

Monitoring Degradation of Phenolic Resin-Based Neutron Absorbers in Spent Nuclear Fuel Pools Technical Letter Report

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Executive Summary

This report compiles and analyzes the available information on Carborundum and Tetrabor to assess the adequacy of surveillance methods for monitoring degradation of phenolic resin-based absorbers. Carborundum and Tetrabor are very similar neutron absorber materials that incorporate boron carbide powder in a binder of phenolic resin. Carborundum neutron absorber material was manufactured in two forms: thick rigid plate and thin flexible fiberglass-reinforced sheet. Tetrabor was produced by a different manufacturer, but is described as being similar to Carborundum plate. Qualification testing was performed on both Carborundum and Tetrabor prior to installation to assess their ability to perform in the spent fuel pool environment. Limited information is available regarding the Tetrabor qualification testing, while much more information is available regarding the Carborundum qualification testing. Operating experience of phenolic resin-based neutron absorbers includes wrapper plate bulging, loss of B-10 areal density, and results from coupon and *in situ* neutron attenuation testing. There have been operating experience events of rack wrapper plate bulging due to offgassing from phenolic resin-based neutron absorbers in sealed panel cavities. Coupon testing, including visual examinations, dimensional and weight loss measurements, and neutron attenuation testing, has found steady weight loss over time, but no degradation outside the acceptance criteria has been identified by visual examination or neutron attenuation testing of coupons. However, the *in situ* neutron attenuation testing campaign performed at Palisades found significant reductions in B-10 areal density below the minimum credited amount. The B-10 areal density plotted as a function of gamma dose for Carborundum plate at Palisades does not appear to show a strong correlation between loss of B-10 and absorbed gamma dose, potentially indicating other factors may influence boron carbide loss.

In order to understand the qualification testing results and operating experience, this report describes the mechanisms of radiolysis of phenolic resins in the spent fuel pool environment. In brief, alpha, beta, and gamma radiation breaks bonds and creates free radicals in the phenolic resin, leading to scission of the polymer backbone and degradation of the polymer structure. In the presence of water and oxygen, degradation is accelerated by the introduction of more aggressive chemical species, including hydroxyl radicals and hydrogen peroxide. A key step in the progression of degradation is the loss of polymer material from the matrix through erosion and dissolution, leading to release of boron carbide from the panel. Erosion and dissolution of the polymer material may be influenced by the rate of flow and water exchange that occurs between the panel cavity and pool. Greater flow and pool water exchange would increase the degradation and dissolution of the phenolic resin by providing fresh water to the panel cavity. The flow rate is highly variable and dependent on the original rack design or modifications made to the racks during service.

Boraflex, a silicone-based polymer neutron absorber, shows a strong correlation between loss of B-10 areal density and absorbed gamma dose. While the radiation chemistry of phenolic resin-based materials would lead one to expect a similar correlation for Carborundum and Tetrabor, the *in situ* neutron attenuation data collected for Carborundum at Palisades does not exhibit this trend. In the Palisades *in situ* neutron attenuation data, panels with apparently

similar absorbed gamma doses had no indicated degradation while others had indications of significant degradation.

It is expected that flow and pool water exchange in phenolic resin-based absorber panel cavities could be a dominant factor in the boron carbide release process. While many spent fuel racks containing Boraflex are open to constant exchange with bulk pool water, phenolic resin-based neutron absorber rack panel cavities were usually designed to be sealed from the pool. Panel cavities in the Palisades spent fuel racks were only vented to the pool through small holes drilled in the wrapper plate to relieve pressure from offgassing after installation. These holes were typically drilled at the top of the wrapper plate and would provide little or no flow or pool water exchange with the cavities surrounding the phenolic resin-based panel. Potentially, the lack of correlation with absorbed gamma dose may be explained by the effect of flow and pool water exchange factors on the process of boron carbide release. However, because the flow and pool water exchange factors at Palisades are unknown, the amount and rate of B-10 release may not be predicted by gamma dose alone.

For several forms of qualification testing, discrepancies between the qualification test data and operating experience encountered during service were identified. These discrepancies are attributed to the accelerated nature of qualification testing, which was non-conservative in two ways: a much higher dose rate and a much shorter exposure time in water.

The report analyzes several forms of surveillance testing for Carborundum. For in-pool coupon testing, given uncertainties in the exact nature of the panel cavity environment and the boron carbide release process, it is difficult to assess whether the design of in-service coupons is representative of the service environment. For *in situ* direct measurement neutron attenuation methods such as BADGER, there are numerous uncertainties (Chapman and Scaglione, 2012). With adequate consideration for these uncertainties, *in situ* data could be valuable in assessing the B-10 loss of individual panels of phenolic resin-based absorbers. However, given the inconsistencies in rack design and flow rates for Carborundum pools, there is additional uncertainty associated with extrapolating the B-10 loss of a limited number of phenolic resin panels to the degradation and B-10 losses of all the panels in a spent fuel pool.

Therefore, the report concludes that even though both Boraflex and Carborundum are polymer-based neutron absorbing materials, for Carborundum the loss of B_4C from the degraded polymer matrix does not show a strong correlation to absorbed gamma dose. The lack of correlation between gamma dose and B_4C loss has two significant implications. First, it precludes the development of a predictive model to inform which panels to interrogate with an *in-situ* B-10 areal density measurement method. Second, one cannot predict the degradation of Carborundum panels throughout the spent fuel pool from a few discrete B-10 areal density panel measurements.

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1. Introduction

NRC regulations, particularly 10 Code of Federal Regulations 50.68 and General Design Criterion 62, require that the subcriticality of spent fuel pools be maintained during both normal operation and under design basis accident scenarios. Over time, many licensees have installed high density spent fuel storage racks that incorporate neutron absorber panels containing boron carbide to ensure subcriticality. These neutron absorbers have come in various forms, including borated stainless steel, aluminum-based composite materials such as Boral and Metamic, and polymer-based materials such as Boraflex, Carborundum, and Tetrabor. In general, polymer-based absorbers have experienced the most significant degradation in service resulting in reduced neutron absorption. The degradation mechanisms and rates for silicone-based Boraflex, which was installed in dozens of spent fuel pools, have been studied extensively. However, the degradations mechanisms and rates for phenolic resin-based absorbers, Carborundum and Tetrabor, have not been studied as comprehensively.

The objective of this report is to analyze the available information on Carborundum and Tetrabor to assess the adequacy of surveillance methods for monitoring degradation of phenolic resin-based absorbers. This analysis considers material composition/structure, the radiation and aqueous spent fuel pool environment, testing results, operating experience, and irradiated polymer degradation theory.

2. Background

This section briefly summarizes the background of spent fuel pool storage, the need for neutron absorbers, and the experience of Boraflex degradation. It also provides a detailed description of the Carborundum and Tetrabor absorber materials and the spent fuel pool environment to which they are exposed.

2.1 Spent Fuel Pool Storage

When most of the current fleet of nuclear power plants were designed and built, spent fuel pools were designed to provide short-term storage for spent fuel before shipping to a reprocessing facility. The pools were designed to use geometrical spacing to ensure subcriticality of the limited number of assemblies anticipated to be stored on-site. However, as the reprocessing and a long-term waste repository options did not materialize, spent fuel pools began to fill up. In order to increase storage capacity to accommodate the accumulating spent fuel assemblies, many licensees chose to replace the original storage racks in the spent fuel pool with high density storage racks that incorporated neutron absorber panels between the spent fuel assemblies to ensure subcriticality per NRC regulations.

2.1.1 Neutron Absorber Materials

Solid neutron absorber materials integrated into high density storage racks have been developed in a variety of forms, but all fundamentally utilize Boron-10 (B-10) atoms to absorb neutrons and prevent criticality. Therefore, the neutron absorption capability of these materials is generally characterized by their B-10 areal density, which is measured in grams of B-10 per square centimeter (g/cm^2). B-10 is generally present in the chemical form of boron carbide (B_4C) within an aluminum matrix or a polymer matrix.

Borated stainless steel incorporates the B-10 atoms into the alloy composition.

Neutron absorber panels are generally enclosed within a panel cavity by a wrapper plate that may or may not allow interaction with the water in the spent fuel pool as illustrated in Figure 2-1 (Haley, 2012). Therefore, the absorber materials may be exposed to borated or unborated water or kept dry. These materials may also be exposed to alpha, beta, gamma, and neutron radiation from the spent fuel. The solid neutron absorber materials can degrade or deform over time in the spent fuel pool environment, reducing their B-10 areal density and capability to absorb neutrons.

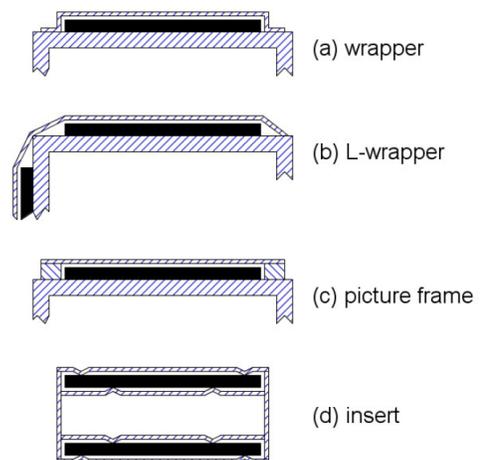


Figure 2-1 Examples of absorber panel wrapper plates (Haley, 2012)

Among the neutron absorber materials credited by licensees, polymer-based materials such as Boraflex, Carborundum, and Tetrabor have experienced the most significant degradation. The degradation mechanisms and rates of silicone-based Boraflex have been studied extensively

and are briefly described in the following section, while the degradation of phenolic resin-based Carborundum and Tetrabor are the primary subject of this report.

2.1.2 Management of Boraflex Degradation

While the polymer in Boraflex is very different from the phenolic resin used in Carborundum and Tetrabor, it is useful to understand the performance of Boraflex when considering the degradation of Carborundum and Tetrabor in the same spent fuel pool environment. A more detailed description of Boraflex and its degradation in the spent fuel pool environment can be found in “Boraflex, RACKLIFE, and BADGER: Description and Uncertainties” (Agencywide Documents Access and Management System (ADAMS) accession number ML12216A307) (Haley, 2012). Boraflex is composed of ~50% boron carbide (B_4C), ~25% elastomeric polymer polydimethyl siloxane (PDMS), and ~25% crystalline silica (SiO_2) filler. Boraflex panels are generally 0.025 – 0.125 inches thick depending on the desired B-10 areal density and cover the entire active fuel length with one panel.

The flexible PDMS polymer serves as the binder for the boron carbide and silica and is therefore the essential component for the integrity of the composite material. The chemical structure of a PDMS polymer chain can be seen in Figure 2-2.

In the presence of radiation, PDMS undergoes three chemical processes: abstraction (bond-breaking) within or of a methyl group, cross-linking between polymer chains, and scissioning

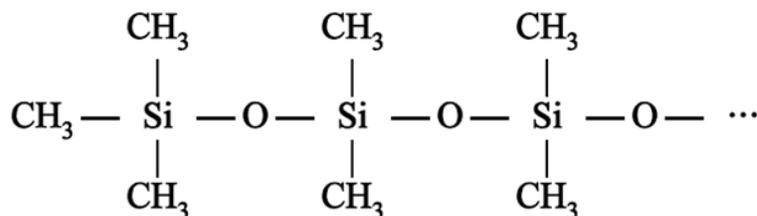


Figure 2-2 PDMS chemical structure (Haley, 2012)

of the polymer backbone. Gamma radiation causes the abstraction of H or CH_3 radicals, which provide sites for cross-linking and lead to offgassing and bubbles in the material. Cross-linking induces shrinkage, gap formation, increases density and hardness, and reduces ductility.

Simultaneously, polymer chain scissioning takes place, which breaks the backbone of the polymer chain and eventually leads to dissolution of the PDMS binder (Haley, 2012). At low to moderate gamma radiation doses, cross-linking is the dominant effect over scissioning and causes Boraflex to shrink and densify (Haley, 2012). Cross-linking also leads to the formation of gaps due to shrinkage around locations where the panel is constrained or pinned by the wrapper plate. Once gamma dose reaches 1×10^{10} rad, cross-linking effects saturate and scissioning effects, which do not saturate, begin to dominate. After 1×10^{10} rad gamma exposure, PDMS has converted to a matrix of amorphous silica and has thus lost its ductility and become hard, brittle, and very susceptible to cracking. Table 2-1 below summarizes the effects of gamma irradiation on PDMS in Boraflex (Haley, 2012).

Table 2-1 Effects of gamma irradiation on PDMS polymer in Boraflex (Haley, 2012)

Dose [Gy]	Dose [rads]	Cross-linking	Effects on material properties
$<1 \cdot 10^4$	$<1 \cdot 10^6$	elastomeric levels	negligible effects
$1 \cdot 10^4 - 5 \cdot 10^6$	$1 \cdot 10^6 - 5 \cdot 10^8$	increasing	increasing Shore A hardness
$5 \cdot 10^6 - 1 \cdot 10^8$	$5 \cdot 10^8 - 1 \cdot 10^{10}$	increasing	increasing Shore D hardness, density, and shrinkage
$9 \cdot 10^7 - 1.5 \cdot 10^8$	$9 \cdot 10^9 - 1.5 \cdot 10^{10}$	becomes saturated	fully hard and brittle, ceramic-like; no further densification or shrinkage
$>1 \cdot 10^8$	$>1 \cdot 10^{10}$	saturated	continued scissioning degradation, including increased porosity

The scissioning process is affected by the aqueous environment. When a polymer chain scissions, the fragments frequently recombine and therefore no permanent damage occurs. However, in the aqueous spent fuel pool environment, dissolved oxygen reacts with the radical sites created by scissioning. This prevents recombination at the site of the scission and causes permanent damage to the polymer by shortening the polymer chains. In this manner, the water and radiation environments work synergistically to cause greater degradation than would be possible by each separately (Haley, 2012). Boraflex degradation is largely dependent on gamma radiation exposure and water flow. As gamma exposure increases polymer chain scissioning, water flow through openings around the wrapper plate increases dissolution of the degraded polymer matrix leading to the *proportional* loss of B-10 from the panel and thus reduced neutron absorption capability. As Boraflex degradation progresses, the breakdown of PDMS causes the slightly soluble silica to be released to the spent fuel pool, which can be measured as silica concentration in the pool at large.

With this understanding of a series of directly proportional correlations among gamma dose, polymer matrix degradation, dissolution of slightly soluble silica, and loss of boron carbide, a computer model known as RACKLIFE was developed. Based on absorbed gamma dose and spent fuel pool silica concentration, RACKLIFE can predict B-10 areal density for each panel in the pool (Haley, 2012). Absorbed gamma dose for each panel is estimated based on tracking the activity levels of the spent fuel assemblies surrounding that panel. RACKLIFE can then estimate the gamma exposure, and thus the degree of degradation and boron carbide loss, of each specific panel relative to the rest of the panels in the pool. Observed silica concentration is used to calibrate the model to account for total degradation in the entire Boraflex panel population of the pool. This model has many uncertainties, particularly the estimate of the exchange of water between panel cavities and the surrounding pool volume, which limit its ability to predict degradation in absolute terms. However, given the high correlation of absorbed gamma dose to degradation, the relative estimate of individual panel degradation to other panels in the pool may be useful for targeting the most degraded panels in the population. In practice, RACKLIFE is used in conjunction with Boron-10 Areal Density Gauge for Evaluating

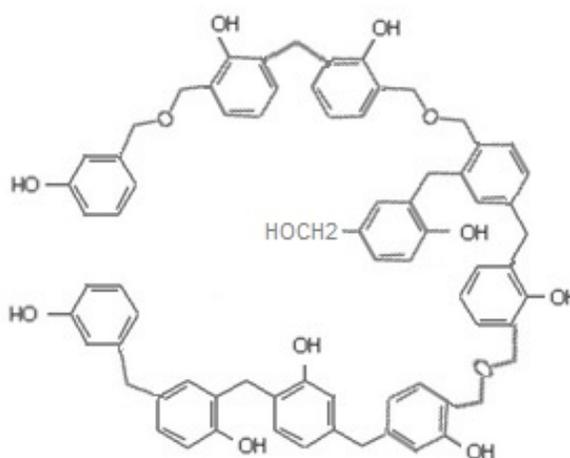
Racks (BADGER) *in situ* neutron attenuation testing to directly assess absorber efficacy and further calibrate RACKLIFE (Haley, 2012).

