Topics:
Spent-fuel storage
Neutron absorbers
Material testing

EPRI NP-6159
Project 2813-4
Final Report
December 1988

An Assessment of Boraflex Performance in Spent-Nuclear-Fuel Storage Racks

Prepared by
Northeast Technology Corp.
Kingston, New York

REPORT SUMMARY

SUBJECTS	High-level radioactive waste management / Light water reactor fuel
TOPICS	Spent-fuel storage Neutron absorbers Material testing
AUDIENCE	Fuels engineers / R&D scientists

An Assessment of Boraflex Performance in Spent-Nuclear-Fuel Storage Racks

Experimental data and theoretical models indicate that Boraflex, a neutron-absorbing material, will shrink during irradiation. Furthermore, the physical properties of Boraflex can change with time and radiation exposure. Thus, EPRI recommends that utilities conduct active surveillance programs to monitor the long-term performance of this material and thereby determine maximum service life.

BACKGROUND

High-density racks for storing spent nuclear fuel in water-filled pools are designed for a 30- to 40-year service life. The use of neutron absorber materials to control reactivity allows fuel storage at maximum density. One such material, Boraflex (manufactured by BISCO), contains boron carbide in a matrix of polydimethyl siloxane or silicone rubber. At one plant, small gaps formed in the Boraflex, and at another plant, Boraflex test coupons deteriorated unexpectedly. EPRI initiated this project to explore the factors determining long-term Boraflex performance.

OBJECTIVES

- To collect and evaluate data from utility coupon surveillance programs and from in-pool neutron radioassay measurements of spent-fuel racks.
- To evaluate data from test irradiations of Boraflex.
- To develop guidelines for Boraflex coupon surveillance programs.

APPROACH

The project team collected and evaluated coupon and neutron radioassay data from nine utilities. They also evaluated data from early Boraflex qualification tests and recent irradiation tests. The team reviewed the literature to identify the mechanisms of radiation damage for materials similar to Boraflex and formulated models to predict the maximum shrinkage. They then compared model predictions with the compilation of experimental data. Using the results of this work, the team developed guidelines for conducting coupon surveillance programs.

RESULTS

Experimental data and theoretical predictions of Boraflex behavior were in general agreement. Cross-linking in the polymer matrix of Boraflex causes the material to shrink when exposed to gamma radiation. The shrinkage

stops when cross-linking saturates at a gamma exposure estimated at about 1×10^{10} rad. The projected maximum shrinkage is 3–4%.

The study also identified mechanisms for gap formation that may result from shrinkage, as well as design and fabrication features of fuel racks that may contribute to gap formation. The maximum cumulative gap size in a storage rack panel is estimated to be about 4–6 in.

Data were not available to estimate the combined effects of gamma radiation and long-term exposure to the aqueous pool environment. Although no study findings suggest a rapid or dramatic change in the physical properties of Boraflex that would affect its neutron-absorbing function, EPRI recommends coupon surveillance programs to monitor its long-term performance. An appendix to the report provides guidelines for such programs.

EPRI PERSPECTIVE

This project makes an important contribution to understanding the factors that affect the performance of Boraflex in spent-fuel storage racks. The study has addressed one of the primary concerns with Boraflex use by presenting data showing that shrinkage of the material will be limited and that employing good design and fabrication techniques can eliminate gap formation.

However, some uncertainty remains about the combined effect of radiation and extended exposure to an aqueous pool environment. Therefore, EPRI cautions that continued surveillance of Boraflex is prudent to assure adequate long-term performance.

PROJECT

RP2813-4
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Research Project 2813-4

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Prepared by
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ABSTRACT

Data from utility surveillance programs, test reactor irradiations and the open literature have been collected and evaluated to assess the effect of service environment in spent nuclear storage racks on the neutron absorber material, Boraflex.

Radiation induced changes in the properties of Boraflex have been identified. The observed formation of gaps in the full length panels of Boraflex in some spent fuel racks has been attributed to one such change, shrinkage, in combination with mechanical restraint. Mechanisms of gap formation and growth are also discussed.

Factors which may influence the ultimate service life of Boraflex in spent fuel storage racks have been identified. Continuation of coupon surveillance programs to verify the serviceability of Boraflex in the spent fuel pool environment is recommended. Guidelines for coupon surveillance programs have been developed.

