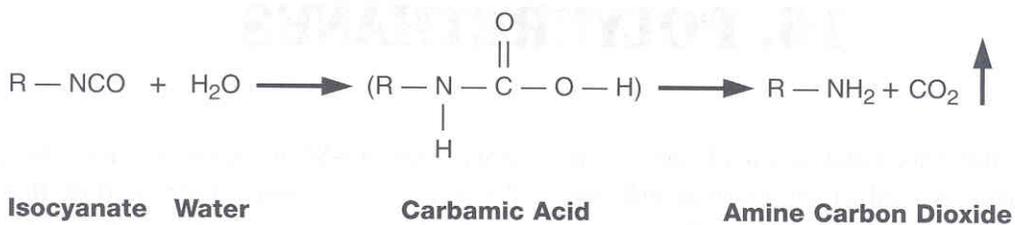


Figure 8. General reaction of polyurethane chemistry (isocyanate + polyol) [22].

Initial reaction produces unstable carbamic acid which immediately dissociates to the amine with the evolution of carbon dioxide



Amine then reacts with a second molecule of isocyanate to form a disubstituted urea

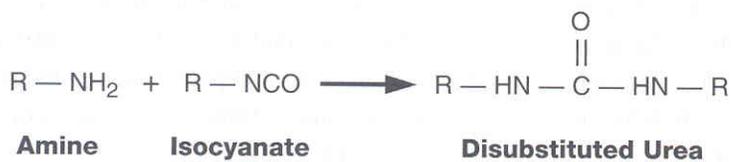
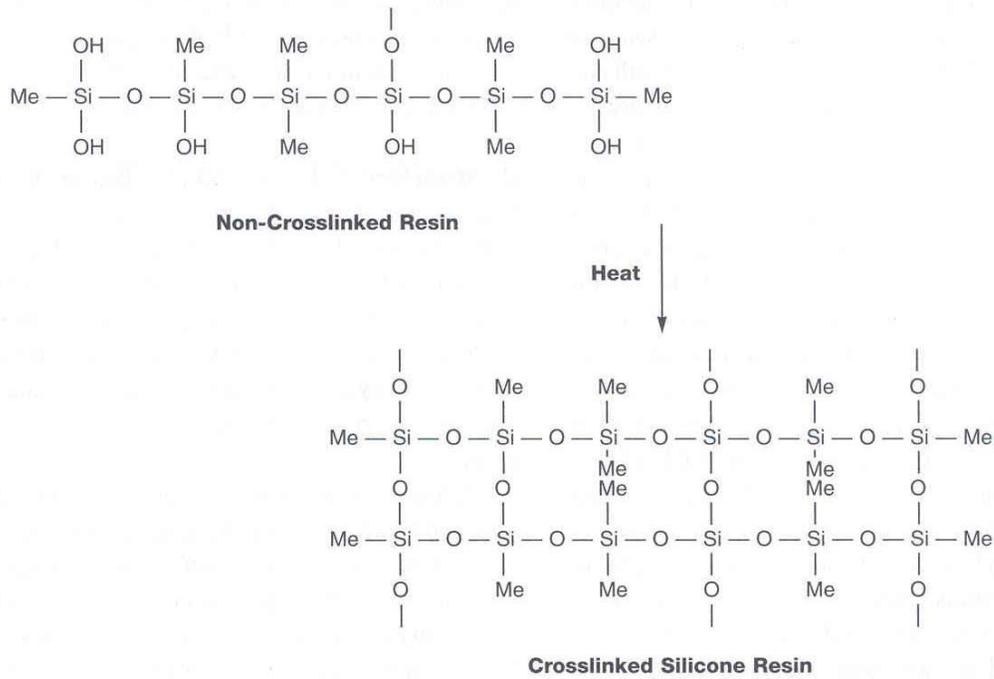


Figure 9. General chemistry of polyurea coatings [22]
(amine + isocyanate yields disubstituted urea)



Where Me is an alkyl group

Figure 10. Basic silicone resin chemistry (alkyl groups are typically methyls or phenyls) [22]



Figure 11. EKOR™ “geopolymer” coating demo at SRS (low tensile strength and self-tearing during curing in absence of applied stress)

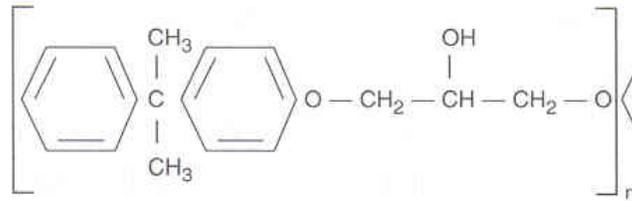


Figure 12. General chemistry of vinyl esters (methacrylic ester of epoxy or epoxy-novolacs) [22]



Figure 13. Stainless steel high activity drain (HAD) tank lined with vinyl ester (vinyl ester protects stainless steel from halide attack)

5.3 VENDOR CONSULTATION

SRNL/Materials Science & Technology contacted several major manufacturers of protective coatings and linings to discuss the Vault #2 application. As the lining will be exposed to ionizing radiation, high pH pore fluid and elevated temperature for at least some time, manufacturers with products qualified for nuclear environments were included.

Per Reference 25, the major manufacturers of nuclear-qualified protective coatings for commercial nuclear power plants (NPPs) are: Ameron International, Carboline, Keeler & Long, Valspar Corporation, Sherwin-Williams, Tnemec, and Wisconsin Protective Coatings. Some of these manufacturers have merged with other companies. For example, both Keeler & Long and Ameron International are now both owned by PPG Industries.

In addition to nuclear coating manufacturers, a few major manufacturers of protective coatings and linings for secondary containments, tank linings, wastewater and other similar chemical services were also consulted. These include: Blome International, Tnemec, Dudick and Ceilcote. Products from several of these companies have been used successfully at SRS. Most of the nuclear-product manufacturers also manufacture non-nuclear coatings, sometimes with superior chemical and/or temperature resistance.

Per ASTM D5144-00, Standard Guide for Use of Protective Coating Standards in Nuclear Power Plants, coating systems used in commercial nuclear power plants may be used in the following categories [26]:

- Coating Service Level I - Term used to describe areas inside the reactor-containment where coating failure could adversely affect the operation of post-accident fluid systems and, thereby, impair safe shutdown.
- Coating Service Level II—Term used to describe areas inside the reactor-containment where coating failure could impair, but not prevent, normal operating performance. The function of Coating Service Level II coatings is to provide corrosion protection and decontaminability in those areas outside the reactor-containment subject to radiation exposure and radionuclide contamination. Service Level II coatings are not safety-related.
- Coatings Service Level III—Term used to describe areas outside the reactor-containment where coating failure could adversely affect the safety function of a safety-related structure, system or component (SSC).

This ASTM guide addresses the concerns of Regulation Guide 1.54 and the replacement of ANSI Standards N5.12, N101.2 and N101.4. The qualification of coatings for Service Levels I and III are different even though they are both safety-related. This standard guide provides the minimum requirements for qualifying Service Level I coatings and also provides guidance for additional qualification tests that may be used to evaluate Service Level I coatings.

All Service Level I coatings for nuclear power plants must resist the effects of radiation and must be design basis accident (DBA)-qualified. These coatings are irradiated per ASTM D4082, which

imposes a 1E+09 rad (1000 Mrad) dose at very high dose rates (typically 1 Mrad/hr) [17]. This is intended to simulate a 40 year dose from normal service, plus additional dose imposed during a DBA event. The acceptance criteria for this test are not qualitative. Discoloration is acceptable, but blistering, disbondment and other degradation is not allowed.

This approach does not fully duplicate many years of aging but it provides a discriminating pedigree for coatings to meet. As with other polymers, degradation of thermosetting coatings at lower dose rates over longer periods may be more severe, but this has not been widely studied. A major difference between the Vault #2 application (and similar applications such as below-grade waterproofing or pipeline coatings) and commercial nuclear power plants is that safety-related coatings in nuclear power plants are monitored and maintained.

In addition to radiation exposure testing per ASTM D4082, Service Level I coatings are subjected to harsh accident exposure conditions as outlined in ASTM D 3911 [27]. This is intended to duplicate a design basis accident event such as a loss-of-coolant accident (LOCA). This typically involves exposure of irradiated coating samples to simulated accident conditions of elevated temperature, steam and cooling cycles. Service Level II coatings may be required to pass irradiation tests and decontaminability tests per ASTM D4236 (now discontinued) but are not subject to DBA conditions. Service Level III coatings must be evaluated for use in accordance with the requirements of plant licensing commitments and the job specifications. Service Level III coatings may include linings used in areas such as service water systems, essential cooling water heat exchanger heads and emergency diesel generator air intakes. There are no specific qualification requirements included in ASTM D5144 for Service Level III coatings or linings.

The chemical resistance of nuclear coatings is evaluated per ASTM Method D 3912 [28]. The specific chemicals to be used should be selected to characterize the anticipated exposure. The chemicals indicated in Test Method D 3912 are shown only as examples and are not mandatory.

Coating manufacturers were provided the service conditions outlined in Section 5.1 and were requested to recommend a lining system if possible. In some cases, manufacturers such as Ameron International, Keeler & Long, and Tnemec could not provide a suitable or recommended system. In most cases, the nuclear-tested products available were not suitable for the chemical/thermal conditions or could not be recommended due to lack of available data.