2.2 Carborundum and Tetrabor

Carborundum and Tetrabor are very similar neutron absorber materials that incorporate boron carbide powder in a binder of phenolic resin. The chemical structure of phenol formaldehyde, comprises a polymer of phenol molecules linked by either methylene or ether bridges (Painter and Coleman, 2009). A representative structure of the resin can be seen in Figure 2-3 below. Carborundum and Tetrabor panels were manufactured and installed in high density spent fuel storage racks in U.S. spent fuel pools in the late 1970s and early 1980s (EPRI, 2009).

2.2.1 Carborundum

Carborundum neutron absorber material was manufactured by the Carborundum Company in two forms: plate and sheet. Carborundum plate material is “a thick rigid plate” consisting of “granular boron carbide bonded in a phenol formaldehyde resin” (The Carborundum Company, 1980). The plate material is composed of 73% natural boron carbide and 27% phenolic resin by weight as shown in Table 2-2 (EPRI, 2009). For mechanical strength reasons, the Carborundum plate material is relatively thick (up to 0.25 inches) and short (30 inches in length).



Carborundum plate therefore requires several pieces stacked on top of one another to cover the active length of a fuel assembly (EPRI, 2009). The relatively thick plates result in high B-10 areal densities of about 0.095 g/cm² (The Carborundum Company, 1980).

Table 2-2 Composition of Carborundum neutron absorber materials (EPRI, 2009)

Constituent	w/o	
	Plate	Sheet
Boron Carbide	73%	64%
Resin	27%	18%
Fiberglass	---	18%

Carborundum sheet material is “a thin flexible glass fabric reinforced composite” containing natural boron carbide powder in a matrix of phenol formaldehyde resin (The Carborundum Company, 1980). The sheet material is composed of 64% boron carbide, 18% phenolic resin, and 18% fiberglass reinforcement by weight (EPRI, 2009). Carborundum sheet material incorporates fiberglass reinforcement to reduce the thickness to less than 0.1 inches with a B-10 areal density of 0.015 – 0.025 g/cm² (NRC, 1980; NRC, 2000). Carborundum sheet material, unlike Carborundum plate, covers the entire active fuel length in one sheet (EPRI, 2009).

Carborundum plate material was installed in spent fuel pools at Haddam Neck (Connecticut Yankee), Millstone 1, and Palisades. Carborundum sheet material was installed in spent fuel pools at Calvert Cliffs 1, Crystal River 3, and LaCrosse.

2.2.2 Tetrabor

Tetrabor neutron absorber material was manufactured by Electroschmelzwerk Kempten (ESK), a major boron carbide supplier in Germany, which is now owned by Ceradyne (EPRI, 2009). Tetrabor neutron absorber plates are composed of [natural] B₄C granule (powder) material mixed with a phenolic resin and catalyst (Energy Northwest, 2010). The 2009 EPRI report on neutron absorber materials, however, states Tetrabor “is manufactured with a phenolic binder with fillers of boron carbide and graphite” (EPRI, 2009). Based on these descriptions, some batches of Tetrabor neutron absorber material may contain graphite. Plates are manufactured by pressing into the approximate shape, followed by heating to 1050°C for 12 hours “to pyrolyze the resin material” (Energy Northwest, 2010).

Tetrabor absorber plates used domestically are 0.21-0.24 inches thick and 19 inches in length with a B-10 areal density of 0.0959 g/cm² (Energy Northwest, 2010; Dominion Energy Kewaunee, Inc., 2009). Similar to the Carborundum plate material, Tetrabor plates are relatively short sections which are stacked on top of one another to cover the entire active fuel length. Two U.S. plants have installed Tetrabor for use in their spent fuel pools: Columbia Generating Station and Kewaunee. In addition to Carborundum plate, Haddam Neck also used Tetrabor, but is now decommissioned with its spent fuel pool dismantled. A summary of the key characteristics of Carborundum and Tetrabor neutron absorbers and the plants that installed these materials can be seen in Table 2-3 below.

Table 2-3 Summary of Carborundum and Tetrabor neutron absorber material characteristics and installations

Material	Components	Typical Thickness (inches)	Typical Length (inches)	Typical B-10 Areal Density (g/cm ²)
Carborundum plate	B ₄ C powder Phenolic resin binder	0.25”	Up to 30”	0.095
Carborundum sheet	B ₄ C powder Phenolic resin binder Fiberglass reinforcement	<0.1”	Full length of active fuel	0.015 – 0.025
Tetrabor	B ₄ C powder Phenolic resin binder Graphite (possibly)	0.21 – 0.24”	Up to 19”	0.0959

3. Qualification Testing and Operating Experience

Qualification testing results and operating experience reports serve as two key sources of information regarding the performance of phenolic resin-based neutron absorbers in the spent fuel pool environment. Qualification testing was performed on both Carborundum and Tetrabor prior to installation to assess their ability to perform in the spent fuel pool environment. Samples were exposed to water and radiation in order to simulate the spent fuel pool environment. Operating experience is accumulated after installation based on reports of the performance of Carborundum and Tetrabor in service. Operating experience may result from surveillance testing performed to ensure neutron absorber performance or may simply be discoveries made during the course of normal plant operations, such as movement of spent fuel assemblies.

3.1 Qualification Testing

3.1.1 Carborundum

The Carborundum Company tested Carborundum boron carbide sheet and plate material at the High Flux Isotope Reactor (HFIR) Spent Fuel Storage Site (SFSS) (The Carborundum Company, 1980). The HFIR SFSS was chosen for this testing due to the high gamma radiation fluxes of 10^6 - 10^8 rad per hour, which allowed a total exposure of 10^{11} rad in about 100 days (The Carborundum Company, 1980). The test arrangement was designed to provide a large volume of uniform flux of full spectrum gamma radiation with minimum neutron flux. Strength (flexural for the brittle plate material and ultimate tensile for the ductile sheet material), elastic modulus, dimensions, and weight data were collected for four exposure conditions: plate and sheet material in deionized and 2500 ppm borated water environments. A range of gamma fluxes from 10^9 – 10^{11} rad were used (The Carborundum Company, 1980). A total of 450 plate samples and 480 sheet samples were involved in the testing to allow at least 12 specimens to be measured per data point for measurements of strength, elastic modulus, dimensions, and weight (The Carborundum Company, 1980). Gas evolution and boron leachability data were also collected over more limited exposure setups with fewer samples.

Test results found that strength and elastic modulus decreased with increasing gamma exposure for both materials in both environments. At exposures up to 10^{10} rad in deionized and borated water environments, plate material strength reduced by around 30%, compared to only about a 10% reduction for the sheet material (The Carborundum Company, 1980). At higher exposures up to 10^{11} rad in deionized water, both sheet and plate materials experienced greater strength losses of about 60 and 65%, respectively (The Carborundum Company, 1980). In separate experiments, soak testing of both plate and sheet material with no exposure to radiation showed that a significant portion of the observed strength losses were due solely to exposure to water, which is typical for fiberglass-reinforced composites (The Carborundum Company, 1980).

In addition to mechanical testing, gas evolution and boron leachability testing were also performed to establish the chemical stability of the Carborundum boron carbide materials in the spent fuel pool environment. Gas evolution testing showed a decreasing amount of gas

evolution with increasing dose. It also showed oxygen (O₂) being consumed, while hydrogen (H₂) and carbon dioxide (CO₂) are produced as gamma dose increases as seen in Table 3-1 (The Carborundum Company, 1980). The majority of the gas evolution data was collected on Carborundum plate material with little data on the sheet material. Boron leachability data showed only a slight increase in the amount of soluble boron during irradiation compared to the unirradiated state: 0.047% in 30 days and 0.025% in 25 days, respectively (The Carborundum Company, 1980).

Table 3-1 Composition of Gas Evolved from Carborundum Plate Material (The Carborundum Company, 1980)

Component	Exposure Level							
	(10 ⁷ gray γ)							
	(10 ⁹ rad γ)							
	1.44		2.95		3.62		5.54	
	LDC*	PSU**	LDC*	LDC*	PSU**	PSU**	LDC*	LDC*
H ₂	13	37	50	69	59	77	75	71
O ₂	16	5	3	1	2	1	1	2
N ₂	68	51	38	18	27	12	10	11
CO ₂	2	6	7	11	11	9	12	14
CO	N.D.	Tr	Tr	Tr	Tr	Tr	Tr	Tr
CH ₄	Tr	N.D.	Tr	Tr	Tr	Tr	N.D.	Tr
Total	100	100	99	100	100	100	100	100

*Analyzed at Lexington Development Center

Tr = Trace

**Analyzed at Pennsylvania State University

N.D. = Not Detected

Weight results found a 5.5% loss for the Carborundum plate material and a 20.2% loss for the sheet material after exposure to 1 x 10¹¹ rad in deionized water as seen in Table 3-2 (The Carborundum Company, 1980). Exposures in borated water were suspended at 1 x 10¹⁰ rad after showing less change in weight and dimensions than those exposed to deionized water. Volume changes based on dimensional measurements increased with dose as seen in Tables 3-3 and 3-4. Carborundum plate's volume increased by around 3-5% at dose levels of 5 x 10¹⁰ to 1 x 10¹¹ rad. Carborundum sheet showed volume increases indicating swelling at lower doses (1 x 10¹⁰ rad) before strongly decreasing in volume by 10 to 15% at the highest gamma exposure doses (The Carborundum Company, 1980).

Table 3-2 Change in Weight of Carborundum Plate and Sheet Material as a Function of Dose (The Carborundum Company, 1980)

Gamma Dose, rad	Sheet			Plate		
	Initial*, g	Final*, g	Weight change, %	Initial*, g	Final*, g	Weight change, %
1 x 10 ⁹	1.761	1.757	-0.2%	9.584	9.596	0.1%
1 x 10 ¹⁰	1.787	1.767	-1.1%	9.566	9.527	-0.4%
1 x 10 ¹⁰	1.687	1.660	-1.6%	9.281	9.232	-0.5%
3 x 10 ¹⁰	1.718	1.653	-3.8%	9.71	9.552	-1.6%
5 x 10 ¹⁰	1.735	1.511	-12.9%	9.456	9.239	-2.3%
8 x 10 ¹⁰	1.704	1.399	-17.9%	9.562	9.097	-4.9%
1 x 10 ¹¹	1.675	1.337	-20.2%	9.482	8.961	-5.5%

*Based on measurements at each exposure on a minimum of 12 samples

Table 3-3 Change in Dimensions and Volume of Carborundum Plate Material as a Function of Dose (The Carborundum Company, 1980)

Gamma Dose, rad	Initial Length*, cm	Final Length*, cm	Initial Width*, cm	Final Width*, cm	Initial Thick.*, cm	Final Thick.*, cm	Initial Volume, cm ³	Final Volume, cm ³	Volume change, %
1 x 10 ⁹	7.615	7.620	1.280	1.280	0.546	0.548	5.322	5.345	0.43%
1 x 10 ¹⁰	7.612	7.645	1.280	1.285	0.541	0.544	5.271	5.344	1.38%
1 x 10 ¹⁰	7.615	7.666	1.285	1.298	0.536	0.538	5.245	5.353	2.07%
3 x 10 ¹⁰	7.633	7.666	1.278	1.283	0.549	0.544	5.355	5.351	-0.09%
5 x 10 ¹⁰	7.617	7.747	1.273	1.293	0.538	0.549	5.217	5.499	5.42%
8 x 10 ¹⁰	7.635	7.732	1.267	1.278	0.541	0.549	5.233	5.425	3.66%
1 x 10 ¹¹	7.633	7.757	1.270	1.285	0.544	0.549	5.273	5.472	3.77%

*Based on measurements at each exposure on a minimum of 12 samples

Table 3-4 Change in Dimensions and Volume of Carborundum Sheet Material as a Function of Dose (The Carborundum Company, 1980)

Gamma Dose, rad	Initial Length*, cm	Final Length*, cm	Initial Width*, cm	Final Width*, cm	Initial Thick.*, cm	Final Thick.*, cm	Initial Volume, cm ³	Final Volume, cm ³	Volume change, %
1 x 10 ⁹	7.668	7.630	1.354	1.367	0.119	0.122	1.236	1.272	2.99%
1 x 10 ¹⁰	7.617	7.617	1.354	1.354	0.119	0.124	1.227	1.279	4.20%
1 x 10 ¹⁰	7.559	7.577	1.308	1.308	0.119	0.122	1.177	1.209	2.77%
3 x 10 ¹⁰	7.557	7.564	1.298	1.293	0.124	0.122	1.216	1.193	-1.90%
5 x 10 ¹⁰	7.557	7.574	1.313	1.306	0.122	0.114	1.211	1.128	-6.85%
8 x 10 ¹⁰	7.579	7.577	1.303	1.285	0.122	0.109	1.205	1.061	-11.91%
1 x 10 ¹¹	7.549	7.539	1.298	1.265	0.122	0.107	1.195	1.020	-14.64%

*Based on measurements at each exposure on a minimum of 12 samples

The report observes that at higher levels of radiation exposure the polymeric bonding phase becomes embrittled and weakened, reducing “the tenacity with which the boron carbide particles are held” and leading to a tendency for material to rub off during handling for both the sheet and plate materials (The Carborundum Company, 1980). The report calls this phenomena “attrition” and attributes the majority of the weight losses observed to attrition during packaging, testing, or other handling, with only minor roles played by gas evolution, boron solubility, and transmutation. The report also cites another study reporting that the exposure of phenolic polymers to radiation leads to swelling, hardening, embrittlement, and “a water soluble degradation product, ‘which causes the material to disintegrate in water’” (Sisman, 1955). Despite the observed attrition and report from Sisman, the Carborundum report provides no further discussion or explanation of why Carborundum is not expected to “disintegrate” over time exposed to water and radiation in the spent fuel pool.

One of the key observations from the Carborundum Company testing program is as follows: “Analysis of the sheet material after exposure to 10⁹ gray (10¹¹ rad) showed a reduction in boron content of 15%, compared to the noted 20% weight loss of the material.” (The Carborundum Company, 1980). It is not clear whether “boron content” refers to B-10 areal density or a mass balance of boron, nor does the report describe which method was used to collect this data. It is also not clear how or whether this one observation might support the use of weight loss as an indicator of “reduction in boron content.”

3.1.2 Tetrabor

Less information is available regarding qualification testing for Tetrabor neutron absorber material than the previously described testing of Carborundum. Tetrabor was gamma irradiated from a Co-60 source (1.25 MeV average energy) to a maximum dose of 2.66×10^{10} rad at 1.6×10^6 rad per hour at a temperature of 50°C (EPRI, 2009). The results of hydrogen evolution during irradiation are plotted in Figure 3-1 showing hydrogen evolution saturating at about 0.2% after a gamma dose of 6×10^9 rad (EPRI, 2009). Thermal cycling of 16 cycles from room temperature to 350°F at $50^\circ\text{F}/\text{hour}$ showed no significant change in the modulus of rupture (EPRI, 2009). Water immersion testing without radiation exposure for 16 days at elevated temperature (exact temperature not reported) showed a 65% reduction in the modulus of rupture and a 30% reduction in the modulus of elasticity (EPRI, 2009).