Given the anticipated service conditions, radiological nature of application, the desired service life (100 years) and the fact that the lining can never be inspected for degradation or maintenance after installation, mat-reinforced thermosetting lining systems were universally recommended. Variations in resins, application sequence and the degree of layer reinforcement were noted. The vendor-recommended systems are generally described in Table 2.

Table 2. Vendor-Recommended Lining Systems for Vault #2Manufacturer

Carboline (Semstone 245AFRC - Aggregate Filled Reinforced Coating)

Carboguard 510 surfacer (if needed)
Semstone 110 Primer (now 110/110EP) - 4-6 mils
Semstone 245 basecoat (25-35 mils)
Semstone Scrim Cloth (lay cloth into basecoat)
Semstone 245 blended mortar at 90-100 mils
Nominal system thickness: 125 mils

Sherwin-Williams:

Surfacer if needed (Kem Cati-Coat or equal)
Corobond Conductive Epoxy Primer @ 4.0-6.0 DFT (dry film thickness)
Putty: Steel Seam FT910 (for repairs and transitions)
Base Coat: Sher-Tuff Epoxy @ 20.0-30.0 mils (80%el)
Laminate Coat: Cor-Cote HP Clear Resin @ 20.0-30.0 mils with 1.0 oz Chopped Strand Mat
Topcoat: ExpressCote HCR @ 20.0-30.0 mils DFT
Total system thickness: 64.0 -96.0 mils DFT

Ceilmate: See Figure 13

380 Primer
Trowel basecoat (68 Lining) with silica filler (68 Lining + S-1 powder)
2 glass-reinforcing mats/2 nexus veil layers, each saturated with 68 lining resin
662 epoxy-novolac lining topcoat (10-15 mils)
Total system thickness: 110-130 mils

Blome International:

Surfacer: 83 MP (if needed, check primer sequence with vendor)
Primer: 75 (2-4 mils) - not conductive, different primer likely needed for holiday testing
2 coats of TL-45S epoxy-novolac with fabric embed between coats; film thickness 30-40 per coat.
Use .5-.75 chopped strand mat.
Total system thickness: 60-80 mils

Note: Vendors should be consulted prior to final specification and installation for details on application sequence, variations for vertical/horizontal surfaces, joint/transition details, environmental conditions and other related aspects.

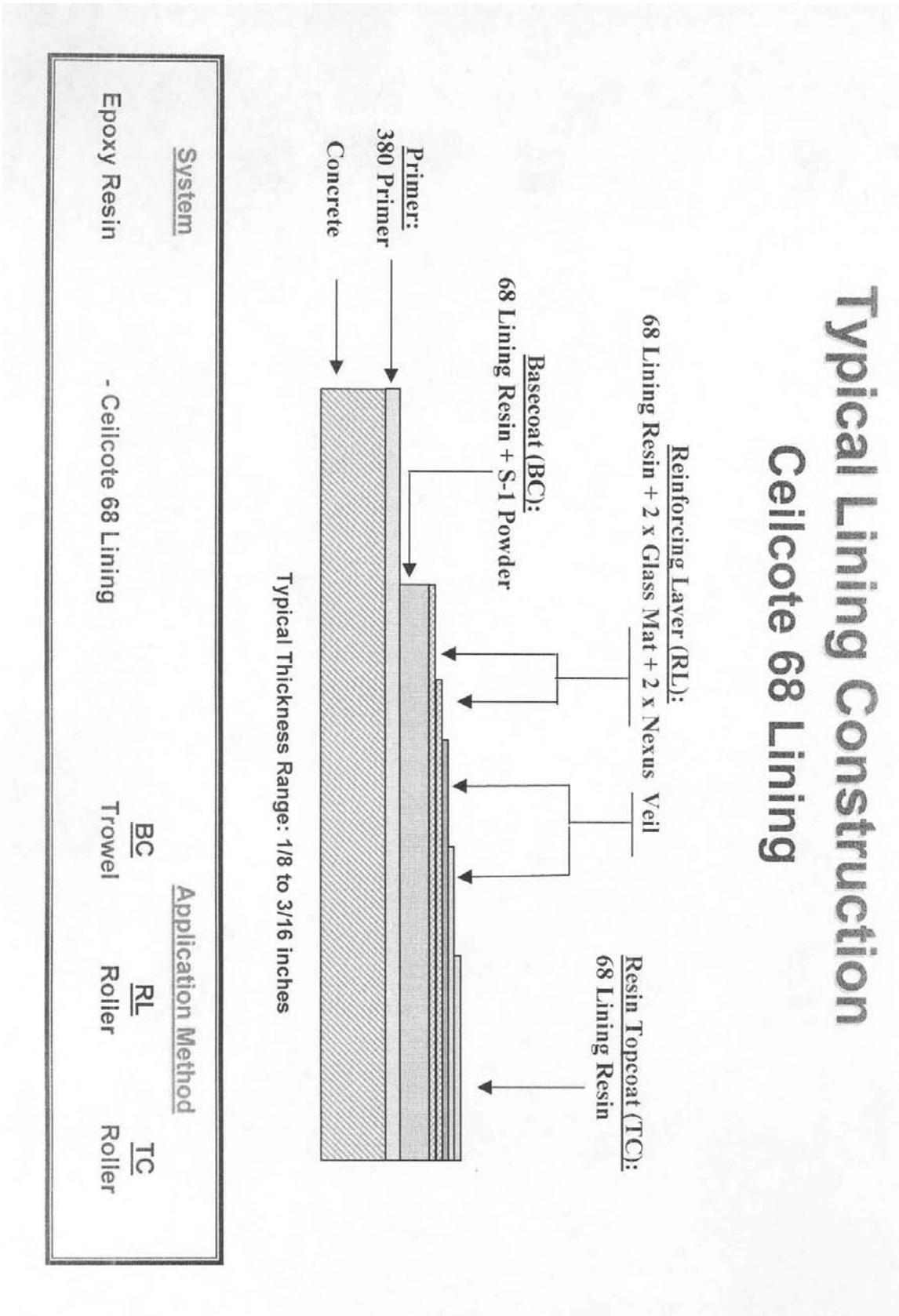


Figure 14. Vendor drawing of Ceilcote 68HT Lining System (662 Topcoat substituted).

5.4 Degradation Mechanisms

In the Vault #2 application, there are several mechanisms that could possibly lead to lining degradation. These are briefly described here for consideration. Additional work may be needed to address these for Performance Assessment purposes. A brief review of literature relevant to the aging of thermosetting polymers and coatings was also performed. Combined or synergistic effects are possible and the degradation mode may change with time. Possible lining degradation mechanisms include:

- Ultraviolet light
- Biological
- Thermo-oxidation
- High Energy Irradiation
- Chemical/Hydrolytic Stability
- Osmotic Blistering
- Moisture Vapor Transmission

5.4.1 Ultraviolet Light

The interior vault lining will not be exposed to ultraviolet light for extended periods. Therefore, degradation due to UV light exposure is not expected. This would be more of concern if the lining were on the exterior of the vault for an extended period prior to burial or closure.

5.4.2 Biological

The lining will not be in direct contact with soils or biological environments. The lining will be exposed to damp, humid conditions for long periods of time, which could theoretically induce biological activity. However, in absence of a significant carbon source (excluding the carbon-based coating itself), degradation due to biological activity is not expected. The presence of ionizing radiation may or may not preclude such behavior. The risk of biological degradation is therefore considered minimal.

5.4.3 Thermal/Oxidation

As discussed in Reference 3 for the HDPE geomembrane on the vault exterior, degradation of polymers is very dependent upon the presence of oxygen. The vault lining will not exist in a completely oxygen-free environment, but oxygen availability is considered to be very limited. Exposure to elevated temperature is also expected to be limited relative to the 10,000 year PA period. Compared to thermoplastic HDPE, thermosetting polymers are more resistant to thermal degradation. Based on the thermosetting nature of the epoxy novolac resins, degradation due to chemical, thermal and even ionizing radiation at the dose levels involved is expected to be minimal over long periods of time. However, some mechanisms such as diffusion-limited oxidation (DLO), hydrolytic breakdown, and dose rate effects are always possible to some extent in an oxygen-bearing environment. Assuming similar oxidation rates as discussed in Reference 3 for HDPE on the vault exterior, the thermosetting linings should provide similar resistance.

5.4.4 High-Energy Radiation

Though a radioactive environment, the total absorbed dose in the lining at 10,000 years (123 Mrad) is far lower than the dose used to qualify protective coatings in the commercial nuclear industry (1000 Mrad). The total dose is comparable to the 50-200 Mrad doses typically used for nuclear motor and cable qualification. The majority of the dose is due to alpha/beta contributions which are more limited to surface layers. The 10,000-year gamma dose is much lower (7.5 Mrad).

In absence of dose rate effects, the thermosetting epoxy/novolac linings are expected to resist degradation by ionizing radiation to doses of at least 10 Mrad (300-400 years total dose, >10,000-year gamma dose). With limited oxidation, doses of 50 Mrad (3000-4000 years total, gamma dose of 5 Mrad) and higher are likely tolerable. Even at 10,000 years, the total dose of 123 Mrad is likely very tolerable assuming the epoxy-novolac coatings have radiation resistance similar to nuclear-qualified epoxy coatings. However, the potential for dose rate effects in highly thermosetting polymers has not been widely studied compared to thermoplastics and elastomers such as used for nuclear cables and elastomeric seals. This behavior is covered in more detail in the following section.

5.4.5 Dose Rate Effects

Since the 1950s, much research has been performed in the area of the radiation resistance of polymers and organic materials. Historically, the approach used to evaluate this behavior has been to expose materials to a high-energy radiation source at very high dose rates (~1 Mrad/hr as in a Co-60 source) and measure general mechanical properties such as tensile strength and elongation. This approach allows for high doses to be achieved within a reasonable period and to gain an understanding of radiation tolerance. Data from References 29-32 are typical of high dose rate exposures.

Unfortunately, high dose rate exposures rarely simulate actual aging environments, unless service dose rates are similar. Therefore, data based on high dose rate exposures cannot be used to accurately predict the service life of materials exposed at much lower dose rates over longer periods. For short duration service or items that can be replaced, dose rate effects are not usually a factor. However, for critical or long-life components or materials that are costly or difficult to replace, dose rate studies are needed for more accurate prediction of service life.

Many studies have shown that most polymers that are required to function in an oxygen-containing environment are susceptible to dose rate effects. These effects are primarily due to diffusion-limited oxidation (DLO) that simply requires longer exposure time to manifest. These effects can be significant, far reducing service life from that predicted by high dose rate exposures.

One of the more notable cases of this behavior was observed at the Savannah River Plant back in the mid-1970s [33]. Control cables for the #5 pump suction valve in K-Reactor were found to be severely embrittled after ~12 years of exposure to an estimated total dose of 2.5 Mrad at a low dose rate (25 rad/hr) at an ambient temperature of 43°C. Additional cables in K-Reactor and other reactors showed similar degradation. The cables were still functional, though severely deteriorated. The cables had been purchased in 1962 (General Cable Co.) and were previously

deemed suitable for 40 years service based on high dose rate exposure tests. These cables were generically constructed of a 20-mil insulation layer of polyethylene, 1-3 mil nylon film, and black PVC jacketing.

Subsequent investigation found that the dose to equivalent damage (DED), defined as 50% loss of elongation, for PVC cable jacketing could vary from 20-50 Mrad at very high dose rates to ~3.5 Mrad at 100 rad/hr (1 Gy/hr), Figure 15 [33]. The effect of dose rate vs. temperature for PVC insulation is shown in Figure 16. These data closely matched the observed degradation at slightly lower dose rates (25 rad/hr) in service.

Similar data were obtained for low-density polyethylene insulation, Figure 17. Figure 17 shows a TED value (time to equal damage, 100% absolute elongation) of ~3 years at 1 Gy/hr (100 rad/hr) and 45°C. Damage is more severe at lower dose rates for a given total dose and less severe at lower temperatures [33]. Interestingly, in the K-Reactor cables, the polyethylene layer was actually found to be more severely degraded than the PVC jacket, even though the outer jacket was more readily exposed to air.

This work led to many subsequent studies by the Sandia National Laboratory and other agencies in the area of dose rate effects in polymers, particularly those types used in nuclear cable applications such as neoprene, PVC, Hypalon[®]/CSPE, EPR/EPDM and polyethylene. Such effects are also observed in polymers known to be highly resistant to oxidation, even at elevated temperature, such as Tefzel[®]/ETFE fluoropolymer.

Some polymers, such as Teflon[®] PTFE, butyl rubber, Delrin[®]/acetal, acrylics and polypropylene are more susceptible to main chain degradation (chain scission) whereas other polymers such as polyethylene primarily degrade by cross-linking. To further complicate matters, some polymers such as PVC can degrade by either mode depending on the service environment and oxygen availability.

Dose rate effects are generally attributed to the following:

- Oxidation, a primary degradation mode for polymers, is diffusion-limited. Testing at highly accelerated conditions can minimize the impact of oxidation, thus indicating falsely optimistic aging performance. This behavior is better evaluated by aging materials at lower temperatures or at lower radiation dose rates for longer periods or by determining the oxygen consumption rate of the material.
- Antioxidants in a given polymer formulation can be depleted at a certain rate over a specific temperature range. Once depleted, the properties of the material can be degraded at a much faster rate than predicted from testing of oxidation-inhibited material. This often results in a “cliff response” where the material behavior is relatively stable for a certain period, then rapidly declines after a threshold aging period is reached.
- Variations in degradation mechanisms can occur at different dose rates or in different environments, primarily related to oxidation above.

5.4.6 Non-Arrhenius aging behavior

Many polymer aging studies are based on the assumption that the degradation mechanism and rate is constant over time or a service temperature range, leading to a constant activation energy for the reaction involved. The classic Arrhenius theory gives rise to the rule of thumb that for every 10 °C increase in temperature, the rate of reaction essentially doubles. However, many studies have shown that this rule of thumb is only valid for certain cases. Several variables can affect the rate of reaction, leading to non-Arrhenius behavior.

An excellent example of non-Arrhenius aging behavior in polymeric materials is given in References 35-36. These studies on EPDM elastomer seals used in nuclear weapon components clearly show the role of antioxidants and the effects of depletion on the mechanical behavior of the material. Life predictions based solely on mechanical property tests at accelerated conditions can give overly optimistic indications of stability. Longer exposure times at lower temperatures revealed a threshold temperature at which oxygen consumption rates begin to significantly increase. Using these data, seal lifetime was significantly reduced from several thousand years at room temperature (predicted from compression stress-relaxation or CSR testing) to ~150 years based on oxygen consumption rates (Figure 18). In the case of weapon components, both lifetime values are highly acceptable, but the difference in predicted values is quite significant.

Subsequent studies have shown oxygen consumption analysis to be very useful for improving the lifetime prediction of polymeric materials used in oxygen-containing environments. The challenge for many real-world applications is how to determine the actual oxygen consumption rate in service. This is easier to do for components such as nuclear cables that are exposed to fresh air, compared to O-ring seals lubricated with silicone grease and compressed in a tight groove, or a protective lining sandwiched between radioactive grout and concrete.

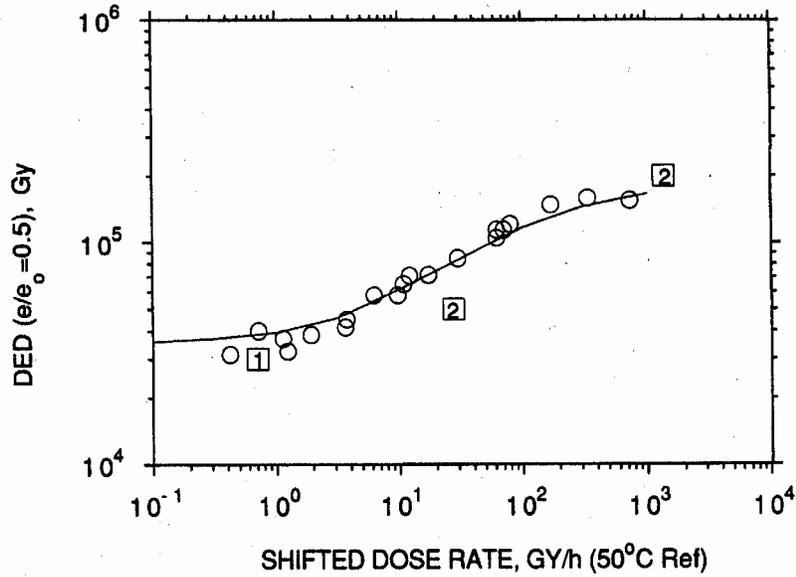


Figure 15. Dose to 50% elongation loss in PVC insulation [33].
 (Data shifted by superposition to a reference temperature of 50°C)

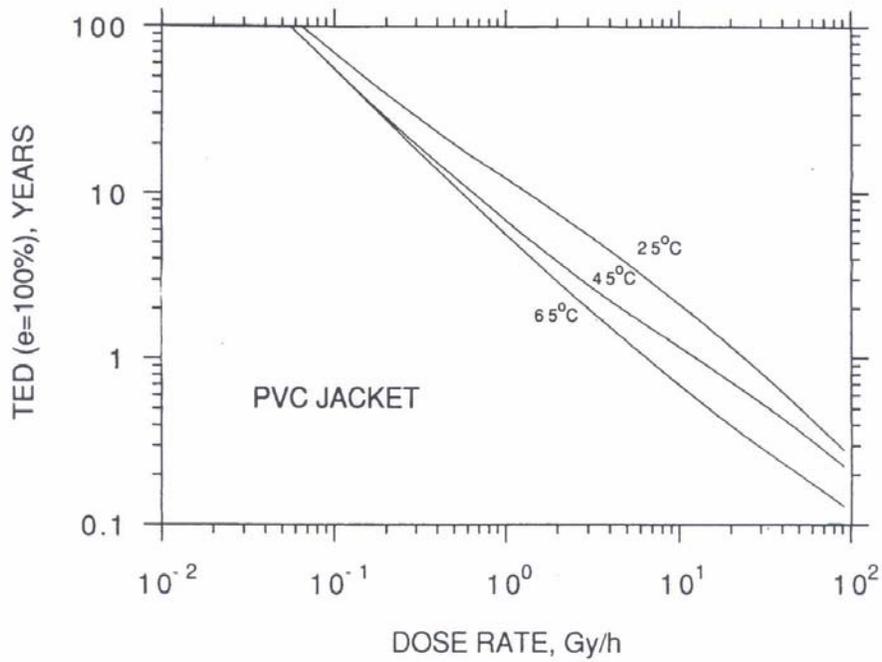


Figure 16. Time to 100% absolute elongation in PVC insulation vs. temperature [33]