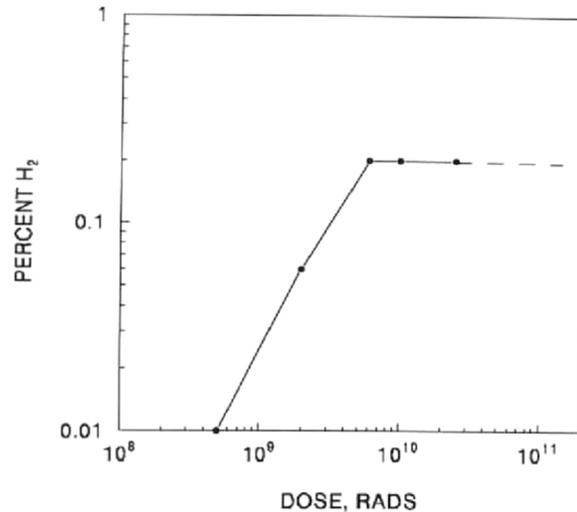


Figure 3-1 Hydrogen gas evolution as a function of gamma dose (EPRI, 2009)

3.2 Operating Experience

Operating experience regarding Carborundum and Tetrabor neutron absorber materials may be a result of complications of normal spent fuel handling activities as well as specific surveillance programs consisting of coupons, *in situ* neutron attenuation testing, and total organic carbon spent fuel pool water sampling. Operating experience includes wrapper plate bulging, loss of B-10 areal density, and results from coupon and *in situ* neutron attenuation testing.

3.2.1 Bulging of Rack Wrapper Plate

There have been numerous reported instances of bulging of the rack wrapper plate due to gas generation from phenolic resin-based neutron absorbers in sealed neutron absorber cavities. This plate bulging has typically been identified during normal spent fuel movement, when it is observed that a fuel assembly has become stuck inside a storage rack cell and cannot be removed, or when an assembly cannot be easily inserted into an empty rack cell. In most cases, wrapper plate bulging has been managed by drilling vent holes in the top of the neutron absorber panel cavity. Venting prevents bulging by allowing gases to escape, but also exposes absorber panels to spent fuel pool water, which may have other effects on the absorber material.

Carborundum Plate at Haddam Neck (Connecticut Yankee)

Haddam Neck Nuclear Power Plant (since dismantled) installed Carborundum plate neutron absorber materials in 1977. Excessive drag when moving spent fuel assemblies led to the discovery of wrapper plate bulging as described in Haddam Neck Licensee Event Report (LER) 78-004 on April 28, 1978 (Connecticut Yankee, 1978). The bulging was attributed to gas generation from the Carborundum plate absorber material causing a pressure buildup within the neutron absorber cavity and subsequent wrapper plate deformation (Connecticut Yankee, 1978). The LER also states: "Connecticut Yankee Atomic Power Company (CYAPCO) believes that offgassing could be the result of radiolytic decomposition of water and/or organic resin used to bind the B₄C powder in plate form." Short-term corrective actions included drilling vent holes "2 ½ inches from the bottom of the storage cell" to relieve the gas pressure buildup.

The LER also includes discussion of test specimens that were inserted in the spent fuel pool in fall 1977 and experienced offgassing (Connecticut Yankee, 1978). Gas chromatography results of the composition of gas present in the test specimen holder after offgassing can be seen in Table 3-5. It is not clear from the LER, but may be reasonably inferred that the starting gas was air. Therefore, the results appear to show that hydrogen, carbon dioxide, and methane are produced, while oxygen is consumed and nitrogen is unaffected. The reduction in nitrogen volume percent may be understood by the increase in the total amount of gas in the specimen holder due to the production of the other gases, rather than any reduction in the amount of nitrogen present.

Table 3-5 Gas Composition from Test Specimen in Haddam Neck (NRC, 1978)

Gas	Volume Percent	
	Starting gas (air)	Offgas sample
Hydrogen (H ₂)	< 1	18
Oxygen (O ₂)	21	3
Carbon Dioxide (CO ₂)	< 1	8
Nitrogen (N ₂)	78	69
Methane (CH ₄)	< 1	1

Tetrabor at Kewaunee

Kewaunee Power Station installed Tetrabor neutron absorber material in 1979 (Dominion Energy Kewaunee, Inc., 2009). On December 19, 1980, Kewaunee observed swelling and bulging of the wrapper plate encasing two coupon specimens and installed fuel storage racks due to offgassing from the Tetrabor material into the sealed panel cavities (Wisconsin Public Service, 1980). The licensee chose to drill vent holes in the top of the racks to relieve the pressure and prevent further bulging (Wisconsin Public Service, 1981). The licensee also reported "the results of a laboratory analysis of the gas generated" showing by volume about 65% hydrogen and 30% nitrogen to be present (Wisconsin Public Service, 1981).

Carborundum Plate at Palisades

Palisades Nuclear Plant installed Carborundum plate neutron absorber material between 1979 and 1981 (Entergy, 2008). Between 1988 and 2007, the plant experienced fourteen instances of

wrapper plate bulging impacting the movement of spent fuel assemblies (Entergy, 2008). According to the licensee: “Originally, the annulus [panel cavity] was designed to be water tight, but cell wall swelling due to internal gas production from gamma exposure necessitated the drilling of 3/16 inch vent holes in the upper region of each cell” (Entergy, 2008). There is little further information regarding the wrapper bulging available. *In situ* testing performed in 2009 revealed a significant reduction in neutron absorption of the Carborundum plates, which is discussed in greater detail in Section 3.2.3 (Northeast Technology Corp, 2009).

Summary

There have been three well-documented operating experience events of rack wrapper plate bulging due to offgassing from phenolic resin-based neutron absorbers at Haddam Neck, Kewaunee, and Palisades, which are summarized in Table 3-6. It should be noted that there are several other plants with these materials that have not documented any wrapper plate bulging events based on the literature review done for this report. However, among the plants without documented wrapper plate bulging events, Crystal River 3, Calvert Cliffs 1, and Columbia are known to have initially installed vented panel cavities as a preventative measure.

Table 3-6 Summary of Documented Wrapper Plate Bulging Events

Plant	Material	Year	Corrective Action(s)	Comments
Haddam Neck	Carborundum plate	1978	Drill vent holes	Gas chromatography of gases from test specimen holder showed by volume 18% H ₂ , 3% O ₂ , 8% CO ₂ , 69% N ₂ , and 1% CH ₄
Kewaunee	Tetrabor	1980	Drill vent holes	Generated gases found to be about 65% hydrogen and 30% nitrogen
Palisades	Carborundum plate	1988 - 2007	Drill vent holes	Continued bulging possibly due to incomplete venting

3.2.2 Coupon Testing Results

Crystal River 3, Calvert Cliffs 1, Kewaunee, Columbia, and LaCrosse have Carborundum and Tetrabor installed as neutron absorbers and use coupon testing surveillance programs to monitor the degradation of the in-service absorber materials. These coupons are placed in the spent fuel pool in order to simulate the environmental exposure and configuration of the in-service panels. To achieve this, they are exposed to pool water and spent fuel radiation typically within sheathing that may be vented similar to the in-service panels. Coupon testing is generally performed every few years and may include visual examination, dimensional measurements, weight/density measurement, and neutron attenuation testing.

Carborundum Sheet at Crystal River

Crystal River 3 Nuclear Generating Plant installed Carborundum sheet coupons along with Carborundum sheet neutron absorber material in their spent fuel racks in 1981 (Progress Energy, 2009). The coupons are all sheathed with a vent hole similar to the actual rack configuration (Progress Energy, 2009). There are two sizes of coupons, which are otherwise identical: small (1" x 2") Type A coupons and larger (2" x 10") Type B coupons (Progress

Energy, 2009). Crystal River's coupon testing program includes a visual examination and weight loss testing, but no dimensional measurements or neutron attenuation testing. Crystal River committed in 2007 to perform coupon testing and *in situ* testing alternately every ten years, so that one surveillance test, either *in situ* or coupons, is performed every five years (Progress Energy, 2010). The most recent surveillance performed in 2004 showed an average weight loss of less than 7% (Progress Energy, 2010). Weight measurements showed a decrease of less than 2% in average weight from 1993 to 2004 (Progress Energy, 2010).

However, Crystal River also reported a sample in 2004 that failed the acceptance criteria of less than 20% weight loss with a weight loss of 21%. The licensee explained this result as "an anomaly" from being "damaged (eroded) by water rinsing/lancing for decontamination during removal of the holder from the spent fuel pool" (Progress Energy, 2010). This coupon was located "directly opposite the vent/inspection hole in the packet," and the only part of the coupon damaged "was the area opposite the vent/inspection hole in the packet" (Progress Energy, 2010). The licensee believes that this type of localized degradation is not expected to occur for the in-service material because the vent/inspection holes in the installed racks are located above the active fuel length (Progress Energy, 2010).

Carborundum Sheet at Calvert Cliffs Unit 1

Calvert Cliffs Nuclear Power Plant Unit 1 installed storage racks with Carborundum sheet material and coupons in or shortly after 1980 (NRC, 1980). No documentation was found discussing the sheathing of the coupons. Coupons are tested by visual examination and length, width, and weight measurements every four years, and benchtop neutron attenuation testing every eight years (NRC, 2008). Calvert Cliffs' coupon program comprises an Accelerated Surveillance Assembly (ASA) and a Long-Term Surveillance Assembly (LTSA) (Constellation Energy, 2007). The ASA conservatively accelerates exposure by moving coupons every outage to a new location with freshly discharged fuel, thereby maximizing radiation exposure. The LTSA, on the other hand, is initially surrounded by freshly discharged fuel, but is simply left in the same location surrounded by the same radioactively decaying fuel to more realistically simulate the exposure of in-service panels (Constellation Energy, 2007). The Calvert Cliffs surveillance program does not utilize *in situ* neutron attenuation testing (NRC, 2008).

A total of six coupons from the ASA have been tested and the weight loss results can be seen in Figure 3-2 (Constellation Energy, 2008). The most recent ASA coupon tested in 2005 showed 9.5% weight loss, which is consistent with a linear projection for weight loss over time (Constellation Energy, 2008). Limited understanding of the mechanism causing the weight loss introduces uncertainty into the continued linearity of the trend.

Projected Life of Carborundum Racks

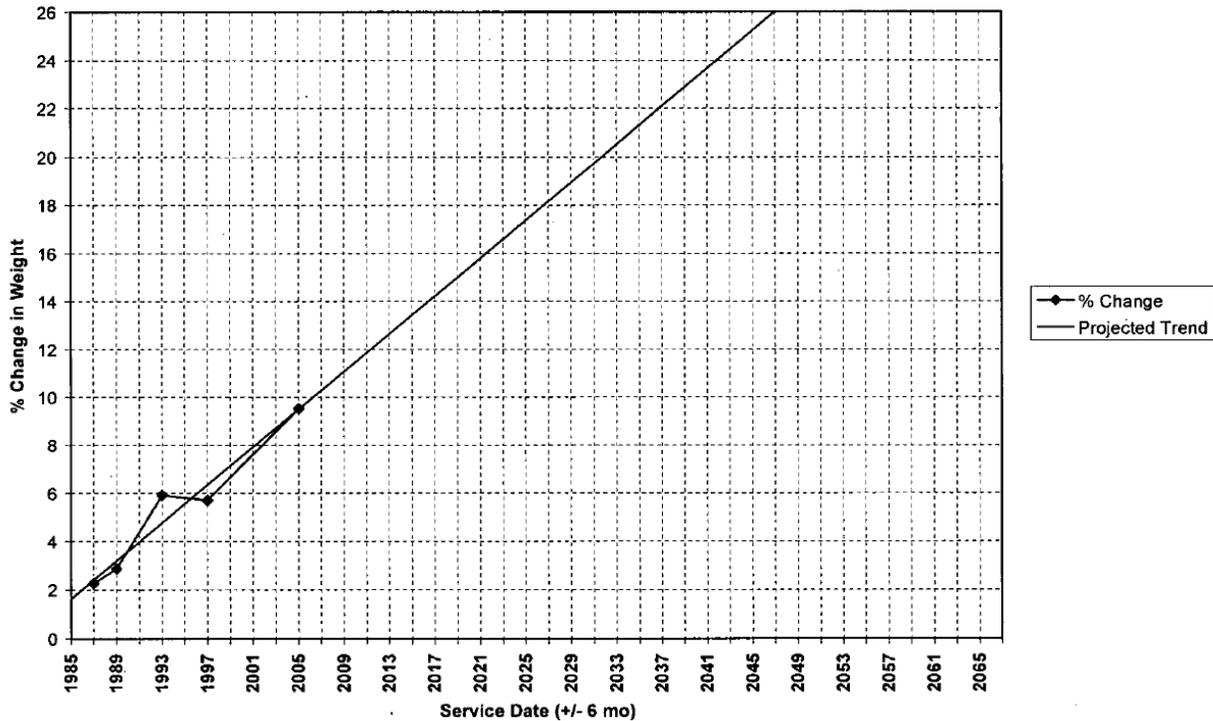


Figure 3-2 Weight loss data and projection over time from ASA Carborundum coupons at Calvert Cliffs (Constellation Energy, 2008)

Carborundum Sheet at La Crosse

La Crosse installed spent fuel storage racks containing Carborundum sheet material and coupons in 1980 (Dairyland Power Cooperative, 2010). The in-service Carborundum sheet material is “essentially sealed” by stainless steel wrapper plates that are tack welded along the edges, while the coupons are exposed to flowing water on two edges and are moved during each outage next to the fresh, newly discharged fuel assemblies (Dairyland Power Cooperative, 2010). The coupon testing program has primarily consisted of visual examination and weight loss measurements at least every six years. Weight loss results have generally shown less than 6% weight loss, except for four samples in 2005 that were measured with weight loss of 10 – 12 %. The licensee noted that coupons tend to show erosion from exposure to water along the exposed edges of the coupons, with up to 1/16 inch of fiberglass exposed along the edges due to erosion of the polymer matrix. They also observed that exposed coupons were “a little more friable” than archival material (Dairyland Power Cooperative, 2010).

In 1997, La Crosse sent two coupons for more extensive testing by NETCO after 16.3 years of exposure to near-maximum gamma fluxes (Dairyland Power Cooperative, 2010). NETCO performed a visual examination, dimensional, weight, and density measurements, a radioassay, and neutron attenuation testing. Neutron attenuation testing showed a B-10 areal density of

0.0211 and 0.0193 g/cm² for exposed samples compared 0.0207 g/cm² for the archived sample, indicating a 2% increase and 7% decrease in B-10 areal density for the two exposed samples compared to the archive (Dairyland Power Cooperative, 2010).

Tetrabor at Kewaunee

A coupon testing program has been in place for the Tetrabor neutron absorber material at Kewaunee since 1982 with testing at least every four years since 1982 (Dominion Energy Kewaunee, Inc., 2009). Coupons are 1 inch x 4 inch x 0.24 inches, vented in stainless steel sheathing, and placed in locations near freshly discharged fuel (Dominion Energy Kewaunee, Inc., 2009). Coupon testing consists of visual examination, dimensional and thickness measurements, and quantitative benchtop blackness testing (Dominion Energy Kewaunee, Inc., 2009). “The boron-10 (B-10) areal density is calculated based on blackness testing results” by comparing “the test rig control plate data of different thicknesses to test coupons from the spent fuel pool” (Dominion Energy Kewaunee, Inc., 2009).