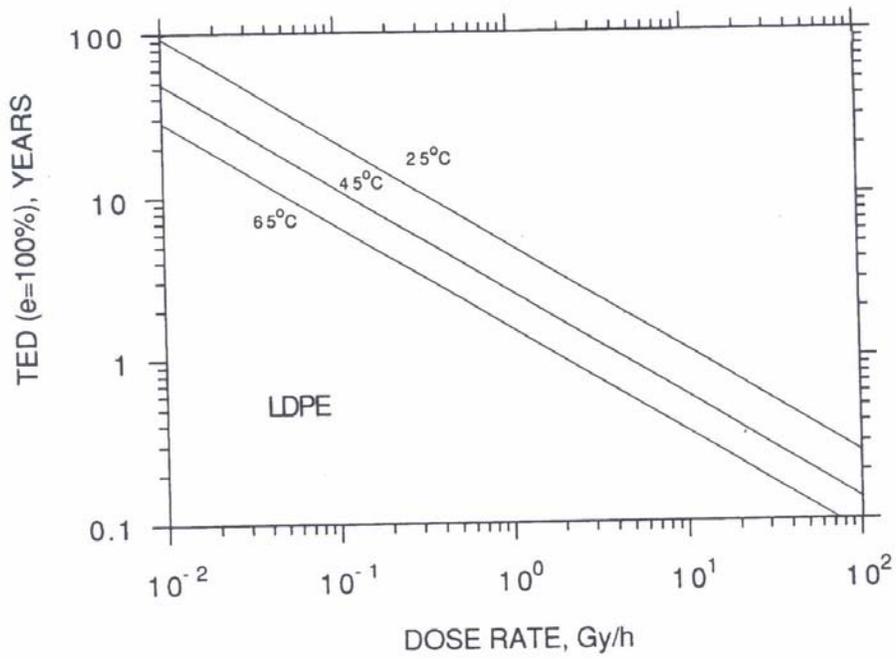


Figure 17. Time to 100% elongation vs. dose rate, LDPE insulation [33].

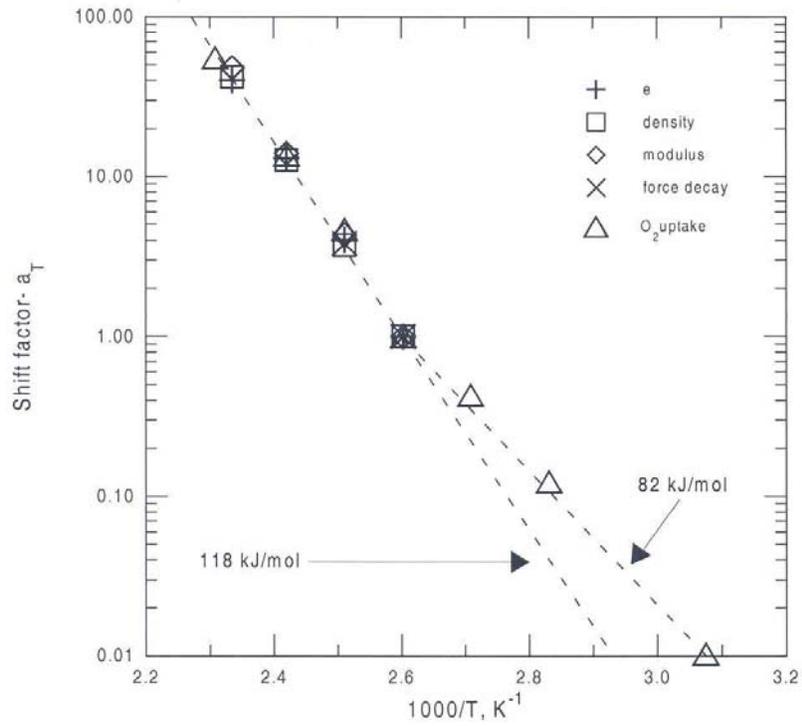


Figure 18. Non-Arrhenius aging behavior in EPDM elastomer seals [35].

5.4.7 Chemical/Hydrolytic Stability

The resistance of thermosetting epoxy-novolac polymers and lining systems to dilute alkaline solutions is known to be excellent. Variation in resistance and permeability is possible with specific formulations and degree of cross-linking. Glass flakes or fiberglass reinforcement can be sensitive to alkaline solutions, particularly at elevated temperature. Resin-rich layers can be used to protect the glass reinforcement from chemical degradation. Mat-reinforcement embedded within the lining is much less subject to chemical attack. For increased resistance to alkaline environments, graphite or carbon fiber or other synthetic reinforcement can be used but at increased cost. This is not considered necessary in the Vault#2 application, as the alkaline solution is not concentrated and the duration of elevated temperature is relatively limited. By thermosetting nature, the linings are intended for direct immersion and resistance to hydrolysis. The specific performance of the vendor-recommended lining systems at all relevant conditions has not been tested, but all systems reviewed are marketed and intended for immersion service.

5.4.8 Osmotic Blistering

A well-documented cause of coating/lining failures in immersion service is osmotic blistering [37-41]. This failure mechanism is primarily attributed to chlorides or other salt contaminants left on the surface prior to coating application. The salts tend to attract moisture through the lining by osmotic forces, eventually resulting in blister formation. This behavior is more often observed in water tanks where chloride levels in the stored media are very low, creating a concentration gradient.

This behavior is more common for steel substrates but it can happen with concrete as well. The mechanism can be avoided or minimized by proper cleaning techniques and testing for soluble salts on the substrate, and also with proper coating formulation and selection. Lower permeability coatings are less susceptible to the problem. Per reference 38, testing of nine epoxy coatings showed a wide range of chloride contamination levels were needed to initiate blistering, ranging from 4-20 $\mu\text{g}/\text{cm}^2$ at 75 °F. For elevated temperature service, even 1 $\mu\text{g}/\text{cm}^2$ levels can have an effect that lowers the maximum service temperature by 10 °F (6 °C). These data were only for coatings on steel substrates, not concrete.

5.4.9 Moisture Vapor Transmission

Moisture vapor transmission (MVT) is a common cause of coating/lining failure, particularly for coatings applied to on-grade or below-grade substrates [42-45]. Moisture vapor transmission failures can occur with or without moisture vapor barriers installed underneath the structure, though failures are much less likely with such barriers installed. Moisture trapped within the concrete from the curing process must come out and if blocked by a well-bonded, low permeability coating, the pressure can eventually result in blistering or gross disbondment. An example of coating failure by moisture vapor transmission is shown in Figure 19.

Even if the concrete is properly cured (28 days is typical), moisture vapor transmission or permeation through the concrete can result in failures. Moisture vapor failures can even occur on slabs of significant thickness. Therefore, moisture content and vapor transmission rates should be confirmed prior to application of a coating or lining to concrete floors and walls (if below-grade).

Various methods for measuring moisture content and moisture vapor transmission rates can be used. Coating/lining manufacturers should be consulted for their specific recommendations. Some manufacturers are more conservative and require lower values. As with other test methods, a limitation is that the measured values can be influenced by atmospheric conditions and recent weather patterns. If moisture testing is only performed under ideal ambient or weather conditions, low transmission rates may be detected and deemed suitable for coating application. However, if measured after a normal or particularly heavy rainfall, transmission rates could be significantly higher.

In cases where a coating is to be applied over substrates without a vapor barrier or with higher than desired transmission values, systems can sometimes be designed to mitigate the problem. The use of low-viscosity, deep penetrating primers can be beneficial, as well as the use of higher permeability, “breathable” coatings. Unfortunately, the higher-permeability coatings are not generally suitable for harsh industrial environments or chemical service. In the case of the Saltstone vault, the HDPE membrane should serve as a durable moisture-vapor barrier in absence of water infiltration in between the membrane and the vault exterior. Therefore, moisture vapor transmission failure of the Vault #2 lining is not expected.

Reference 42 discusses several coating types and properties, particularly with regard to moisture vapor transmission (MVT) or water vapor transmission (WVT). Acrylic emulsions, polyesters, vinyl esters, Bisphenol A and F-type epoxies, novolac epoxy, elastomeric polyureas, polyurethanes, and furans were all discussed. Of the general types, novolac epoxies were rated the highest for chemical resistance (widest range of suitability), also with high adhesion to concrete (several types), medium-high heat resistance, and medium-high resistance to permeation (all other types rated same or lower). The biggest drawbacks identified for the epoxy novolac coatings were limited flexibility and resistance to UV degradation (not applicable to the Saltstone vault).

Reference 42 also discusses that the permeability or permeation of coatings is evaluated by ASTM E96, with WVT measured in grains per square foot per hour per inch of mercury or grams per square meter per second per Pascal. One perm equals $5.72E-08$ grams per square meter per second per Pascal. Permeability is the product of permeance and coating thickness, with permeance being independent of thickness. Another method used is ASTM D1653, which measures the parameter in terms of grams per square meter per 24 hours. Chemical resistance and permeation is primarily attributed to the degree of cross-linking, which is determined largely by the functionality value. A bisphenol A-type epoxy typically has a functionality of 1.9, whereas a bisphenol F epoxy may have a functionality of 2.1. A typical bisphenol F novolac epoxy has a functionality of 2.6-3.5, which increases both heat and chemical resistance.

Reference 43 discusses protection of concrete in wastewater/sewer treatment systems against hydrogen sulfide (H_2S) and sulfuric acid attack, primarily attributed to microbial activity, most notably from SRB (sulfate-reducing bacteria) microorganisms. Sulfate resistant concrete is not sufficiently resistant to these environments, thus coatings are often used to prolong facility service life. Bisphenol A epoxies, novolac epoxies, polyureas and polyurethanes are most often used for these applications.

The author notes that permeability tests have shown that bisphenol A epoxies are actually less permeable by H_2S than the novolac epoxies, even though the novolac epoxies have a higher functionality and generally superior acid/chemical resistance. This permeability variation is not perceived to be an issue for the Saltstone vault lining, as H_2S exposure is not anticipated. Permeability of the alkaline pore fluid (with sulfates) is expected to be less though actual values are unknown. No specific references were noted. The author also notes that several failures of polyureas have been observed, primarily due to fast cure times and limited wetting/penetration of concrete substrates.



Figure 19. Floor coating failure on below-grade concrete, typical of moisture vapor transmission

5.5 Aging of Thermosetting Coatings

Synthetic polymers and coatings based on such resins and binders have only been developed in the last 50-75 years. Therefore, there are no cases of protective coatings or linings with any significant aging time relative to the hundreds or thousands of years discussed as part of the 10,000 year Performance Assessment period for the Saltstone vault.

Epoxy chemistry was initially developed in the late 1920s, with many developments and improvements since [22]. Therefore, as a class, epoxy resins have only been commercially viable for the last ~70-80 years. In comparison, HDPE of any form has only been in existence for approximately 57 years (invented in 1951). In addition, given various formulations and chemistry advances over the years, most specific products have been in service for much shorter periods.

Some of the oldest synthetic coatings used for corrosion protection of steel and concrete are solution-vinyl coatings, chlorinated rubber and early coal-tar based epoxies. These types of coatings were commonly used from the 1940s until the 1960s and into the 1970s. Coal tar epoxies are still used today but are less commonly used due to health and toxicity concerns. Vinyl and chlorinated rubber coatings are still used for specialized applications but are generally avoided because of high VOC levels and presence of lead and polychlorinated biphenyls (PCBs). Some of these products can be found in excellent condition today, depending on service conditions.

In below-grade applications with limited oxidation and in absence of ultraviolet light radiation, these coatings generally age very well unless the coating is subject to moisture vapor transmission or other external causes. Even at SRS, chlorinated rubber and solvent-based vinyl coatings have shown excellent aging behavior in indoor and below-grade applications. However, these coatings are not generally exposed to moisture or chemicals on a continuous basis. Due to low permeability, these coatings also tend to be susceptible to moisture vapor transmission failures.

The majority of commercial applications involving the use of thermosetting coatings and linings such as corrosion protection, tank linings, secondary containment or nuclear power plant containment coatings are usually limited to design life periods of 20-40 (now 60) years. It is noted that spent fuel storage pools at commercial U.S. nuclear power plants are typically lined with stainless steel and not organic linings [46]. The use of stainless steel was likely for several reasons including leak detection capability, fuel pool water chemistry requirements as well as to longevity. In contrast, most of the spent fuel basins at SRS built in the 1950s and 1960s were lined with organic coatings such as solution-vinyls or epoxy-phenolics.

With the exception of foundation waterproofing and other below-grade applications (e.g. pipelines), protective coatings and linings can often be inspected and repaired if needed. Even underground and offshore applications are generally not intended for hundreds of years of service, though 100-year service life requirements are more recently being specified. Therefore, research in the area of long-term aging performance of thermosetting coatings and linings is limited. This does not mean that such linings will not perform satisfactorily for longer periods, particularly in low oxygen environments and in absence of other harsh environmental factors, but the data are limited.

In contrast, since HDPE and other flexible membrane liners have been used for many years in sanitary and hazardous waste landfill applications where stability over long periods is desired, such materials have been more extensively studied. Per Reference 3, HDPE was identified as being able to last for hundreds or thousands of years as a functional diffusion barrier. This document summarized work by several researchers that conclude that HDPE geomembranes in landfill service will slowly degrade by thermooxidation. Oxidation will generally be limited by the availability of oxygen within the subsurface, and such slow oxidative degradation will not result in the disintegration or disappearance of an HDPE geomembrane within 10,000 years.

The models referenced above for polyethylene cannot likely be directly applied to a mat-reinforced thermosetting polymer lining. However, assuming similar oxygen availability and oxidation rates as well as comparable if not superior chemical, thermal and radiation stability of the thermosetting linings, it is reasonable to assume that such linings will exhibit similar aging behavior. It is acknowledged that the aging performance of thermosetting polymers and linings has been less widely studied. Therefore, additional testing and research is needed in this area to validate these assumptions.

5.6 Literature Review – Aging of Thermosetting Polymers

SRNL/MS&T performed a brief literature review of the aging of thermosetting resins and coatings. The aging behavior of fiber-reinforced polymer (FRP) materials was also included, as thermosetting resins are also used and the aging of such materials can be critical. Additional review of these aspects may be needed for Performance Assessment purposes.

FRP materials are typically constructed of fiberglass, carbon-fiber or synthetic fiber reinforcement saturated with a thermosetting resin such as epoxy, polyester or vinyl ester. The resins and properties of the composites can vary significantly. Compared to coatings and linings, composite structures are likely to have been studied more extensively for aging behavior, particularly for structural components such as tanks, piping, construction materials and military/aerospace vehicles. The resins used in these materials are in some cases very similar to those used in thermosetting coatings. However, the ratio of polymer resin to fiber reinforcement is much different for most composite materials.

An excellent reference of methodologies for predicting the service life of coating systems is given in Reference 47. This text focuses on the use of probabilistic/reliability-based methodologies for coating service life prediction, particularly with regard to newer low-VOC or water-based systems that may have different aging characteristics. The coatings industry, as with other industries, has moved from using long-term in-service testing to reliance on short-term laboratory tests for life prediction. This reference gives an excellent discussion on fault trees, failure modes, and probabilistic/reliability-based methodologies for coating service life prediction. Unfortunately, this reference is primarily focused on the outdoor aging performance of coatings, particularly for the automotive industry. The authors do highlight a notable difficulty in predicting the service life of coatings, which is that there are many different failure modes and the dominant mode of failure can vary with a particular system or environment.

References 48-49 by the same primary author as Reference 46 discuss a systems approach for service life prediction of coating systems. Much of the same information as in Reference 47 is discussed. One of the most notable aspects of these reports was that no study or method has been found to ideally reproduce outdoor exposure results. Though not applicable to the Saltstone vault lining (no UV exposure), it is important to note that short-term laboratory tests rarely simulate real-time aging in any multivariable environment.

Reference 50 summarizes work to evaluate the sorption and diffusion characteristics of an amine-cured epoxy and an isophthalate polyester coating when exposed to an alkaline solution (pH 13.5, 0.23 M KOH, 0.14 M NaOH, 0.002 M $\text{Ca}(\text{OH})_2$ in distilled water) at 60 °C and 22 °C. Diffusion of the solution was observed to follow a Fickian process at both temperatures. However, the increase of the epoxy coating diffusion coefficient was more than three times that of the polyester coating at 60°C.

Changes in the glass transition temperature of the epoxy were more substantial, dropping from 80.1 to 68.4 °C as measured by DSC. The values for the polyester coating only changed slightly from 105.0 to 98.3 °C. No evidence of mass reduction up to 400 hours at either temperature for the epoxy coating, with mass loss observed for the polyester at elevated temperature, likely attributed to base-catalyzed hydrolysis. This could lead to pathway formation through the coating, accelerating corrosion of the substrate.

Reference 51 details research on the effects of radiation dose rate and design basis accident conditions on thermal properties of epoxy coating systems in nuclear power plants. This report is one of only a few studies found to address potential dose rate effects in protective coatings used in nuclear power plants. Two epoxy coatings were irradiated at dose rates of 0.5 and 1 Mrad to a total dose of 200 Mrad. Following irradiation, the coatings were then subject to DBA exposures. The glass transition temperature and thermal stability of the coatings were studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

The authors found that even with the limited variation in dose rate and a lower total dose than used for coating qualification in commercial U.S. nuclear plants (1000 Mrad), thermal properties of the epoxy systems varied with both dose rate and DBA exposures. Since the dose rates used in this study are relatively close, the effects of lower dose rates and longer irradiation times may be even more significant. Irradiation to higher doses (1000 Mrad) at lower dose rates may show even different behavior.

Reference 52 discusses the managing of aging of coatings for nuclear power plants. Coatings applied to the interior surfaces of primary containment structures, classified as Service Level I. Weaknesses have been identified in the existing programs for Service Level I coatings, evident as blistering, cracking or peeling. Coatings must maintain integrity during an accident scenario so as not to clog sumps, screens and other safety-related equipment. For extended life and license renewal, nuclear plant owners are required to show that in-place coatings are qualified, the amount of unqualified coatings will not affect safety-related equipment, and that coating condition is assessed at prescribed frequencies.