Areal density results can be seen in Table 3-7 below (Dominion Energy Kewaunee, Inc., 2009). There is a fairly large amount of variability from one testing date to the next, particularly looking at the data between 1990 and 1995. In this date range, areal density results for all seven coupons appear to increase and then decrease together. This may indicate issues with the calibration associated with the testing procedure and may reduce confidence in the absolute values for B-10 areal density generated. Overall, the trend in areal density appears to be decreasing over time with data shown in Table 3-7,; however, the coupons continued to meet the acceptance criteria of 0.086 g/cm² B-10 areal density

Table 3-7 Areal density results from blackness testing of Tetrabor coupons at Kewaunee (Dominion Energy Kewaunee, Inc., 2009)

Date	#79-1	#79-2	#79-3	#81-1	#81-2	#88-1	#88-2	Source
3/82	0.114	0.107	0.107	0.101	0.095	*	*	AmBe 3.38
8/82	0.118	0.118	0.118	0.103	0.118	*	*	AmBe 3.2
3/83	0.117	0.117	0.112	0.128	0.134	*	*	AmBe
9/83	0.117	0.134	0.125	0.117	0.134	*	*	AmBe 3.4
6/84	0.136	0.126	0.126	0.130	0.131	*	*	AmBe 3.4
1/85	0.104	0.100	0.108	0.110	0.112	*	*	AmBe 3.4
8/85	0.100	0.109	0.131	0.138	0.125	*	*	AmBe 3.4
2/86	0.100	0.100	0.105	0.108	0.103	*	*	AmBe 3.4
9/86	0.110	0.980	0.110	0.092	0.110	*	*	AmBe 3.4
1/87	0.119	0.107	0.094	0.105	0.119	*	*	AmBe 3.4
1/87	0.097	0.100	0.095	0.094	0.090	*	*	PuBe
2/88	0.099	0.102	0.093	0.097	0.104	*	*	AmBe 3.4
10/88	0.096	0.103	0.095	0.095	0.095	0.102	0.093	AmBe 3.4
10/89	0.092	0.100	0.094	0.098	0.097	0.097	0.102	AmBe 3.4
7/90	0.098	0.088	0.089	0.094	0.088	0.094	0.098	AmBe 3.4
10/91	0.097	0.101	0.094	0.094	0.101	0.098	0.098	PuBe 4.6
9/92	0.115	0.124	0.123	0.116	0.123	0.117	0.121	PuBe 4.6
10/93	0.104	0.108	0.101	0.104	0.107	0.102	0.102	PuBe 4.6
10/94	0.111	0.104	0.101	0.104	0.106	0.108	0.113	PuBe 4.6
11/95	0.099	0.098	0.095	0.100	0.096	0.107	0.097	PuBe 4.15
7/99	0.100	0.106	0.104	0.103	0.106	0.102	0.102	PuBe 4.6
6/02	0.093	0.091	0.096	0.094	0.091	0.097	0.098	PuBe 3.4
2/05	0.106	0.107	0.106	0.108	0.108	0.103	0.105	PuBe 4.6
8/08	0.089	0.087	0.094	0.102	0.090	0.097	0.094	PuBe 4.59

* These test coupons were installed when additional racks were installed at a later date.

Tetrabor at Columbia

Columbia Generating Station installed Tetrabor neutron absorber material between 1979 and 1983 (Energy Northwest, 2010). Columbia’s installation of Tetrabor is very unique, because “the Spent Fuel Rack enclosures are vented above storage pool water surface through an arrangement of tubing and sampling valves at the pool curb” (Energy Northwest, 2010). This system prevents pressure buildup in the panel cavities, but also allows the Tetrabor to be sealed from the spent fuel pool water. Columbia reported finding “less than ¼ cup of water” when venting the line connected to the panel cavities, which may indicate leakage from the pool into the panel cavities (Energy Northwest, 2010).

Columbia has performed visual examination of coupons every four years since 1999 and has observed “no signs of degradation” (Energy Northwest, 2011). Columbia’s program includes coupons both sealed from the spent fuel pool water and vented to the pool water configurations to simulate a leak into the panel cavities (Energy Northwest, 2010). Isotopic abundance analyses performed in 1995 showed at least 20 atomic percent of isotope B-10 out of all boron atoms in all samples (Energy Northwest, 2011). Columbia committed in 2011 to perform coupon

visual examinations every four years, coupon neutron attenuation testing “at an interval not to exceed ten years,” and *in situ* testing at least every ten years (Energy Northwest, 2011).

Summary

Coupon testing has been performed at several plants that credit phenolic resin-based absorbers, including visual examinations, dimensional and weight loss measurements, and neutron attenuation testing as shown in Table 3-8. Coupon testing results have shown steady weight loss over time in Carborundum sheet coupons at Crystal River and Calvert Cliffs, including one sample with over 20% weight loss. Visual examinations at some plants have not shown visual degradation. Finally, neutron attenuation testing of Tetrabor coupons at Kewaunee have shown acceptable neutron attenuation over 25 years of testing, but also a high degree of variability.

Table 3-8 Summary of Coupon Testing Programs and Results

Plant	Material	Environment		Coupon Testing Methods	Results
		In-Service Material	Coupons		
Crystal River 3	Carborundum sheet	Vented to pool	Vented to pool	Visual exam and weight loss testing	Average coupon weight loss of 7% in 2004; one failed coupon showed 21% weight loss
Calvert Cliffs 1	Carborundum sheet	Vented to pool	Unknown	Visual exam; length, width, and weight measurements; and neutron attenuation testing	Accelerated coupon in 2005 showed 9.5% weight loss after about 25 years
La Crosse	Carborundum sheet	Vented to pool	Vented to pool	Visual exam and weight loss testing	Neutron attenuation testing in 1997 showed 7% reduction in B-10 areal density for one sample; Coupons in 2005 showed 12% weight loss
Kewaunee	Tetrabor	Vented to pool	Vented to pool	Visual exam, dimensional and thickness measurements, and blackness testing	Blackness testing areal density results show variability over time, and overall downward trend
Columbia	Tetrabor	Vented to air above pool	Both sealed and vented to pool	Visual exam and neutron attenuation testing	No visual signs of degradation; isotopic abundance analysis in 1995 normal

3.2.3 *In Situ* Testing Results

In situ neutron attenuation testing has been used to directly monitor B-10 areal density in pools both with and without coupons. The most common *in situ* testing method is the Boron-10 Areal Density Gauge for Evaluating Racks (BADGER) system, which was originally developed by NETCO for use in conjunction with the RACKLIFE computer code to monitor Boraflex degradation. However, BADGER operates by measuring neutron absorption and is therefore potentially applicable to any absorber material integral to spent fuel pool racks. BADGER places a Californium-252 source on one side of the panel and four BF₃ neutron detectors on the opposite side of the panel to measure neutron count rate and estimate B-10 areal density (Northeast Technology Corp., 2009). A technical letter report describing the uncertainties associated with the BADGER system, "Initial Assessment of Uncertainties Associated with the BADGER Methodology," can be found in ADAMS under accession number ML12254A064.

Carborundum Plate at Palisades in 2008

As discussed in Section 3.2.1, Palisades experienced fourteen instances of wrapper plate bulging from 1988 to 2007. During the license renewal process, Palisades presented several justifications to demonstrate adequate management of aging effects for Carborundum. Palisades stated that it had been monitoring total organic carbon (TOC) in the spent fuel pool since 2000 and found "very low, stable TOC values (typically less than 0.2 ppm)" (Nuclear Management Company, 2005). The licensee concluded from this monitoring "that the B₄C absorber [Carborundum plate] is not degrading" and that "periodic confirmatory sampling" would provide assurance that no degradation is occurring (Nuclear Management Company, 2005). In addition, the licensee stated that it is and would continue monitoring a coupon testing program of the same absorber material at another spent fuel pool to provide information about the performance of the material at their plant (Nuclear Management Company, 2005).

To confirm that the bulging was not due to degradation of the Carborundum plates and to gain NRC's approval for license renewal, the licensee committed to perform BADGER testing on selected cells in the Palisades spent fuel pool before the beginning of the period of extended of operation. The first BADGER campaign, conducted in July 2008, indicated that B-10 areal densities of several panels in the pool were below the minimum areal density assumed in the criticality analysis (Northeast Technology Corp., 2009). A follow-on BADGER campaign was conducted in March 2009 to more rigorously measure the panel areal densities (Northeast Technology Corp., 2009). The nominal and minimum B-10 areal densities of the sixty panels tested can be seen plotted as a function of gamma radiation dose in Figures 3-3 and 3-4. Minimum B-10 areal density values are calculated conservatively with respect to count rate uncertainty by assuming the minimum count rate from the calibration panel and the maximum count rate from the observed panel. For this BADGER campaign, test panels were compared to a 0.0705 g/cm² maximum calibration standard panel. Therefore, any data points with a count rate less than that for the highest calibration standard (indicating a higher B-10 areal density) were simply recorded as 0.0705 g/cm² to avoid extrapolation.

can therefore be proportionally correlated to gamma dose. However, the same trend is not observed for Carborundum plate at Palisades. While only one data set, the Palisades results suggest that gamma dose alone is not a clear indicator of reduction in B-10 areal density. This lack of correlation is further discussed in Chapter 5.

As described previously, Palisades used TOC sampling and monitoring of a coupon testing program at another plant to manage this degradation. However, significant degradation of the Carborundum plate was detected by *in situ* neutron attenuation testing without any indication from TOC or the coupons at another plant, indicating the failure of these techniques in this instance.

Carborundum Plate at Millstone 1 in 2007 and 2011

Millstone 1 is known to have performed two BADGER campaigns, one in 2007 and another in 2011 (NRC, 2010; NRC, 2011). Unlike the 2008 Palisades BADGER campaign, detailed reports from these campaigns at Millstone 1 were not available for this report. An NRC inspection report mentions that the 2007 BADGER campaign at Millstone 1 found a reduction in B-10 areal density (NRC, 2010). A second BADGER testing campaign is mentioned in an NRC inspection report as having taken place in June 2011 at Millstone 1, but no results are available (NRC, 2011).

Summary

BADGER testing campaigns have only been performed at two plants with phenolic resin-based absorbers, both of which were Carborundum plate material. The BADGER testing campaign of Carborundum plate at Palisades found significant reductions in B-10 areal density below the minimum credited amount. Based on the information available, it is not clear whether this degradation is unique to Carborundum plate material or more generally applicable to Carborundum sheet and Tetrabor materials, which also use phenolic resin binder material. It is important to note that the significant degradation of the Carborundum plate at Palisades occurred without any indication from TOC or the coupons at another plant, indicating the failure of these techniques in this instance.

4. Radiation Chemistry of Phenol Formaldehyde Resins

In order to better explain the qualification testing data and operating experience, it is important to understand the degradation mechanisms of phenol formaldehyde resin in the spent fuel pool environment. This section will describe the degradation process of phenolic resin-based neutron absorbers employed in spent fuel pools using well-established radiation chemistry theory. This discussion focuses on the effects of radiation, water, and oxygen on phenolic resin polymers, and also considers other variables such as temperature, pool chemistry, and local flow.

4.1 Degradation of Polymers in the Spent Fuel Pool Environment

There are several important processes that affect the degradation of polymers in the spent fuel pool environment. First, ionizing radiation has a direct effect on the polymeric material by breaking bonds and inducing scission and cross-linking. Second, radiolysis of water produces hydroxyl radicals and hydrogen peroxide, which can attack polymer bonds. Finally, the presence of dissolved oxygen allows for oxidation of free radicals that can enhance degradation (Wilson, 1974).

4.1.1 Direct Radiation Effects: Scission and Cross-linking

Ionizing irradiation induces the formation of anions, cations, and free radicals in polymers on a time scale of about 10^{-12} to 10^{-6} s. The early events in the interaction of ionizing radiation with polymers are the production of ionized and excited polymer molecules. These ions and excited polymers undergo various reactions to produce free radicals, additional ions, and hydrogen atoms. The most probable mechanisms of radical and cation formation in the radiolysis of polymers, for which there are varying degrees of evidence, include the following in Equations 1-10:



Where:

RH = polymeric material RH^* = excited molecule

R^\bullet = free radical

RH^+, RH_2^+ = cations

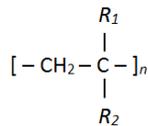
In general, upon the irradiation of polymers, the following processes will take place:

1. Cross-linking: the formation of covalent bonds between the polymer chains
2. Scission: bond-breaking in the backbone of the polymer molecule
3. Changes in the concentration and the nature of double bonds
4. Oxidative and degradation reactions (in the presence of oxygen)
5. Evolution of gases such as hydrogen (H_2) and methane (CH_4)

The predominance of these processes depends on the chemical structure of the polymers, the irradiation dose, dose rate, the linear energy transfer (LET) of the irradiation, the presence of oxygen, and the presence of antioxidants.

Whether a particular polymer undergoes scission or cross-linking upon irradiation depends entirely on its backbone's chemical structure. The presence of quaternary carbon atoms (bonded to four other carbon atoms) in the backbone of the polymer enhances radiation-induced scission, while the presence of secondary and tertiary carbon atoms (bonded to two or three other carbon atoms) in the backbone enhances cross-linking reactions as seen in Table 4-1 below (Woods and Pikaev, 1993). Bonds broken by radiation-induced scission can be repaired by recombination, and the backbone's chemical structure affects the recombination process to repair scission damage.

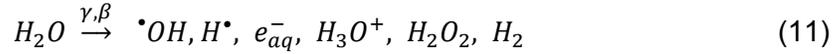
Table 4-1 Radiation Induced Changes to Common Polymers (Woods and Pikaev, 1993)



Polymer	R_1	R_2	Radiation-Induced Change
Polyethylene	H	H	Cross-linking
Polypropylene	CH_3	H	Cross-linking
Poly(vinyl chloride)	Cl	H	Cross-linking
Polyacrylonitrile	CN	H	Cross-linking
Polyacrylates	CO_2R	H	Cross-linking
Polystyrene	C_6H_5	H	Cross-linking
Poly(vinylidene chloride)	Cl	Cl	Scission/Degradation
Polyisobutylene	CH_3	CH_3	Scission/Degradation
Polymethylstyrene	C_6H_5	CH_3	Scission/Degradation
Poly(methyl methacrylate)	CO_2CH_3	CH_3	Scission/Degradation
Polytetrafluoroethylene	Varies	Varies	Scission/Degradation
Natural rubber	Varies	Varies	Cross-linking
Cellulose and derivatives	Varies	Varies	Scission/Degradation

4.1.2 Radiolysis of Water

Radiolysis is the disassociation of water molecules in the spent fuel pool water by interaction with beta and gamma radiation from the spent fuel to break chemical bonds. Radiolysis produces radicals, aqueous electrons, and stable compounds that can be seen in Equation 11 below:



Radiolysis of water by gamma radiation has the following radiation-chemical yields in micro moles produced per joule of deposited energy (Spinks and Woods, 1990):

$$G(\cdot OH) = G(e_{aq}^-) = G(H_3O^+) = 0.28$$

$$G(H\cdot) = 0.062$$

$$G(H_2) = 0.042$$

$$G(H_2O_2) = 0.082$$

Water radiolysis changes the chemical environment in which the neutron absorbers are located. Hydroxyl radicals ($\cdot OH$) are very powerful oxidizers that react with aromatic compounds via addition to the phenyl rings to produce various isomeric adduct radicals ($\cdot Ar(OH)$), which begins the degradation of the polymer structure. Meanwhile, aqueous electron (e_{aq}^-), are very strong reducing agents, which react with the phenyl structure as well as ether, ketone, and carboxylic groups. However, in the presence of oxygen, aqueous electrons may be scavenged very rapidly by the soluble oxygen in water, producing superoxide radicals with reaction rate constant of $2 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ as seen in Equation 12:



Therefore, effectively all aqueous electrons will be scavenged by the dissolved molecular oxygen.

Hydrogen atoms are also scavenged by the dissolved oxygen, producing perhydroxyl radicals (HO_2^{\bullet}) at a diffusion-controlled reaction rate of $1-2 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ in Equation 13:



HO_2^{\bullet} has a pKa value of 4.7 that governs the following reaction seen in Equation 14:



Therefore, at pHs less than 4.7, there will be more HO_2^{\bullet} than $O_2^{\bullet -}$ present. HO_2^{\bullet} is more reactive than $O_2^{\bullet -}$. HO_2^{\bullet} will abstract hydrogen from the polymer structure to form corrosive hydrogen peroxide (H_2O_2) as follows in Equation 15:

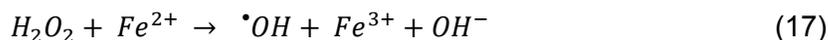


At pHs greater than 4.7, most of the HO_2^* will be converted to $O_2^{\bullet-}$, which is less reactive than HO_2^* and reacts bimolecularly to also produce the corrosive H_2O_2 in Equation 16:



H_2O_2 is one of the main corrosive radiolytic products of nuclear reactor operation as well as spent fuel aqueous storage. Both HO_2^* and $O_2^{\bullet-}$ will produce hydrogen peroxide, but at pHs less than 4.7, degradation will be increased due to HO_2^* abstracting hydrogen from the polymer structure.