Reference 53 discusses the service life of epoxy-coated reinforcing steel used in concrete structures. Though not the same formulation or chemical environment as the Saltstone vault lining, fusion-bonded epoxy-coated reinforcing steel (FBECR) is a relatively common material of construction. FBECR steel was principally developed as a physical chloride barrier to increase the time to corrosion of the reinforcing steel, which leads to spalling of the concrete due to increased volume of the corrosion product. This study found that the mode of coating failure is different for laboratory conditions compared to field conditions. Field aging experiments showed that the principal mode of failure was coating debondment before chlorides could initiate corrosion, providing very little long-term corrosion protection. This research found that laboratory tests were unreliable for predicting corrosion protection in actual service. The authors concluded that the performance of the epoxy-coated steel was heavily dependent on surface preparation, chloride levels on the steel surface and in the surrounding concrete, porosity and permeability of the coating, coating thickness and many other factors. Debondment of some systems were observed within 15-17 years in bridge decks. The fusion-bonded epoxy coatings used in this case are not equal to the epoxy-novolac linings being considered for the Saltstone vault lining.

Reference 54 evaluated the performance of a mat-reinforced epoxy coating for sulfuric acid exposure in wastewater and industrial facilities. The authors found that after 5 months of hydrostatic tests and 3 years of chemical testing, the coating system passed hydrostatic water pressure of 105 kPa with no visible defects after 5 months. The lifetime of coated concrete was estimated at being extended by a factor of 70 compared to uncoated concrete. Coated wet concrete without holidays did not fail during 3 years of exposure to 3% sulfuric acid. These service conditions are much different than the Vault #2 application. Note the authors stated that coatings should be inspected after 500 days for possible degradation and maintenance, which cannot be performed in the Saltstone vault.

Reference 55 discusses the 18-year performance of epoxy-coated rebar in a tunnel structure, subject to aggressive chloride environment. Epoxy-coated reinforcement (ECR) was developed in the 1970s, also known as fusion-bonded epoxy (FBE). Conclusions from this report indicate that a concrete structure (tunnel roof) built in 1984 shows minimal signs of degradation caused by corrosion of the steel reinforcement. The fusion-bonded epoxy coatings did not provide total protection for the rebar, mainly due to the permeation of water/moisture and accumulation at the metal surface. However, the corrosion initiation period was significantly extended compared to uncoated bars. Again, direct comparison of FBE coating results for rebar protection to the linings recommended for the Saltstone vault lining application is not valid. The increased lining thickness, reduced porosity and permeability and incorporation of mat-reinforcement all make the vault lining system much more robust.

Reference 56 discusses the acoustic monitoring of a prestressed concrete tank (water reservoir), presumably similar to the proposed Vault #2 design. This subject was not researched in detail but the article is included as a matter of interest. The acoustic monitoring project was largely successful in identifying and locating broken prestressing wires. Lack of accuracy in some locations was attributed to density variations in the mortar and the gunite surface layers. Inspection of vault prestressing wires over time may be worth consideration by Saltstone operations, if it can be reasonably incorporated into the design. Further research into this topic, including the technical interpretation and accuracy of the data and installation/monitoring costs should be considered.

In Reference 57, additional research into the physiochemical properties of epoxy coatings for nuclear power plants was performed. Irradiation of polyamide-cured epoxy coatings to a total dose of 200 Mrad was performed at two different dose rates, 0.5 and 1 Mrad/hr. Irradiated coatings were then subjected to DBA test conditions per ASTM D3911. The authors found that irradiations to 200 Mrad resulted in a decrease of the T_g value, even though the total dose was less than the 1000 Mrad dose required from ASTM D4082. This reduced dose may be based on the specific plant operating conditions. Immersion in hot water required a post-cure of the epoxy system which improved adhesion strength. The variation in dose rates evaluated in this study are not significant, but a variation in properties was observed. This indicates that some degree of dose rate effects in thermosetting epoxy coatings are possible.

Reference 58 discusses the characterization and modelling of aging in composites, particularly when exposed to water. The composite in this study was a DGEBA epoxy resin cured with a diamine hardener, reinforced with an E-glass matrix. Balance of the composite was not given but a 70% fiber/30% resin ratio by weight is typical. Conclusions of this study indicated a reversible decrease in rigidity due to humidity and irreversible change due to cracking by mechanical loading. A numerical model was proposed, accounting for hygrothermo-mechanical degradation at all times during water absorption during which the water concentration profile is not uniform. Rigidity of the epoxy/glass fiber composite was shown to decrease by approximately 10% over about one year at 60 °C, with the data trend appearing to level off.

Reference 59 outlines an accelerated-aging method for predicting the long-term properties of glass-fiber reinforced epoxy pipe. Glass reinforced plastic (GRP) or fiber-reinforced plastic (FRP) piping is used in a variety of industrial applications. However, prediction of GRP/FRP aging properties remains a difficult task due to extensive mechanical tests are necessary to quantify changes due to the aging process. Resistance to chemical or hydrolytic attack is significantly dependent on the binder resin as well as the inner resin-rich veil thickness and quality.

Time-temperature superposition principles commonly used for aging of polymers and other materials was applied to the FRP piping. However, conclusions from this work indicate that it is difficult to apply the time-temperature superposition method in practice to the GRP/FRP piping materials. Dynamic mechanical analysis (DMA) was used to evaluate creep properties. A master curve of creep strength vs. time to failure was developed.

The radiochemical aging of amine-cured epoxy was studied in Reference 60. An aromatic amine-cured epoxy network was irradiated in air at 30 and 120 °C at two dose rates (2 and 20 kGy/hr) for doses up to 70 MGy (1 Gy = 100 rad; 70 MGy = 7E+09 rad or 7000 Mrad). The basis for the dose rates and total doses was not provided. The doses and dose rates are significantly higher than expected in the Saltstone vault liner. In fact, assuming the reported units are correct, they are much higher than normally evaluated for nuclear coatings (1000 Mrad). The materials were principally characterized by changes in glass transition temperature (T_g) and mechanical properties. The conclusions of this work were that the flexural strength and T_g values were highly dependent upon the thickness of the oxidized layer (TOL). This is consistent with other studies by Gillen et. al. and others that show diffusion-limited oxidation as the controlling parameter. Degradation at these high doses cannot be compared to materials exposed to lower doses, but are presented for information. Time to failure parameters were not defined. The epoxy resins studied were not specific to nuclear-qualified coatings or resins for electric motor insulation systems.

Reference 61 is an extension of work presented in Reference 60. A kinetic model was established for the chain scission process induced by gamma radiation in an aromatic-amine cured epoxy network. Much analytical work is presented, with characterizations by NMR spectroscopy and ESR experiments. The focus is on thermal effects upon the T_g value and how to predict such changes at varying conditions. The work presented is not directly comparable to the epoxy/novolac coating systems for the Vault #2 application, but it is a presentation of data not generally found in the literature. Thermosetting polymers are much less studied due to inherent radiation and thermal stability, at least as demonstrated by traditional methods.

Burnay provides an overview of polymer aging studies in Reference 62, with emphasis on seals and electrical insulation, but some discussion of coatings. NPPs (nuclear power plants) were initially designed for 40 years, with 20-year life extension now being pursued. Burnay points out that little work has been done on the aging of coatings or methods to predict lifetime. Coatings are assessed by qualification testing before installation and they are inspected routinely for degradation or signs of failure.

Damian et. al. in Reference 63 investigated the effects of thermal oxidation, radiochemical and hydrolytic aging on the structure and gas transport properties of epoxy-amine networks. This work was primarily done to evaluate the use of an epoxy material for embedment of low activity radioactive wastes. Samples of four epoxy-amine network polymers were exposed to five doses of gamma radiation (42, 84, 854, 1700 and 3400 kGy) at 4 kGy/hr. Different dose rates (130, 500, 4000 Gy/hr) were also studied for doses lower than 100 kGy. The conclusions from this work are:

1) thermal oxidation can be characterized by an oxidation rate, 2) radiochemical aging leads to an increase in the polarity of the network, with no significant degradation observed at the doses evaluated, 3) hydrolytic aging had a higher effect on one commercial network polymer than the others. This was attributed to water-soluble components in the system. Thermal oxidation behavior was modeled to predict long-term behavior. Thermal aging was performed at temperatures of 30, 50 and 70 °C, similar to the 68 °C peak temperature in Vault #2.

Reference 64 describes work to study the ageing and yielding of epoxy thermosets. The effect of physical aging on the DSC heat flow and yielding behavior was investigated for two series of epoxy resins in which the crosslink density is varied without significant compositional variation. DGEBA epoxy cured with various curing agents. Physical aging at 50, 70, 90 and 160 °C for periods of up to 3840 minutes was performed, with changes in T_g values and heat capacity determined. The room temperature yield stress was also determined as a function of aging time (up to 30 days). For the epoxy resins examined, the yield stress was observed to increase for all aging conditions, with values leveling off after 20 days or so for resins aged at 50 °C. Longer aging times would be needed to evaluate the potential for diffusion-limited oxidation effects.