In the presence of impurities such as Fe^{2+} , H_2O_2 will decompose to produce more hydroxyl radicals through Fenton's reaction seen in Equation 17, which will serve to further enhance the polymer degradation:



4.1.3 Effect of Oxygen Presence

The presence of oxygen plays a major role in the degradation of polymers through peroxidation seen in Equation 18. The vast majority of the free radicals created by radiation, particularly the carbon-centered free radicals, react with oxygen to produce the corresponding peroxy radicals (HRO_2^*). Oxygen greatly impedes cross-linking reactions seen in Equation 19 by reacting very quickly with the carbon-centered radicals before they can cross-link with one another.



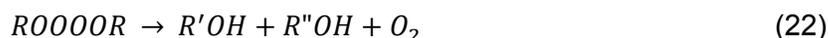
As oxygen concentration increases, the peroxidation reaction dominates over cross-linking reactions. Peroxidation of free radical leads over time to degradation of the polymer molecules. HRO_2^* can also initiate a chain reaction seen in Equation 20 by abstracting a hydrogen atom from the neighboring molecules producing another free radical and organic peroxide:



Another important reaction of the peroxy radicals seen in Equation 21 is the formation of an intermediate molecule called tetraoxide:



The tetraoxide will then decompose to aldehyde and alcohol as seen in Equation 22:



These products will undergo further decomposition and degradation reactions.

In the open spent fuel pool, the oxygen concentration is expected to remain relatively constant with a level of $\sim 2.2 \times 10^{-3} \text{ mol L}^{-1}$ due to the atmosphere above serving as an oxygen source. However, the panel cavity may not be as oxygen-rich as the pool itself depending on the amount of exchange between the panel cavity and pool water.

4.2 Radiation Chemistry of Phenol Formaldehyde Resins

As described previously in Chapter 2, a detailed description of the phenolic polymer materials used in Carborundum and Tetrabor is not available, so a generic phenol formaldehyde resin is assumed for this discussion. The chemical structure of phenol formaldehyde resin is shown in Section 2.2.1 and includes primarily phenol, ether, and methyl groups.

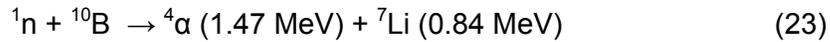
4.2.1 Degradation Process in the Absence of Water or Oxygen

This section discusses the degradation process in the absence of water or oxygen. This environment is expected to be present in the bulk interior of the neutron absorber material whether in a vented or sealed configuration as well as at the surface of the neutron absorber material if sealed from the spent fuel pool water. The direct effects of the ionizing radiation of the spent fuel pool on phenol formaldehyde resins are a result of beta particles, gamma rays, and alpha particles.

Radiation-Induced Degradation

Given the light elements present in the phenol formaldehyde resin, beta particles (fast electrons) and gamma rays (high-energy photons) from the spent fuel are not expected to interact significantly with atomic nuclei. However, gamma and beta will interact with the electrons of the elements in phenol formaldehyde and impact the chemical bonds that are present. It is well known that the presence of the aromatic group (in this case, phenol) in the polymer structure greatly enhances its resistance to ionizing radiation. The pi (π) structure in the aromatic group is very effective at dissipating the energy of the ionizing radiation. It is also known that the OH groups of the phenol structures act as excellent hydrogen donors (antioxidants) to the radiolytically-produced free radicals, thereby converting them to stable molecules by the hydrogen transfer mechanism. However, despite containing the resilient pi structure and antioxidant OH groups, phenol formaldehyde resins also contain ether bonds, which are very susceptible to ionizing radiation, in their backbone. As a result, it is expected that the ether bonds connecting phenyl groups (phenyl-C-O-C-phenyl) undergo a scission reaction in the presence of ionizing radiation such as beta particles and gamma rays from spent fuel.

In addition to beta particles and gamma rays from the spent fuel, alpha particles produced from neutron absorption by B-10 may also contribute to degradation of phenol formaldehyde resins. Alpha particles from the spent fuel are absorbed before reaching the neutron absorber material, and neutrons from the spent fuel have insignificant direct effects on the phenolic resin due to the low molecular weight and small neutron cross section of the atoms composing the phenolic resin. However, when neutrons from the spent fuel are absorbed by B-10 within the absorber material, alpha particles are produced by the following nuclear reaction seen in Equation 23:



Alpha particles lose their energy rapidly when passing through liquid or solid materials and have a very limited penetration (or range) in such condensed systems. However, in this case, the alpha particle is produced within a boron carbide particle embedded within the neutron absorber material. Similar to beta particles and gamma rays, the interactions of alpha particles with matter primarily cause ionization. Alpha particle irradiation is considered high linear energy transfer (LET), since alpha particles lose their energy very rapidly when passing through a material.

Beta particles, gamma rays, and alpha particles are all expected to have similar radiation chemistry effects on the phenol formaldehyde resin. Scission through the ether bonds is most likely and can be seen in Figure 4-1 below. Scission through the ether bonds breaks the polymer backbone, shortens, and leads to the formation of phenoxy and carbon-centered free radicals. Breaking the polymer backbone shortens the polymer chain length and degrades the polymer as chain length decreases with successive breaks in the backbone.

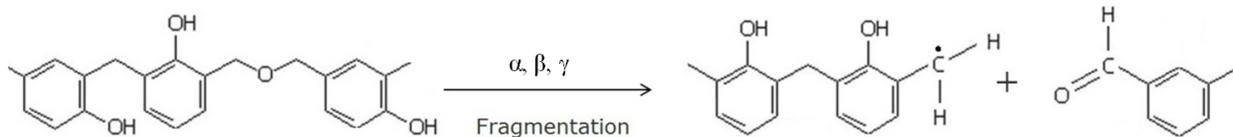


Figure 4-1 Scission of ether bond in phenol formaldehyde resin by ionizing radiation

Another reaction that may occur is hydrogen abstraction as seen in Figure 4-2 below. In this reaction, the radiation excites the polymer structure, leading to abstraction of the hydrogen atom from the methyl group. However, due to the chemical structure of the phenol formaldehyde resin, the probability of hydrogen abstraction is much lower than scission the ether bond.

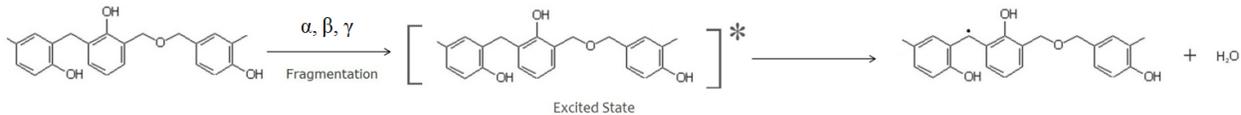


Figure 4-2 Hydrogen abstraction in phenol formaldehyde resin by ionizing radiation

This section focused on the direct effects of radiation of phenol formaldehyde resin, but the degradation process may be affected by the presence of water or oxygen. It is known that several plants have vented their neutron absorbers to the pool, which would place them in contact with water and likely oxygen. The role of water and oxygen in the degradation process of phenol formaldehyde resin will be discussed in the following sections.

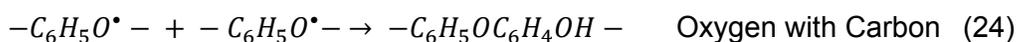
4.2.2 Degradation Process in the Presence of Water

Although phenol formaldehyde resins are insoluble in water, they are in contact with water at their surfaces if submerged. Therefore, it is expected that the radiolytically-produced species from water discussed in Section 4.1 would interact with the phenol formaldehyde resins at these interfaces. The most important radiolytically-produced species is the strongly oxidizing hydroxyl radical ($\cdot\text{OH}$), which reacts rapidly with phenol formaldehyde resins through addition to the phenol group and abstraction of hydrogen (Neta and Steenkin, 2003).

Addition to the Phenol Group

As mentioned earlier, hydroxyl radicals react with the phenyl group at a very high reaction rate constant with a value of $1 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$. The hydroxyl radical reacts by addition to yield dihydroxycyclohexadienyl radicals as shown in Figure 4-3 below, which then may undergo a spontaneous, acid-catalyzed, or base-catalyzed dehydration to yield phenoxyl radicals.

Phenoxyl radicals do not react with oxygen since they are oxidizing radicals and are primarily short-lived intermediates. Phenoxyl radicals undergo a dimerization reaction with a second-order decay of the order of $1 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ producing various dimers. Since the electron (unpaired spin) is delocalized on the oxygen and on the *ortho*-carbon and *para*-carbon, various dimers can be produced through the following cross-linking reactions seen in Equations 24 and 25:

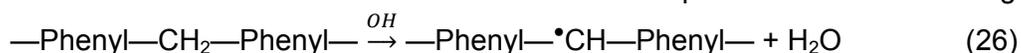


The carbon with carbon cross-linking reaction will be predominant because of the absence of a delocalized electron.

Hydrogen Abstraction

In addition to reacting with the phenol group, hydroxyl radicals will abstract hydrogen to produce carbon-centered radicals as shown in Figure 4-3 below. The abstraction of hydrogen takes place from two sites: methylene and ether.

1. At the methylene site, a hydrogen atom reacts with the hydroxyl radical to form water and a carbon-centered radical as shown below in Equation 26 and seen in Figure 4-3:

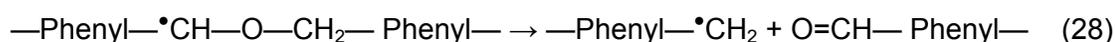


In the absence or low concentration of oxygen, the carbon-centered free radical will undergo a cross-linking reaction. However, in the presence of oxygen, it is not expected that the cross-linking reaction would take place.

2. At the ether site, a hydrogen atom reacts with the hydroxyl radical to form water and a carbon-centered radical as shown below in Equation 27 and seen in Figure 4-3:



Because of the delocalization of the unpaired spin on the carbon, oxygen, and phenyl group, it is expected that the ($-\text{Phenyl}-\dot{\text{C}}\text{H}-\text{O}-\text{CH}_2-\text{Phenyl}-$) free radical is relatively stable and its cross-linking reaction rate is slow. However, it is also expected to undergo scission as seen in Equation 28, because this bond is weak and susceptible to breaking.



In the absence or low concentration of oxygen, $-\text{Phenyl}-\dot{\text{C}}\text{H}_2$ is expected to undergo cross-linking reactions. However, the presence of the neighboring phenyl will enhance the delocalization of the unpaired spin and make this free radical less reactive with a slow cross-

linking reaction rate. The presence of water alone will enhance degradation on the surface of the polymer as compared to a dry state.

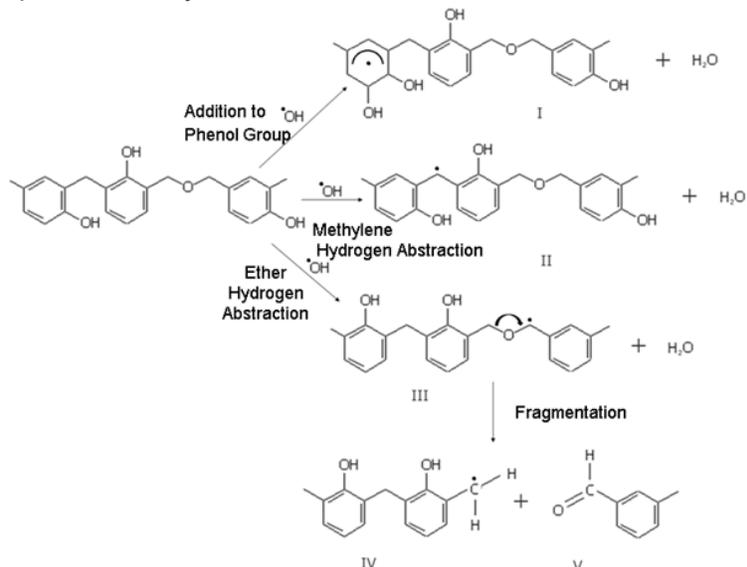
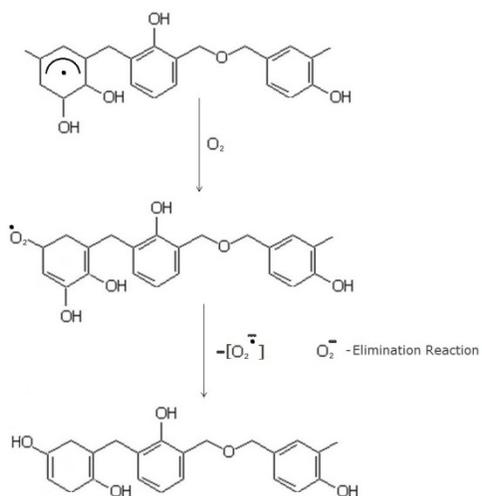


Figure 4-3 Reactions of hydroxyl radicals with phenol formaldehyde resins

4.2.3 Degradation Process In the Presence of Oxygen

In general, phenol formaldehyde resins produce carbon-centered free radicals by reaction with hydroxyl radicals as discussed in the previous section. In the presence of oxygen, these free radicals react with molecular oxygen to produce the corresponding peroxy radicals. However, the reactivities of the free radicals toward oxygen depend strongly on their chemical structure and the presence of the delocalization of the unpaired spin. The delocalization of the unpaired spin decreases the reductive tendency of the carbon-centered radical and hence makes it less reactive with oxygen. As Figure 4-3 shows, the interactions of phenol formaldehyde with hydroxyl radicals produce primarily free radicals with delocalization of the unpaired spin.

The subsequent reactions that the phenol formaldehyde peroxy radicals can undergo are superoxide elimination, bi-molecular reaction, and hydrogen abstraction. These reactions with oxygen increase the degradation rate by providing more opportunities for degrading reactions to occur. After an addition to the phenol group reaction with a hydroxyl radical, molecular oxygen can react with the phenol group followed by a superoxide ($\text{O}_2^{\cdot-}$)- elimination reaction leading to the formation of the cyclohexene structure as shown in Figure 4-4 below. After a methylene hydrogen abstraction reaction with a hydroxyl radical, a bi-molecular reaction with the production of a tetraoxide intermediate can occur as shown in Figure 4-5. The tetraoxide intermediate undergoes a decomposition reaction with the formation of alcohol and ketone structures, based on Russell's and Bennett's type mechanisms as seen in Figure 4-5. Oxygen can also lead to a chain reaction of methylene hydrogen abstractions as shown in Figure 4-6. After a methylene hydrogen abstraction reaction with a hydroxyl radical, oxygen reacts at the methylene to form a peroxy radical. This leads to a hydrogen abstraction reaction from the neighboring phenol formaldehyde molecules by the phenol formaldehyde peroxy, which produces carbon-centered free radicals as seen in Figure 4-6.



VI

Figure 4-4 Reactions of phenol formaldehyde resin free radicals producing peroxyl radicals followed by superoxide elimination

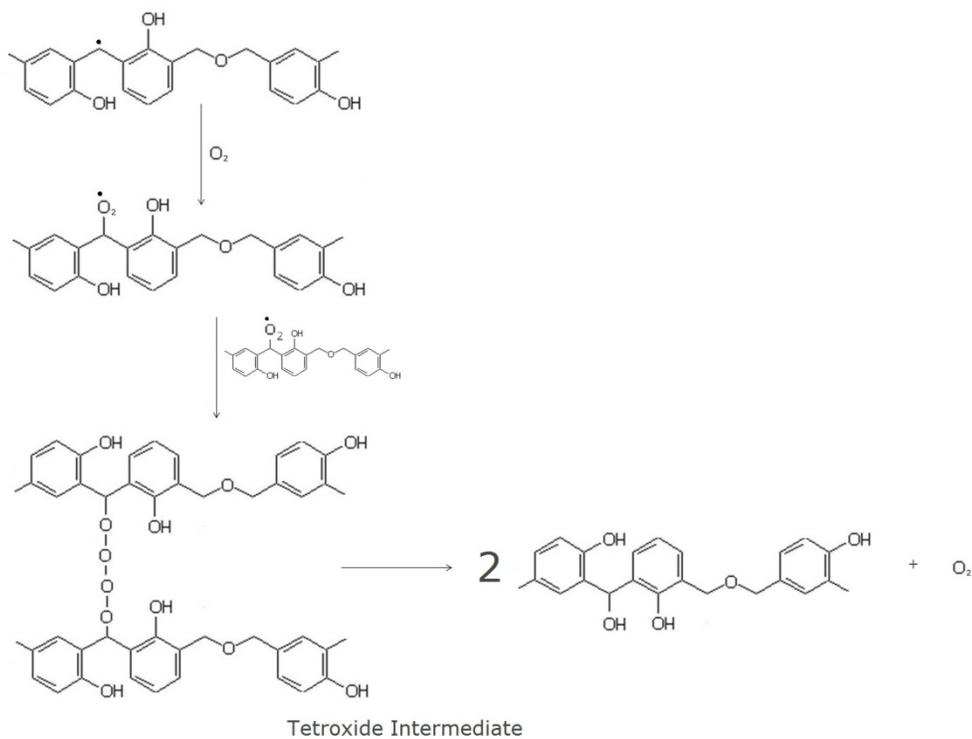


Figure 4-5 Reactions of phenol formaldehyde resin free radicals producing peroxyl radicals followed by the tetraoxide intermediate formation and decomposition

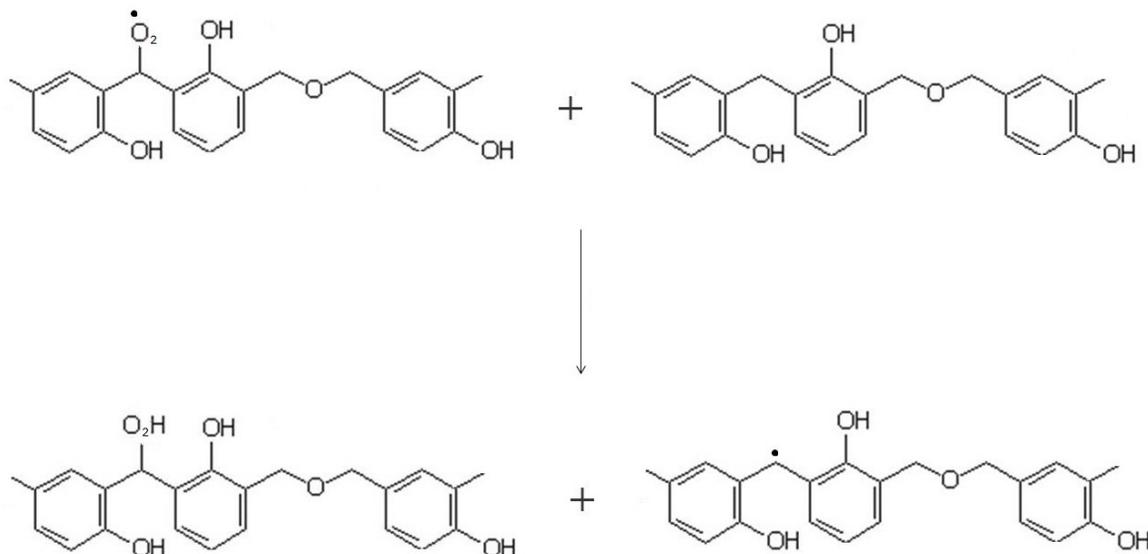


Figure 4-6 Methylene hydrogen abstraction by peroxy radical

It is important to note the very rapid rate of reactions involving oxygen. The reaction rate constants of carbon-centered free radicals with the dissolved oxygen are estimated to be 10^7 - $10^8 \text{ M}^{-1}\text{s}^{-1}$. These reactions are very fast, but still slower than the reaction of alkyl carbon-centered free radicals with oxygen, which have reaction rate constants around $10^9 \text{ M}^{-1}\text{s}^{-1}$. Meanwhile, oxygen reacts most quickly with aqueous electrons at a rate constant of $2 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$. This indicates that most of the oxygen will be consumed by scavenging electrons, but the other degradation reactions involving oxygen are also very rapid.

4.2.4 Degradation Products of the Phenol Formaldehyde Resin

The degradation products described in Sections 4.2.1, 4.2.2, and 4.2.3 are further broken down by radiation as well as chemical processes. Various other intermediate products and free radicals are produced at intermediate steps, but are not soluble or expected to be removed from the material prior to further decomposition. Ultimate degradation products from this process will include water-soluble low molecular weight compounds such as phenols, aldehydes, and muconic acids and partially water-soluble gases such as hydrogen (H_2), carbon dioxide (CO_2), methane (CH_4), and carbon monoxide (CO). Depending on the type of ionizing radiation and polymer additives, the total radiation chemical yields (G-values) of the gases may range from 0.1 to 1.0 molecules/100eV (Milinchuk, Tupikov, and Kemp, 1989).

4.2.5 Radiation Dose Tolerance of Phenol Formaldehyde Resins

While radiation chemistry theory can describe conceptually and qualitatively the degradation of phenol formaldehyde resins by radiation, water, and oxygen, experimental data is needed to quantitatively measure degradation as a function of dose. Figure 4-7 shows that phenol formaldehyde resin loses 50% of its ductility after irradiation in air to $10^6 - 5 \times 10^7 \text{ Gy}$ ($10^8 - 5 \times 10^9 \text{ rad}$) depending on dose rate. Likewise, Figure 4-8 shows that irradiation in air of phenol formaldehyde resins to a dose level of $3 \times 10^7 \text{ Gy}$ ($3 \times 10^9 \text{ rad}$) leads to 50% loss of flexural

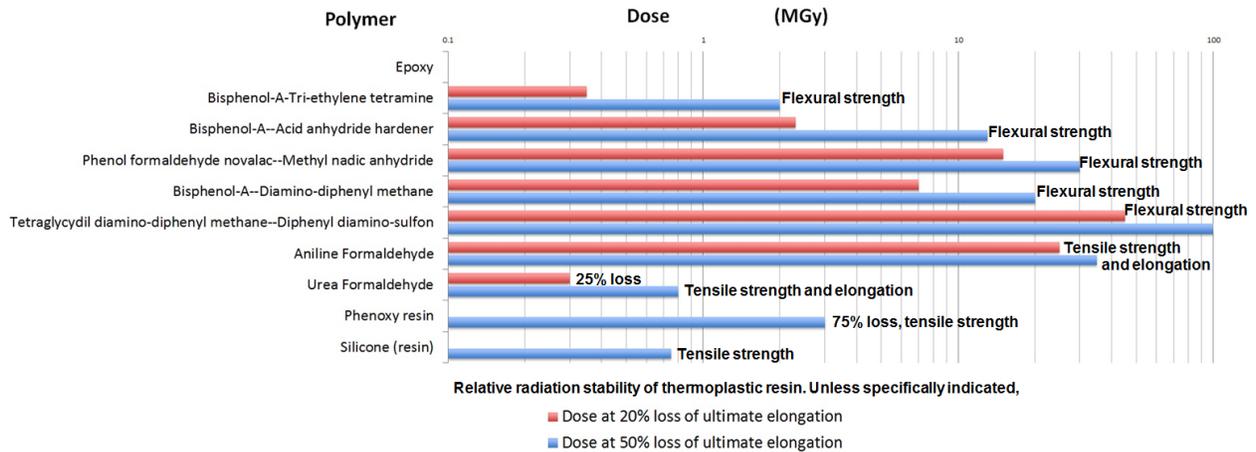


Figure 4-8 Degradation of mechanical properties of polymers as a function of absorbed dose (Tabata, Ito, and Tagawa, 1991, reprinted by permission of CRC Press © 2013)

Based on the Palisades BADGER testing report, licensees have exposed phenolic resin-based neutron absorbers to dose levels of higher than 10^8 Gy (10^{10} rad), which is significantly higher than the doses shown in Figures 4-7 and 4-8. It should also be noted that the results shown in Figures 4-7 and 4-8 were performed in air and therefore reflect only the effects of radiation and oxygen. It is expected that degradation will be enhanced with the additional stressor of water.

4.3 Effect of Variables in the Surrounding Environment

It is important to understand the effects of different environmental variables on the degradation process of phenol formaldehyde resins in the spent fuel pool environment. This may allow for better understanding of what conditions are bounding or conservative relative to others, which may be essential when assessing the adequacy of surveillance methodologies. Several key variables considered in the sections below include water temperature, filler material, the presence of oxygen, pool chemistry, the exchange rate between the panel cavity and the pool, and flow rate within panel cavity.

4.3.1 Water Temperature

Pool water temperature is expected to affect the oxidation rate, the decomposition rate of hydrogen peroxide, and the oxygen content of the water; all of which affect the degradation process of the phenolic resin.

In general, higher temperatures enhance and increase the reaction rate of oxidation-induced degradation. At high temperatures, peroxidation of the carbon-centered free radicals will be enhanced leading to the formation of more peroxy radicals. Furthermore, the increased decomposition of the phenolic aldehyde tetraoxide (ROOOOR) leads to more degraded products. The abstraction of hydrogen atoms from the phenol formaldehyde resin by the peroxy radicals will also be enhanced, which will lead to the formation of more carbon-centered radicals and hydroperoxide as seen in Figure 4-6 and the following reaction: $RO_2^{\bullet} + RH \rightarrow R^{\bullet} + RO_2H$.

This reaction initiates a chain reaction that creates more free radicals and hydroperoxide (RO₂H) and faster degradation.

As described previously, gamma radiolysis of water produces hydrogen peroxide (H₂O₂) with a radiation chemical yield (G-value) of 0.75-0.8 molecules per 100 eV (0.8 μmole per joule). At high temperatures, hydrogen peroxide decomposes to form more hydroxyl radicals (•OH). An increased hydroxyl radical concentration enhances the degradation of the phenol formaldehyde resin because hydroxyl radicals are a very oxidizing species. The decomposition of one molecule of H₂O₂ leads to the formation of 2 •OH radicals: H₂O₂ → 2 •OH.

The solubility of oxygen in water at room temperature and at atmospheric pressure is about 0.23 x 10⁻³ M. This solubility of oxygen decreases dramatically as the temperature of the system increases. For example, at atmospheric pressure, the concentration of oxygen in water decreases from 8.8 mg per liter at room temperature to 5.6 mg per liter at 50°C. The soluble oxygen molecule in aqueous solutions is consumed with about 0.75 kGy (75 kRad) of absorbed dose radiation dose. The consumption of soluble oxygen in water is a result of the reaction of the aqueous electron (e_{aq}⁻) with molecular dissolved oxygen in water: e_{aq}⁻ + O₂ → O₂^{•-}. Since the spent fuel pools are open to air, it is expected that the system reaches equilibrium with the atmosphere. Therefore, increasing temperature will decrease the amount of dissolved oxygen in the water, but there should still be sufficient oxygen in the pool water to initiate the oxidative degradation based on reaching equilibrium with the air above the pool.

4.3.2 Filler Materials: Fiberglass, Graphite, and Boron Carbide Particles

As described in Chapter 2, Carborundum sheet material is described as containing fiberglass reinforcement, while Tetrabor is described as possibly containing graphite. In addition, all of the phenolic resin-based neutron absorbers contain boron carbide particles. Fiberglass and graphite are not expected to affect the radiation chemistry of phenol formaldehyde resin due to their nuclear and chemical stability in the presence of ionizing radiation. As discussed earlier, the presence of boron carbide produces alpha particles which degrade the phenol formaldehyde resin, but other components of the neutron absorber panel are generally stable.

Another key distinction between Carborundum sheet compared to Carborundum plate and Tetrabor is that Carborundum sheet is much thinner. This difference is not expected to alter the fundamentals of the degradation process beyond the effect on the surface area to volume ratio. Dissolution occurs at the surface of the material where it interfaces with water, so the thinner Carborundum sheet would be expected to be more susceptible due to its greater surface area to volume ratio.

4.3.3 The Presence of Oxygen

As discussed earlier in the report, oxygen has a crucial and effective role in the degradation of phenol formaldehyde resin. The amount of oxygen present in the panel cavity may be dependent on the amount of exchange between the panel cavity and pool, because fresh oxygenated water from the pool is expected to be the source of oxygen as it is consumed in the degradation process. Given sufficient exchange between the panel cavity and pool, molecular

oxygen should be present in both the panel cavity water and in the bulk phenol formaldehyde resin. Therefore, the peroxidation of the phenol formaldehyde carbon-centered radicals should occur in both the bulk and the surface of the resin, leading to continuous degradation of the resin in the bulk and at the surface. However, more degradation is expected to occur on the surface due to greater availability of hydroxyl radicals and oxygen on the surface than in the bulk.

4.3.4 Pool chemistry: pH, Soluble Boron, and Metal Ions

Panel cavity chemistry around the phenolic resin-based neutron absorber materials can have a significant impact on the degradation process. However, the exact chemical conditions in the panel cavity are not well-known. The pH of panel cavity water may be influenced by radiolysis of water from spent fuel radiation as well as exchange between the panel cavity and pool and the presence of soluble boron. The pH decreases during radiolysis of water by producing hydronium (H_3O^+) with a radiation chemical yield of $G(\text{H}_3\text{O}^+) = 0.29 \mu\text{mol J}^{-1}$. Without significant pool water exchange to reduce hydronium concentrations, they cause pH to decrease. In addition, the presence of boric acid (soluble boron) in PWR pools also reduces pH. In general, more acidic conditions would be expected to enhance the degradation, because of the role of perhydroxyl radicals as discussed in Section 4.1.2.

Radiolysis also produces hydrogen peroxide (H_2O_2), which is a very powerful oxidizer that can degrade the phenol formaldehyde resins. While hydrogen peroxide is produced through the radiolysis of water, it also decomposes to hydroxyl radicals and reacts with metals and organic materials in the pool such as phenol formaldehyde resin. Additionally, dissolved metal ions such as ferrous ions (Fe^{2+}) may react with hydrogen peroxide to form more hydroxyl radicals by Fenton's reaction. This reaction enhances the hydroxyl radical concentration, which leads to greater degradation of the phenol formaldehyde resin.

4.3.5 Water Exchange between Panel Cavity and Pool

It is expected that the amount of water exchange between the panel and pool affects the degradation rate of the polymer matrix. However, the actual amount of water exchange between the panel cavity and the pool is not well-known and will vary from pool to pool depending on rack design. Therefore, the following subsections describe the potential scenarios of significant water exchange and no or insignificant water exchange.

Water-Filled Panel Cavity with Pool Water Exchange

In the case of a panel cavity with significant pool water exchange, fresh water from the bulk pool entering the panel cavity would have high oxygen concentrations. This replenishment of oxygen in the panel cavity can enhance the peroxidation of the radiolytically-produced carbon-centered free radicals on the surface of the phenol formaldehyde resin and therefore increase the degradation rate of the phenol formaldehyde resin. Conversely, a continuous exchange of water may also reduce the buildup of hydrogen peroxide (H_2O_2) concentrations in the panel cavities since they can be regarded as open systems. This decrease in the concentration of the corrosive radiolytically-produced hydrogen peroxide would consequently decrease the degradation rate of the phenol formaldehyde resin.

Water-Filled Panel Cavity without Pool Water Exchange

In the case of no or insignificant pool water exchange, the panel cavity may be treated as an essentially closed system. This situation may exist in the case of very small or clogged vent holes that allowed water to enter the cavity, but allow little or no pool water exchange. Assuming an essentially closed system filled with stagnant water in a radiation field, three key effects are expected: hydrogen peroxide will build up, pH will decrease, and oxygen will be consumed.