The aging of a cycloaliphatic epoxy resin (Araldite CY 192, curing agent HY 918) irradiated under vacuum and in moisture saturated air was investigated in References 65-66. The effects of gamma radiation doses of 0.1, 0.5 and 1.5 Mgy imposed at a dose rate of 5 kGy/hr. A post-irradiation thermal treatment (3 days at 80 °C) was performed under vacuum to remove free radicals produced during irradiation that could cause oxidative degradation in air. In the first part of the study (vacuum conditions), the main effects of degradation were a slight increase in the

degree of crosslinking and minor changes at doses < 1.5 MGy (1.5E+08 rad or 150 Mrad), which is bounding for the 10,000-year total dose anticipated for the Saltstone Vault #2 liner.

In part 2 of this study, the properties of the same resin were evaluated after irradiation to the same doses and at the same dose rate in moisture saturated air. Before irradiation, samples were kept for 60 days in a moisture saturated air environment at room temperature. Samples were irradiated in the presence of water. Moisture absorption was found to have an effect (slight swelling which imposes stress), but the structure and mechanical properties were not significantly affected. Of course, at the dose rates involved (5 kGy/hr = 0.5 Mrad/hr), long-term aging behavior in air cannot be determined.

Thermal and photochemical aging of epoxy resin and the influence of curing agents was investigated in Reference 67 using photoacoustic-FTIR spectroscopy. A DGEBA epoxy (DER 331, Dow Plastics) cured with anhydride or amine curing agents was thermally aged at 100 °C for periods of up to 1960 hours. An oxidation induction period was observed at around 400 hours for the amine-cured resin vs. 900 hours for the anhydride-cured resin, as evident by changes in the PAS-FTIR spectra. Based on these results, DGEBA cured with anhydride was observed to be much more resistant to photochemical aging and thermo-oxidation than the amine-cured resin.

Reference 68 discusses some interesting work with regard to oxidation-induced shrinkage of thermally aged epoxy networks. Though not directly applicable to the vault lining, the behavior described could have implications for a bonded lining under stress after thermal aging. Aging was performed on an aromatic epoxy cured with an aromatic diamine, with 30% of the polymer also a thermoplastic polyethersulfone polymer for impact strength. The epoxy matrix was aged at 120 °C for 10,000 hours, with embrittlement of surface layers induced by thermal oxidation leading to shrinkage and development of spontaneous cracks. As the aging temperature used in this study is much higher than anticipated in the Saltstone vault application, the results are not directly comparable. However, longer-term oxidation at lower temperatures may result in similar behavior. This can only be predicted by long-term testing of lining materials at various elevated temperature conditions.

An excellent summary of long-term thermo-oxidative aging in composite materials and failure mechanisms is provided in Reference 69. Two epoxy/carbon fiber reinforced composite systems were aged at 350 °F for up to 10,000 hours. Though not designed for this service temperature, significant degradation was observed to help reveal failure mechanisms and properties to characterize during long-term aging. The properties of interest for a structural composite are different than for a lining. Recommendations from this study were: 1) accelerated methods should reproduce failure mechanisms that occur during aging, 2) test conditions should be below the glass transition temperature to avoid anomalous degradation, 3) possible use of higher air pressure to accelerate the oxidation process at temperatures that are closer to actual use temperatures, rather than using the traditional method of using various higher temperatures.

Reference 70 discusses the durability and service life prediction of GFRP (glass-fiber reinforced polymer) for concrete reinforcement. Unlike steel, GFRP (or FRP) is much more resistant to chloride-induced corrosion. However, GFRP may deteriorate in an alkaline environment such as concrete due to attack of the fiber reinforcement. Carbon fiber reinforcement is much more resistant to alkaline environments than glass fibers, but is also much more expensive. For the

purposes of concrete reinforcement, the required service life is normally on the order of 100 years or less.

In this case, researchers subjected four types of GFRP reinforcement bars from two manufacturers with either E-glass or AR-glass reinforcement and vinyl ester or polyester resins to various exposure conditions. One condition was an alkaline solution of pH 13.7, similar to the pH of Saltstone pore fluid. Some bars were embedded in concrete at 60 °C for up to a year. Conclusions from this research were that the E-glass/vinyl ester systems have the best durability in alkaline environments, compared to the polyester system. Epoxy-novolac resins were not tested and are likely less common for FRP resins (typically either epoxy, polyester or vinyl ester). Also, the researchers noted that the alkaline solution was more aggressive than moisture saturated concrete, even for the same pH value. Aging data indicated that strength retention after 18 months in concrete at 60 °C corresponds to 100 years under outdoor conditions in south-west Sweden.

A number of other good general papers on the selection and installation of chemical-resistant, thermosetting polymer linings are given in References 71-76.

Literature Summary

The aging behavior of thermosetting polymers used in protective coatings and linings or resins in fiber-reinforced composite materials has been studied to various extents. Organic linings are typically used in applications and facilities that allow for periodic inspection, maintenance and repair, though such activities are not always practical. The design life of facilities in which such linings are installed is typically 20-60 years, though 100-year design periods are more recently being specified. Therefore, compared to HDPE used as landfill membranes, the aging performance of thermosetting linings has been less studied.

Case histories of protective coatings and linings of 50+ years are rare, with varying degrees of success. Failure of coatings in underground/interior vault-type applications is often caused by moisture vapor transmission problems from the substrate rather than aging or degradation of the coatings themselves. Though thermosetting linings are anticipated to be more resistant to chemical, thermal/oxidative and radiation damage than HDPE and other flexible membrane linings, additional research is needed in the area of long-term aging performance of thermosetting coatings/linings and composites, particularly with regard to radiation dose rate effects and combined effects of relevant service conditions.

5.7 Gas Generation Rates

All organic materials and polymers will offgas or evolve volatile species in the presence of ionizing radiation. The specific amount and type(s) of gas liberated depends on several factors, including the base polymer type, specific formulation, additives/curing agents, total dose, radiation type, dose rate and presence of oxygen. Gas generation is usually of less concern for well-ventilated systems or open environments, but closed systems require more scrutiny. Some gases liberated may be toxic or hazardous (flammable), while others may be relatively benign. Therefore, an estimate of gas generation rates from the lining was requested by the project to aid in any necessary resolution strategies.

An excellent discussion of gas generation rates for polymers comes from Reference 77. Gas generation rates are usually expressed in terms of G-values, which represent moles of gas formed or consumed per 100 electron volts (eV) of energy absorbed by a material. G-values for a given material may vary with the type of radiation absorbed by the material due to the linear energy transfer (LET) effect. For example, alpha radiation has a relatively high LET value (value) as much energy is imparted to the material. However, alpha particles are easily stopped within the first 1-2 mils (0.001-0.002 in.) of most polymers. So, though the absorbed dose from alpha radiation can be quite high, the amount of material affected is usually much less.

In most cases, G-value data are based on exposure to gamma radiation as this is the most common approach used for material exposures. Data for G-values as a function of exposure to alpha or beta radiation are less available.

From Reference 77, the bounding G-value (H_2) for saturated hydrocarbon polymers is 4.0 for polyethylene. Polymers having ether functional groups generate gases that contain oxygen, even when the polymers are irradiated in a vacuum. G-values for cellulose and ureaformaldehyde have been shown to be strongly dependent on the absorbed dose. For absorbed doses greater than 10 Mrad, the maximum G(H) value for ether polymers is 3.2. One of the polymers in this family (acetal or polyoxymethylene) generates other flammable gases that cause the G(flam gas) value to exceed 4.1. Another polymer (polyvinyl formal) has a measured G(total gas) value that is 1.4 times the G(total gas) value for polyethylene.

Polymers containing chlorine are usually stabilized to reduce the catalytic effect of HCl generated by radiolysis or thermal degradation. The strong effect of the plasticizers and stabilizers on the radiolysis of PVC is demonstrated by the differences in the composition of the radiolysis gas, which can vary from x-85% H₂, 2 to 83% HCl, and 2 to 70% CO, depending on the specific polymer formulation and whether oxygen is present.

G-values for cross-linked thermosetting polymers such epoxies are not readily available. Reference 77 gives a G-value of 0.8 (total) for generic epoxy resin (Table 3). Specific resins and coatings based on resins and other additives may give different values.

In reference 77, the rate of radiolytic gas generation (n) in moles per second from a material is given by:

$$n = W \sum_i (F_i G_i) \times C_i$$

where:

W = total decay heat (watts),

F = fraction of energy emitted that is of radiation type i and is absorbed i by the material (range 0 to 1),

G = number of molecules of gas produced (or consumed) per 100 eV of energy i absorbed from radiation type i , and

C = conversion constant = (1 joule/W-sec) \times (1E7 erg/joule) \times (1 eV/1.6E-12 erg) \times (1 g-mole/6.02E23 molecules)

$$= 1.04E-5 \text{ (g-mole)(eV)/(molecule)(W-s)}$$

$$= 1.04E-7 \text{ (g-mole)(100 eV)/(molecule)(W-s)}.$$

A G value may be positive (as in the generation of hydrogen or carbon dioxide) or negative (as in the depletion of oxygen). F depends on the nature of the emitted energy and the materials being irradiated. In the case of short-range radiation, F also will depend on the spatial distribution of radioactivity, especially when several different materials are present, such as in wastes.