As described previously, hydrogen peroxide (H_2O_2) is a very corrosive and oxidative radiolytic product of the radiolysis of water, which is produced inside the panels by gamma irradiation. Due to the continued production of hydrogen peroxide and lack of exchange with the pool water, hydrogen peroxide concentration will increase as a function of dose. Hydrogen peroxide concentration can be estimated based on the radiation chemical yield ($G = 0.75$ mole per 100 eV) and the absorbed dose in Gy as seen in Equation 29:

$$G(H_2O_2) = 9.648 \times 10^6 \left(\frac{\text{Chemical yield (mol.liter}^{-1}\text{)}}{\text{Absorbed Dose (Gy)} \times \rho} \right) \quad (29)$$

Assuming the water pool receives a gamma dose of 10^8 Gy and the density of the H_2O_2 is 1.45 g/cm³, the concentration of the produced H_2O_2 is 113 moles per liter, which is extremely high. Usually, while hydrogen peroxide is being produced through the radiolysis of water, it also decomposes to hydroxyl radicals and reacts with metals and organic materials in the pool such as phenol formaldehyde resin. Its corrosive and oxidative nature will effectively degrade the phenol formaldehyde resins by the following mechanism involving hydroxyl radicals and hydrogen peroxide as illustrated in Figure 4-9.⁷

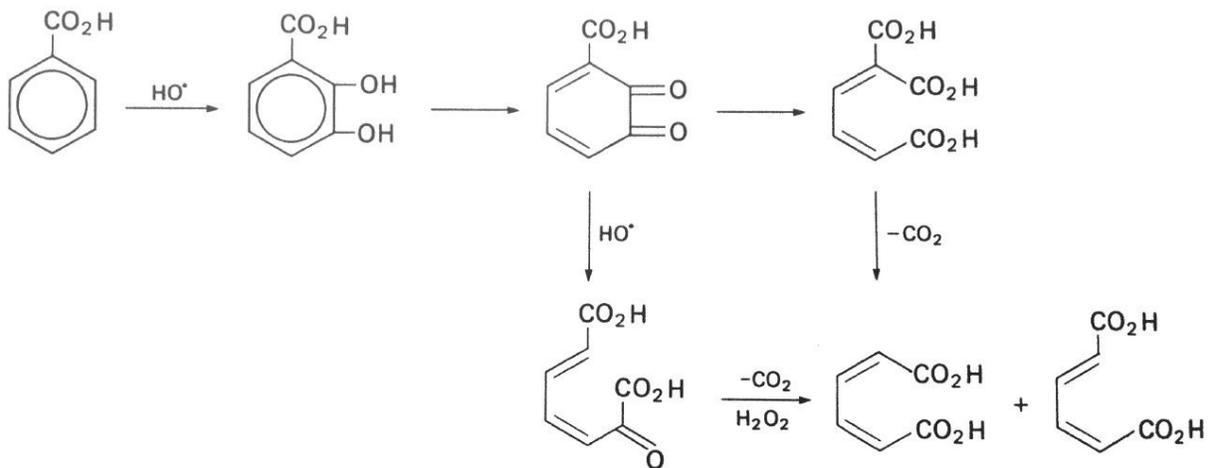


Figure 4-9 Reaction of hydroxyl radical and hydrogen peroxide with phenyl (Patai, 1983)

This mechanism involves the addition of a hydroxyl radical to the pi (π) structure of the phenyl ring followed by opening of the ring. The phenols are further oxidized by hydroxyl radicals and hydrogen peroxide, leading to decarboxylation and the formation of muconic acids. These muconic acids are prone to further oxidation by hydroxyl radicals and hydrogen peroxide. The cumulative effect of these types of oxidation/degradation reactions inside the panels is dissolution of the resin.

Continuous irradiation without pool water exchange also increases the hydronium (H_3O^+) concentration according to: $\text{H}_2\text{O} \xrightarrow{\gamma} \cdot\text{OH}, \text{H}^*, \text{e}_{\text{aq}}^-, \text{H}_3\text{O}^+, \text{H}_2\text{O}_2, \text{H}_2$. The continuous increase in hydronium concentration leads to a continuous decrease in the pH. It is known that phenol formaldehyde resin has a reasonable resistance to acidity (Schnabel, 1992). However; it is expected that the combination of radiation and low acidity can cause increased degradation.

Continuous irradiation without pool water exchange leads to dissolved oxygen consumption due to reaction with aqueous electrons and hydrogen atoms produced by radiolysis of water. Assuming an initially air-saturated solution, complete scavenging of the aqueous electrons and hydrogen atoms by oxygen ($\text{O}_2 = 0.24 \text{ millimol L}^{-1}$) occurs. For a closed system, the O_2 consumption yield $G(-\text{O}_2)$ is $0.32 \mu\text{mol J}^{-1}$. The dose required to consume all dissolved oxygen can be estimated by Equation 30:

$$\text{Dose} \left(\frac{\text{J}}{\text{kg}} = \text{Gy} \right) = \frac{0.24 \times 10^{-3} \text{ mol/L}}{(1 \text{ kg/L}) \times (3.2 \times 10^{-7} \text{ mol/J})} = 7.5 \times 10^2 \text{ Gy} \quad (30)$$

Therefore, all oxygen will be consumed in the submerged panels at a very low dose of only 0.75 kGy (0/75 kRad). Without oxygen present, the degradation of the phenol formaldehyde resin from irradiation of water will still occur from both the direct interactions of the hydroxyl radicals and the oxidation by hydrogen peroxide as described above.

Water Exchange Effect on Dissolution in Water

As degradation progresses, the degraded phenol formaldehyde resin may be removed from the panel surface by dissolving in the bulk water of the panel cavity. Degraded radiolytic resin products, such as phenols and muconic acids, dissolve very easily in water. This dissolving process enhances further degradation by exposing more resin from the bulk polymer directly to the water. In panel cavities with significant pool water exchange, the concentration of the degraded resin dissolved in the water of should remain below saturation due to dilution with fresh pool water, promoting further dissolution. Conversely, in panel cavities without significant pool water exchange, the stagnant water may eventually be saturated with degraded resin products due to the lack of diluting pool water exchange. Therefore, dissolution of degraded resin will occur in stagnant water, but the dissolution process is slowed when the concentration of degraded resin products approaches solubility limits. Dissolution is expected to occur more rapidly with significant pool water exchange by maintaining the concentration of degraded resin below the solubility limit.. Therefore, it is expected that the degraded phenol formaldehyde resin in panels with significant pool water exchange would dissolve faster than resin in panels without significant pool water exchange.

The gases produced from the irradiation of water and phenol formaldehyde resin (such as hydrogen gas (H_2), carbon dioxide (CO_2), methane (CH_4), and carbon monoxide (CO)) dissolve to a certain extent in water. However; solubility in water varies from one gas to another, and gas produced above the solubility limit will come out of solution and form gas bubbles. It is therefore expected that their release to the environment does not depend only on their G-values, but also on their solubility in water.

4.3.6 Flow Rate within the Panel Cavity

Another key factor that may affect the erosion and dissolution process is the flow rate within the panel cavity. The nature of water flow rates within the panel cavity of plants with phenolic resin-based absorbers is not well known. However, it is important to consider how flow within the panel cavity may affect the degradation rate and the physical erosion of degraded resin. Increasing flow rate within the panel cavity is expected to enhance the kinetics of the erosion and dissolution process by chemically increasing the interaction between the degraded polymer and flowing water. In the case of Boraflex, flow is known to be a key factor to increasing the severity of degradation. Therefore, flow rate should also be considered as a potentially important factor in the erosion and dissolution process.

4.4 Summary

Radiation chemistry theory shows that phenol formaldehyde resins are expected to degrade in the spent fuel pool environment. Radiation directly interacts with the polymer itself to break bonds and cause scissioning of polymer chains. Radiation also affects the water environment through radiolysis by creating aggressive hydroxyl radicals and corrosive hydrogen peroxide. The presence of oxygen increases the opportunities for chemical reactions that degrade the polymer structure. Other important variables that may significantly impact the degradation process, but are not well-known include water exchange between the panel cavity and pool and flow rate within the panel cavity.

Table 4-2 below summarizes the expected degradation process in four potential panel cavity environments: dry without oxygen, dry with oxygen, wet without oxygen, and wet with oxygen. With the information available, it is not possible to quantify the degradation rate. However, Table 4-2 shows the relative degradation rate in each of the four environments. It is expected that the presence of water and oxygen accelerate degradation, while a dry environment without oxygen is expected to show the least degradation. However, it is important to note that these rates are only relative. A dry environment without oxygen may still cause significant degradation.

Table 4-2 Summary of degradation process in possible environments

Environment	Primary Causes of Degradation	Relative Degradation Rate
Wet with oxygen	<ul style="list-style-type: none"> • Beta and gamma radiation from spent fuel • Alpha particles from B-10 neutron reaction • Hydroxyl radicals and hydrogen peroxide • Oxygen 	Highest
Wet without oxygen	<ul style="list-style-type: none"> • Beta and gamma radiation from spent fuel • Alpha particles from B-10 neutron reaction • Hydroxyl radicals and hydrogen peroxide 	High
Dry with oxygen	<ul style="list-style-type: none"> • Beta and gamma radiation from spent fuel • Alpha particles from B-10 neutron reaction • Oxygen 	Lower
Dry without oxygen	<ul style="list-style-type: none"> • Beta and gamma radiation from spent fuel • Alpha particles from B-10 neutron reaction 	Lowest

5. Discussion

Chapter 3 surveyed the current empirical knowledge of the behavior of boron containing phenolic resin composite neutron absorber materials under spent fuel pool conditions: initial qualification studies, testing of in-pool coupons, and in-pool operational experience of racks. Chapter 4 provided a mechanistic background of the radiation-assisted degradation of phenol formaldehyde resin polymers. Chapter 5 will compare the empirical knowledge with mechanistic understanding to assess whether initial qualification testing, in-situ testing, or coupon programs can adequately capture and predict the degradation of phenolic-resin based neutron absorbers.

5.1 Radiation-Assisted Degradation of Phenolic Resins and Empirical Data

The degradation product and mechanical property observations from qualification testing and operating experience in Chapter 3 are consistent with the degradation mechanisms from radiation chemistry theory in Chapter 4. Radiation chemistry theory predicts the production of hydrogen (H_2) and carbon dioxide (CO_2) as the ultimate degradation products due to bond-breaking in the phenol formaldehyde resin by gamma radiation. This is in good agreement with the empirical data described in Section 3.1. Qualification testing and operating experience have found offgassing from Carborundum and Tetrabor to be primarily hydrogen and carbon dioxide. For example, Palisades observed continued swelling problems from 1988 to 2007 even after drilling vent holes indicating continued offgassing for an extended period of time.

Radiation chemistry theory shows that gamma radiation causes degradation of phenol formaldehyde polymers by scissioning polymer chain backbones. Degradation is expected to occur in the presence of spent fuel radiation (particularly gamma) even in a dry sealed environment. However, the presence of water and oxygen should influence the kinetics of the polymer degradation process. Degradation is expected to occur more rapidly in wet environments with oxygen present than in dry environments without oxygen. Degradation physically weakens the phenolic resin by shortening polymer chains and is consistent with observations of “friability” of these polymers after irradiation described in the qualification testing of Carborundum in Chapter 3 and in the coupons from La Crosse.

5.2 Rack Conditions and Boron Carbide Release

The mechanism of releasing boron carbide from radiation degraded polymer is postulated to be influenced by two effects. First, bulk dissolution of water-soluble phenolic resin degradation products such as phenol, as described in Section 4.3.5, may remove enough resin to cause particles of insoluble boron carbide to be released from the panel by gravity. If stagnant water is present in the panel cavity, dissolution and simple gravity release can potentially occur even if there is little or no water exchange with the bulk pool. Second, boron carbide release may be effected by water flow within the panel cavity and exchange between the panel cavity and the surrounding pool water. Water flow, in turn, is highly dependent on rack configuration. Racks containing Boraflex are open to constant flow and exchange with bulk pool water and show a strong correlation between B-10 areal density and absorbed gamma dose. In contrast, phenolic resin-based neutron absorber rack panel cavities are generally less exposed to flow

and pool water exchange and do not show a strong correlation between B-10 areal density and absorbed gamma dose. Therefore, gamma dose alone may not be a good predictor of B-10 areal density for phenolic resin panels depending on water flow and exchange conditions. The postulated influence of flow and pool water exchange in the panel cavity on the release of boron carbide is discussed in greater detail below.

Section 2.1.2 reviewed the mechanism for the degradation of Boraflex polymer-B₄C neutron absorber panels. In general, the degradation is a two-step process. First, gamma radiation degrades the backbone of the PDMS matrix from a flexible polymer to brittle amorphous silica which is only slightly soluble in water. Second, water flow in the pool erodes the panel, releasing both silica and boron carbide from the panel at known rates proportional to each other. Through a series of directly proportional processes based on a silica transport model, the B-10 areal density loss from a panel as measured by *in situ* testing can be correlated from boron carbide release proportionally to polymer degradation and then to the panel's gamma exposure history. This proportionality of the boron carbide release rate to silica release has not been observed directly, but is inferred based on the correlation between B-10 areal density and gamma dose found for Boraflex, and is integral to the model for RACKLIFE (Haley, 2012).

If the rate of boron carbide loss in phenolic resins is proportional to polymer matrix degradation, similar to what is inferred for Boraflex, then it would be expected that the B-10 areal density of a phenolic resin panel would follow that of Boraflex; i.e., B-10 areal density should decrease with increasing gamma dose. However, the BADGER B-10 areal density data plotted as a function of gamma dose for Carborundum plate at Palisades, shown in Figure 3-3, does not appear to indicate a strong correlation between loss of B-10 and dose. At Palisades, panels with low gamma dose may show large losses of B-10, while panels with high gamma dose still retain B-10 above the maximum calibration areal density of the 0.0705 g/cm² standard. While this is only one data set, the apparent lack of a correlation suggests that the boron release process for Carborundum plate, and by extension for Carborundum sheet and Tetrabor, may not occur proportionally with radiation-induced polymer degradation as it does for Boraflex. Two postulated reasons for this behavior, variations between panel cavities with respect to flow and pool water exchange and solubility of the degradation products are discussed below.

As described in Chapters 3 and 4, significant degradation of the mechanical properties of phenolic polymers has been observed at dose levels in the range of 10⁹ – 10¹⁰ rad as well as the production during irradiation of “a water soluble degradation product, which causes the material to disintegrate in water” (Sisman, 1955). Although there is clear evidence that the polymer structure is degraded at these high doses, degradation of the phenolic resin matrix does not necessarily lead to a proportional amount of B-10 loss from the panel, unlike Boraflex, as evidenced by the absence of a correlation between B-10 areal density and gamma dose observed at Palisades. Operating experience with Boraflex shows that both flow and exchange with the pool have significant effects on the rate of dissolution of polymer materials. Flow in the panel cavity accelerates the dissolution process by mixing otherwise stagnant water. Greater water exchange with the pool can increase the driving force for dissolution by removing dissolved degradation products from the panel cavity and introducing fresh water which can dissolve the panel further, as discussed in the technical letter report on RACKLIFE (Haley

2012). Although the assertion that boron carbide release from the panel is dominated by flow and pool water exchange rather than by polymer degradation from gamma dose alone cannot be confirmed directly, it can be inferred from the consistent correlation of loss of B-10, as observed by in-situ methods such as BADGER, with accumulated gamma dose.

It is expected that flow within the cavity and water exchange with the bulk pool will have similar dissolution effects on phenolic resins as they do on Boraflex, as described in Chapter 4. Similar to Boraflex, the boron carbide release process from degraded phenolic resins likely involves an erosion or dissolution interaction with the water that removes the fragments of degraded polymer binder, exposing and releasing the boron carbide. However, there are two key factors which affect the predictability of B-10 release in Boraflex racks and phenolic resin-based absorber racks

The first key factor is the degree of interaction between the panel cavity and the bulk pool. Boraflex rack panel cavities are generally open to the pool with only skip or spot welds attaching the wrapper plate to the rack. This allows for significant water exchange and even areas of strong flow into the panel cavity. Meanwhile, phenolic resin-based neutron absorber rack panel cavities, as described in Chapter 2, were usually designed to be sealed from the pool, and were only vented to the pool through small holes drilled in the wrapper plate to relieve pressure from offgassing after installation.

A single small hole will only allow a small amount of water exchange with the bulk pool. Without flow and water exchange to spur the erosion and dissolution process, boron carbide may be retained in a severely degraded polymer matrix due to factors that are difficult to observe, model, or predict. An additional confounding factor in the boron release process is that the degradation products of polymer resins such as phenols are very soluble in water compared to amorphous silica, the degradation product of the silicone rubber matrix in Boraflex. Bulk dissolution of degraded phenolic resin matrix in water may lead to release of boron carbide particles by gravity even in a no-flow environment, although that effect may be slowed or limited by saturation of the stagnant water with degradation products. Therefore, while high flow may accelerate loss of B_4C , low or no flow does not necessarily prevent the loss of B_4C . Potential loss of B_4C in the absence of flow contributes additional uncertainty to the effect of flow and rack environment on extent of boron carbide release.

The series of correlations from gamma dose to measured B-10 loss depends both on predictable polymer degradation and on proportional release of B-10 from the degraded polymer. Therefore, if the lack of flow and pool water exchange leads to a lack of proportional B-10 loss, then gamma dose will no longer be a reliable predictor of B-10 loss. This may explain why, at Palisades, an *in situ* test such as BADGER detected an acceptable level of B-10 present in severely degraded phenolic resins that are exposed to high gamma doses above 10^{10} rads.

The second key factor in predicting B-10 release from Boraflex racks or phenolic resin racks is their consistency of design. Although there were several variations in design, all Boraflex racks allowed for the significant exchange between the panel cavity and the bulk pool. In contrast, phenolic resin rack designs can vary greatly from pool to pool. For example, a rack that leaked or was drilled with large holes would be expected to experience less water exchange with the

bulk pool than an open Boraflex rack. A panel in a rack that had very small or potentially clogged vent holes drilled may experience little to no exchange with the bulk pool, leading to partial or full submersion in fairly stagnant pool water. A panel in a rack that remained airtight during venting, as at Columbia, may be exposed to a dry but oxygenated environment. The effect of each of these postulated environments on degradation of the polymer matrix and on the release of B-10 is discussed in greater detail in Section 4.3.

The inconsistent flow in panel cavities and inconsistency in rack designs leads to uncertainties in the amount and rate of B-10 release as a function of dose, which will affect the adequacy of the surveillance methods.

5.3 Adequacy of Qualification Testing and Surveillance Methods

The lack of clear understanding of the boron carbide release process and inconsistency of environments based on varying rack designs makes speculation or predictive modeling about the state of phenolic resin-based neutron absorber panels difficult. Therefore, the adequacy of qualification testing and surveillance methods becomes paramount to assessing the neutron absorption capabilities of these panels.

Qualification testing of Carborundum and Tetrabor materials was performed at the time they were installed to establish their performance over the range of radiation doses anticipated for service. Initial qualification testing programs are intended to provide the technical basis to show that the material will perform throughout its design life for the specified environment. Surveillance methods are employed to ensure neutron absorber performance during service and should be designed to detect degradation in a manner that captures the degradation mechanism or is at least reliably representative of the condition of the in-service material, if not conservatively bounding. The three surveillance methods described in Chapter 3 that have been employed to monitor the performance of phenolic resin-based neutron absorbers are monitoring of total organic carbon (TOC) in the spent fuel pool, coupon testing, and *in situ* testing.

5.3.1 Qualification Testing

Qualification testing was performed on Carborundum and Tetrabor neutron absorber materials as described in Chapter 3. Limited information is available regarding the Tetrabor qualification testing, although it is known that hydrogen gas was evolved during gamma irradiation as described in greater detail in Section 3.1.2. Much more information is available regarding the Carborundum qualification testing, which was carried out at gamma fluxes of $10^6 - 10^8$ rad per hour up to a total exposure of 10^{11} rad in about 100 days (The Carborundum Company, 1980). The Carborundum qualification testing program concluded that Carborundum would maintain its performance up to 10^{11} rad with only 20% weight loss and 15% boron loss. However, BADGER testing at Palisades showed greater than 50% boron loss at about 10^{10} rad, representing much greater loss of neutron absorption at ten times lower dose.

The BADGER results from Palisades and Millstone 1 may be explained by shortcomings in the applicability of the Carborundum qualification testing to in-service materials. Most importantly, the qualification testing was greatly accelerated compared to the amount of time in service.

These materials have been used in service for over 30 years, while qualification testing was condensed to 100 days. This accelerated testing is non-conservative in two ways. First, in order to reach a 10^{11} rad dose in 100 days, very high dose rates approaching 10^8 rad per hour were used. However, it is well-established that for a given accumulated dose, damage is less severe at higher dose rates due to greater likelihood of recombination as described in Section 2.4.2, Section 4.1., and Woods and Pikaev, (1993). At low dose rates, the radical-oxygen reaction that causes polymer degradation is predominant, but at higher dose rates, the radical-radical reaction that causes cross-linking is predominant. Therefore, qualification testing with high dose rates over a short time may result in phenolic resin binder that is less degraded than it would be in-service with lower dose rates for a longer time.

Second, as discussed in Section 5.2, one BADGER data set suggests that the loss of boron carbide from phenolic resin-based absorbers may not be dependent only on degradation from radiation exposure, but also strongly affected by dissolution and erosion in water. Therefore, the exposure time in water of only 100 days would not be conservative or representative of degraded phenolic resin binder exposed to pool water and flow for over 30 years. These two non-conservative aspects of the qualification testing may help explain why the Carborundum qualification testing results are not consistent with operating experience.

5.3.2 Total Organic Carbon Monitoring

There is one occurrence available in the literature of using total organic carbon (TOC) monitoring as a surveillance method for phenolic resin-based neutron absorbers. As discussed in Chapter 3, during the license renewal process in 2005 Palisades described a TOC monitoring program in their spent fuel pool as evidence of the lack of degradation of their Carborundum plate neutron absorbers. Palisades informed the NRC of periodic sampling since 2000 of spent fuel pool water showing low, stable levels of TOC less than 0.2 ppm. Subsequent BADGER testing of the absorber materials in 2008 found significant degradation of the Carborundum plate material at Palisades, including greater 50% loss of B-10 areal density in some panels. The finding of significantly degraded Carborundum plate material indicates that TOC monitoring at Palisades did not provide effective indication of degradation of the Carborundum plate materials.

This TOC monitoring may be considered an analogue to silica concentration measurements used to monitor Boraflex degradation. Through the RACKLIFE program, Boraflex degradation and subsequent loss of B-10 can be calculated from measuring the concentration of the Boraflex degradation product, reactive silica, through a well-established model which accounts for all forms of silica released from a degraded panel of Boraflex (Haley, 2012). In addition, the RACKLIFE model assumes that release of boron carbide from the panel is proportional to the release of silica from the panel. As discussed in Chapter 4, the degradation of phenolic resins produces a variety of degradation polymer fragments along with hydrogen and carbon dioxide gases. These degradation products may bubble from the pool water or remain in sealed racks where it is not available to TOC analysis. The discrepancy between the TOC monitoring as described and the release of boron carbide measured by BADGER can be explained because, unlike silica with Boraflex, it appears that TOC monitoring for phenolic resins does not

necessarily detect all the products of radiation-induced degradation of phenolic resins. Current understanding of the events at Palisades shows that TOC monitoring is not an effective surveillance method for the degradation of phenolic resin-based neutron absorbers.

5.3.3 Coupon Testing

Crystal River 3, Calvert Cliffs 1, La Crosse, Kewaunee, and Columbia credit phenolic resin-based neutron absorbers and utilize coupon testing programs as a surveillance method to monitor degradation of the absorber materials. These coupons are placed in the spent fuel pool in order to simulate the environmental exposure and configuration of the in-service panels. To achieve this, they are exposed to pool water and spent fuel radiation within sheathing that may be vented similar to the in-service panels. Coupon testing may include visual examination, weight and dimensional measurements, and neutron attenuation testing.

The primary considerations of the effectiveness of coupon surveillance programs are how representative the coupons are of the population of in-service panels and whether the coupon test procedures can adequately detect degradation. In order to capture the degradation of the service material, the coupon surveillance programs must be designed to expose the coupons to the same stressors that degrade the service material. In order to determine those stressors, the primary degradation mechanism must be known. For example, if the degradation mechanism is known to be dependent on radiation dose, then coupons that are exposed to the same or greater radiation dose as the service material will be representative of the in-service panels.

Coupon testing methods must also be able to detect expected degradation. If a coupon degrades by weight loss without losing volume, then measuring dimensions of the coupon may not capture the degradation. Further, uncertainties in coupon testing must be considered. For example, if a coupon is sensitive to damage by abrasion, there is uncertainty whether a negative test result such as weight loss is reflective of degradation in service, or by damage from handling of the coupon during the test procedure, as reported by Crystal River as seen Section 3.2.2. Also, measuring the B-10 areal density of coupons by laboratory neutron attenuation testing must consider the uncertainties of the attenuation test. An example of this is the inconsistencies in the neutron attenuation results of the Kewaunee coupons in Section 3.2.2.

For phenolic resins, there is good understanding that the degradation of the overall panel begins with degradation of the polymer binder due to polymer chain scission from gamma radiation, which is exacerbated in the presence or absence of oxygen and water. However, as described in Section 5.2, the factors which control the subsequent release of boron carbide particles and loss of neutron absorption are not well understood, making it difficult to assess whether the performance of coupons are representative or conservative regarding the boron carbide release process of in-service panels. For example, if the coupon assembly does not represent pool water exchange as in the in-service panels, then coupon performance may not be a reliable indicator of panel performance.

Since the mechanism of boron carbide release is not well-established, operating experience was used to assess the effectiveness of coupon surveillance in this report. However, only

limited direct information is available on the condition of current in-service phenolic resin-based absorber materials to provide a reliable comparison. One key operating experience event involving coupon testing programs occurred at Palisades in 2008. During the license renewal process in 2005, Palisades informed the NRC that it was monitoring the coupon testing program at another plant with the same absorber material. The coupon testing from the other plant gave no indication of significant degradation, but as described previously, Palisades found significantly degraded absorber material by *in situ* testing in 2008. This limited experience demonstrates the limitations of relying on the comparison of coupons from another pool to predict the release of boron carbide and loss of neutron absorber performance, particularly considering the inconsistencies in rack design as discussed in Section 5.2.

5.3.4 *In Situ* Testing

In situ methods such as BADGER testing has been used primarily to measure B-10 areal density in neutron absorber materials at plants that credit Boraflex; but it is also known to have been conducted at two plants with phenolic resin-based absorbers (Palisades and Millstone 1). BADGER uses a neutron source and detectors on opposite sides of a panel in adjacent storage cells to measure neutron transmission count rates which are then correlated to B-10 areal density, albeit with significant uncertainty (Chapman and Scaglione, 2012). Given adequate considerations for these uncertainties, an *in situ* method such as BADGER can provide a comparative assessment of the B-10 areal density of individual panels of phenolic resin-based absorbers.

In situ methods are valuable in that they directly measure the ability of an in-service neutron absorber panel to perform its function of absorbing neutrons without introducing uncertainties from pool chemistry models or potentially non-representative coupons. However, *in situ* neutron attenuation methods cannot observe degradation of the phenolic polymer binder unless that degradation has led to boron carbide loss, nor can these methods provide predictive information. Therefore, while an *in situ* method may assess the neutron absorbing capabilities of a single panel, without a consistent method to relate individual panel results to environmental conditions such as gamma dose, there is uncertainty in its ability to extrapolate the B-10 areal density results of a limited number of panels to the degradation and B-10 losses of all the panels in a spent fuel pool.

In the case of Palisades, BADGER results showed that B-10 content cannot be correlated to one specific property, gamma dose. However, this lack of correlation between B-10 content and gamma dose may not necessarily extend to other spent fuel pools containing phenolic resin-based neutron absorbers. As described in Section 5.2, the absence of a correlation at Palisades may be explained by a lack of predictable release of B-10 from the degraded polymer due to a low or inconsistent flow between the rack cavity and the pool. It is possible that another pool may have a different rack design where flow is sufficiently strong and consistent that the release of B-10 is proportional to polymer degradation and dose. In that case, the series of proportional correlations which relate gamma dose to B-10 loss may exist, similar to the series of correlations observed for Boraflex. Each spent fuel pool should examine its rack

design in this light to determine whether the B-10 areal density results of an *in situ* method can be extrapolated from a few panels to the entire spent fuel pool.

BADGER results from the two spent fuel pools tested with phenolic resin-based absorbers represent the only information available that directly assesses the performance of phenolic resin-based neutron absorbers in-service. The only two BADGER campaigns known to have been conducted have shown significant panel degradation at both pools. Although in-situ methods are known to have uncertainty in results for individual panels and for the extrapolation of results to the pool, it can still provide at least a qualitative measure of B-10 areal density. Therefore, these results of significant phenolic resin absorber degradation at both plants tested by BADGER, which represent the only information available to directly assess absorber performance, are noteworthy and concerning.

6. Conclusion

This report assesses the adequacy of current surveillance methods to monitor the degradation of phenolic resin-based neutron absorbers in the spent fuel pool environment. Background information describing the absorber materials, qualification testing results, and operating experience is compiled in Chapters 2 and 3. Qualification testing showed some degradation in mechanical properties and weight loss at doses of 10^{10} to 10^{11} rad, but not excessive degradation. Meanwhile, operating experience includes two instances of BADGER testing showing greater than 50% loss of boron carbide. Interestingly, BADGER testing data from Palisades does not appear to show a strong correlation between B-10 areal density and absorbed gamma dose, potentially indicating other factors may influence boron carbide loss in these materials.

Radiation chemistry theory provides a mechanistic theory of the radiolysis of phenolic resins in the spent fuel pool environment in order to understand the qualification testing results and operating experience. Radiation breaks bonds and creates free radicals in the phenolic resin, leading to scission of the polymer backbone and degradation of the polymer structure. In the presence of water and oxygen, degradation is accelerated by the introduction of more aggressive chemical species, including hydroxyl radicals and hydrogen peroxide. A key factor in the progression of degradation may be the amount of flow and water exchange that occurs between the panel cavity and pool. Greater flow and pool water exchange may increase the degradation and dissolution of the phenolic resin by providing fresh water to the panel cavity.

The Palisades BADGER data that does not appear to show a strong correlation between B-10 areal density and absorbed gamma dose may be explained by the predominance of flow and pool water exchange factors on the process of boron carbide release. Phenolic resin-based neutron absorber rack panel cavities were usually designed to be sealed from the pool and were only vented to the pool through small holes drilled in the wrapper plate to relieve pressure from offgassing after installation. This effect of flow and pool water exchange in phenolic resin-based absorber panel cavities, in addition to gamma dose, may be a dominant factor in the boron carbide release process. Some boron carbide may be released by dissolution and gravity, but without flow and water exchange to spur the erosion and dissolution process, even severely degraded phenolic resins that are exposed to high gamma doses above 10^{10} rads and susceptible to erosion and dissolution may not release boron carbide proportionally to gamma dose.

Discrepancies between qualification testing results and operating experience are believed to be due to the accelerated nature of qualification testing, which was non-conservative in two ways: a much shorter exposure time in water and a much higher dose rate. Operating experience at Palisades and understanding of the expected degradation products shows that TOC monitoring is ineffective. It is difficult to assess the adequacy of coupons given uncertainties in the exact nature of the panel cavity environment and the boron carbide release process. Given adequate considerations for uncertainties (Chapman and Scaglione, 2012), BADGER may be similarly effective on phenolic resin-based absorbers as on Boraflex. However, uncertainties associated with extrapolating boron carbide loss results from measurement of a limited number of panels to

all the panels in a spent fuel pool are significant when the degradation mechanism is not well understood.

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