Temperature will also drive gas generation rates, with higher rates generally expected for higher temperatures. Assuming Arrhenius behavior, for most polymers, the radiolytic gas generation rate at 55°C should be no greater than approximately 1.6 times the gas generation rate at room temperature (25°C) [77]. Assuming this ratio holds for higher temperatures, the gas generation rate at 68°C (the peak grout temperature) should be approximately 2.3 times the gas generation rate at room temperature, but this temperature is only reached for a relatively short period.

Measured total gas G values depend on the atmosphere in which the irradiation occurs, especially whether or not any oxygen is present. In most polymers, oxygen retards or completely eliminates formation of a cross-linked network. Even polymers that otherwise would crosslink will degrade in the presence of oxygen. Radiation-induced oxidation initially consumes dissolved oxygen that has diffused into the material from the surrounding oxygen-containing atmosphere. The efficiency of radiolytic oxidation of polymers under otherwise equal conditions will therefore depend on the dose rate (i.e., the oxygen consumption rate) and on other factors determining the rate at which oxygen can permeate the sample.

Table 3. Material G (gas) Value Relative to Polyethylene
(From Table 4.8-2, Reference 77)

<u>Polymer Type</u>	<u>G-Value</u>
cellulose nitrate	1.5
polyvinyl formal	1.4
polyethylene	1.0
allyl diglycol carbonate	0.6
ethyl cellulose	0.5
methyl methacrylate	0.5
cellulose propionate	0.5
cellulose acetate butyrate	0.4
nylon (polyamide)	0.4
phenolics (no filler, or cellulosic or mineral filler)	<0.3
urea formaldehyde (cellulosic filler)	0.3
Silastic®	0.3
cellulose acetate	0.3
butyl rubber	0.3
natural rubber-butyl rubber mixtures	<0.3
melamine formaldehyde (cellulosic filler)	0.2
Selectron 5038R polyester	0.2
natural rubber with fillers	<0.2
natural rubber	0.1
Thiokol STR	0.09
Neoprene	<0.06
casein plastic	0.05
Mylar® film	0.05
Plaskon® alkyd	0.03
triallyl cyanurate	0.02
aniline formaldehyde	0.01
furane resin (asbestos & carbon filler)	<0.01
polystyrene	<0.01
styrene-butadiene copolymer	<0.01
epoxy resin	0.8

For the epoxy-based linings proposed for the Vault #2 design, SRNL/MS&T requested SRNL/Actinide Technology to estimate gas generation rates due to radiolytic degradation. This was an estimate only, not a formal calculation. To determine gas generation rates, SRNL/Actinide Technology performed separate dose rate calculations independent of those documented in Reference 16. These were performed to provide a separate basis for gas generation rate estimates, not as a specific check on previous calculations. Assuming a liner density of 1.7 g/cc for a glass-filled epoxy resin, the dose rate results obtained were slightly conservative, but within 3% of the earlier dose rate calculations.

The total absorbed dose estimated at 10,000 years by SRNL/Actinide Technology is approximately 1.26E+08 rad or 126 Mrad. This dose is approximately 2.44% higher than the dose rate calculation (123 Mrad) in Reference 16. Variations in the calculations are believed to be due to minor differences in the radionuclides included as contributing to the total dose and other minor factors. For the total doses involved, such minor variations are not considered significant.

SRNL/Actinide Technology provided an Excel spreadsheet based on previous calculations of the absorbed dose in the grout, performed by standard radioactive transport computer codes. This converts the computer code calculations to a more user-accessible spreadsheet format and adds gas generation calculations to the dose calculations. The calculation spreadsheet gives the total gas generation rate in L/year, given an exposure time in years and activity levels for the radionuclides contained in the saltstone grout. The calculations are valid for a time interval up to 10,000 years; after this time in-growth of daughters from long-lived isotopes make the spreadsheet calculation increasingly inaccurate.

In summary, for a lining with a density of 1.7 g/cc and a G-value of 0.8 (total), the gas generation rate estimates performed by SRNL/Actinide Technology indicate that without a top liner, the initial gas generation rate is 48 L/year, and the rate after 10,000 years is 0.17 L/year. With a top liner, the initial rate is 78 L/year, and the rate after 10,000 years is 0.27 L/year. These rates do not account for slightly higher rates during initial period at higher temperatures but the increase is likely negligible over the 10,000 year period. These values are documented here for general reference. A more formal calculation can be provided at a later time if needed.

6.0 CONCLUSIONS AND RECOMMENDATIONS

6.1 Based on described service conditions and project requirements, the following lining systems were recommended by vendors for the Vault #2 application:

- 68 Tank Lining System (Ceilcote)
- TL-45-S High Build Novolac Epoxy Tank Lining (Blome International)
- Semstone 245AFRC (Carboline)
- Expresscoat HCR/Sher-Tuff Epoxy (Sherwin-Williams)

Of these, the Ceilcote and Carboline systems are more robust but are likely more labor-intensive and expensive to install. Systems recommended by Blome International and Sherwin-Williams are less robust but are suitable for the application. The Sherwin-Williams system provides for greater flexibility and crack-bridging capability if needed. Sherwin-Williams is the site strategic supplier for protective coatings and linings.

6.2 Comparison of systems on an equal basis is difficult as some vendors are more conservative than others with regard to lining system design for this type of application. Primary concerns shared by all vendors are that the lining cannot be inspected or maintained once in service, as well as the 100-year service life requirement.

6.3 The vendor-recommended systems use epoxy-novolac resins (at least topcoats) for superior chemical resistance. The primary limitation of these coatings is low flexibility. More elastic linings such as flexible epoxies, elastomeric polyureas and polyurethanes could not be recommended due to lower radiation, chemical and thermal stability, particularly during early periods of operation at peak temperatures. These may be an option for future vaults with different service conditions.

6.4 Unbonded membrane linings such as HDPE are not recommended due to concerns about leakage behind the lining and long-term degradation due to radiation/oxidation. The 2.6 Mrad threshold dose previously established for HDPE on the vault exterior would be reached within 40-50 years (gamma) or 15-20 years (total dose) if used on the vault interior. Bonded EPDM linings (Marseal 8000 or equal) may be suitable but long-term resistance to radiation/oxidation and organic compounds is less certain. This option can be reviewed for future vaults.

6.5 Service life prediction of polymeric materials in multivariable environments is complex. There are no known 100-year case histories of synthetic polymer linings in any environment, much less in radiological service. Many accelerated-aging studies have been performed using various failure criteria. The mat-reinforced thermosetting linings are reasonably expected to maintain integrity for the first 50-100 years based on anticipated service conditions and several assumptions, including: limited oxidation and elevated temperature exposure, tolerable radiation dose, minimal differential settlement and proper installation. Avoidance of known failure modes such as osmotic blistering and moisture vapor transmission is critical. The linings will likely remain physically intact and act as a diffusion barrier for much longer periods, though the time to absolute failure is difficult to predict without product-specific testing.

6.6 With no dose rate effects, the thermosetting linings are expected to resist degradation by ionizing radiation for at least 300-400 years (10 Mrad total, 3.7 Mrad gamma). A higher dose of 50 Mrad is also likely tolerable and would not be reached until 3000-4000 years (gamma dose ~5 Mrad). The 10,000-year radiation dose to the lining (123 Mrad total, 7.5 Mrad gamma) is far less than the dose used to qualify nuclear power plant coatings (1000 Mrad). Dose rate effects for the lining materials involved are unknown.

6.7 Though high radiation tolerance is expected, the specific thermosetting lining systems have not been tested. Therefore, radiation exposure testing of these linings is recommended. Linings should be exposed at various dose rates over longer periods to evaluate the potential for dose rate effects. Linings should also be exposed to simulated service conditions to evaluate combined effects. An accelerated-aging test program is needed to validate conclusions and to provide a model for lining service life prediction.

6.8 The aging behavior of thermosetting coatings and linings has been studied much less extensively than flexible membrane linings such as HDPE used in landfills. This is mainly because such linings are normally used in facilities with a much shorter design life (20-60 years) and they are often accessible for inspection and maintenance. The aging behavior of thermosetting coatings and/or composite materials may require additional review to support the PA process.

6.9 For any lining system, vendor application instructions must be strictly followed. Proper installation is crucial for systems that cannot be later accessed for inspection or maintenance. Moisture vapor transmission testing of the concrete should be performed as this is a common cause of lining failures, particularly for on-grade or below-grade structures. The use of HDPE as an exterior membrane reduces this concern. Surface contaminants (chlorides) should be removed to prevent osmotic blistering in immersion service. Holiday detection is recommended, with a conductive primer generally needed for concrete substrates. Details should be discussed with the lining manufacturer.

6.10 Lining systems should be installed by qualified personnel. Experience with the specific products involved is recommended in order to minimize errors. On-site support and inspection by lining manufacturer representatives is recommended to insure satisfactory results. Installation of sheet drain systems should be planned so as to minimize damage to the lining system as well as limiting penetrations for attachment. Adhesive bonding may be needed.

6.11 Gas generation rates due to radiolytic degradation of the epoxy-based linings are estimated at less than 100 L/year (total gas). Without a top lining, the initial gas generation rate is estimated at 48 L/year, with a rate after 10,000 years of 0.17 L/year. With a top liner, the initial rate is 78 L/year and the rate after 10,000 years is 0.27 L/year. Ventilation strategies should account for these values.

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Paul Whitehead, Ameron

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