ACKNOWLEDGMENTS

In the course of this project Northeast Technology Corp (NETCO) has had discussions with nine utilities. The data and comments provided were invaluable to this project and NETCO hereby acknowledges and expresses its sincere appreciation for their help. Specifically, these utilities were:

- Alabama Power Company
- Carolina Power and Light
- Commonwealth Edison Company
- Duke Power Company
- Florida Power and Light Company
- Northeast Utilities
- Northern States Power Company
- Sacramento Municipal Power District
- Wisconsin Electric Power Company

In particular, the contributions of Commonwealth Edison Company and Wisconsin Electric Power Company are gratefully acknowledged. The valuable comments of the Electric Power Research Institute staff and, in particular, R. Lambert, on the final report as well as assistance provided throughout the project is sincerely appreciated. The test irradiation data provided by BISCO, the manufacturer of Boraflex, are also acknowledged.

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Section 1

INTRODUCTION

When the nuclear power stations now in operation or under construction were designed it was envisioned that spent nuclear fuel would be stored at the reactor site for a period of 6 months to one year. After this interim cooling period, the fuel was to be shipped to a reprocessing plant for separation of the fissile isotopes and recovery from the residual fission products. In the mid 1970's, delays in commercial reprocessing and ultimately a moratorium eliminated fuel reprocessing as a near-term option. Reactors at the time had storage capacity for one full core plus one or two additional discharge batches of fuel. Accordingly, the abandonment of commercial reprocessing and subsequent delays in the Federal Repository have caused a severe shortage of at-reactor spent fuel storage capacity.

One alternative to expand fuel storage capacity was to remove the original storage racks and replace them with racks which offered higher fuel packing density. The original racks supplied with these plants relied on large center to center spacing between fuel assemblies to control reactivity. Typically, PWR fuel assemblies were arranged in the racks in a square array with a spacing of as much as 21 inches between centers. Higher packing density, i.e., closer center to center assembly spacing, was achieved by taking credit for the stainless steel structure of the storage racks and/or by incorporating plates or sheets containing a neutron absorber material for reactivity control.

One such neutron absorbing material used quite extensively since the late 1970's for reactivity control utilizes a polymer, dimethyl polysiloxane or silicone rubber, as a matrix to contain the neutron absorber material, boron carbide. This material is Boraflex (Trademark of BISCO). The sole purpose of Boraflex is to provide

reactivity control in the spent fuel storage racks.

Recent examinations of surveillance coupons and an irradiated Boraflex sheet at Point Beach (1) as well as neutron radioassay measurements of the Boraflex in the spent fuel storage racks at Quad Cities (2) have indicated unanticipated behavior of the Boraflex absorber. For example, the Point Beach coupons showed a discoloration of the initially shiny black Boraflex to a steel gray color and some tendency of the material to soften and rub off when handled. Also, some of the coupons exhibited mechanical damage such as broken corners and chipping attributed to handling when the coupon cladding was removed. While the overall condition of the full length panel was good, some discoloration and softening of the Boraflex along the edges, similar to the color of the coupons, were observed.

Subsequently, a neutron radioassay technique was used at the Quad Cities Pool to verify the presence of Boraflex in the spent fuel racks. This investigation showed the presence of small gaps (or the absence of Boraflex) in some of the fuel storage cells. The gaps ranged in size from about 1/2 in. (approximately the limit of detectability) to 4 in.. In a separate study, funded by Commonwealth Edison, the neutron radioassay measurements were evaluated (3). The formation of gaps and their subsequent growth was postulated to result from shrinkage of a restrained sheet of Boraflex due to radiation induced crosslinking between adjacent chains in the polymer (3).

The present evaluation is a follow-on to the work performed for Commonwealth Edison and represents a broadening of the scope to include data collection and evaluation from a number of surveillance and test programs currently underway in the industry. Specifically the scope of this project includes:

- Utility Poll and Data Collection: A poll of utilities with spent fuel racks utilizing Boraflex was conducted. The status of each coupon surveillance program was established and where available, data were requested.
- Data Evaluation: The data received from the utility

coupon programs has been reviewed and evaluated. In addition, recent test irradiation of Boraflex samples in a Co-60 facility as well as a test reactor at the University of Michigan were also evaluated. These later irradiations were performed by BISCO, the manufacturer of Boraflex, after the Quad Cities gap phenomenon was observed.

- Literature Search: A computerized search of the literature was conducted to identify relevant studies of radiation effects in materials similar to Boraflex. This study was initiated to quantify the radiation damage mechanisms in Boraflex and to provide a basis for projecting the long term effects of irradiation on Boraflex.

- Gap Formation and Gap Growth: Based on the data collected and evaluated, postulated mechanisms for gap formation and growth have been developed. A gap growth model provides a method for projecting the maximum gap size and a basis for evaluating the worst case reactivity effects of gaps.

- Recommendations: Based on this comprehensive evaluation of the available data, recommendations as to areas where further research, testing and surveillance may be desirable have been developed. These recommendations are intended to provide data to determine the adequacy of Boraflex in the spent fuel pool environment for extended service life.

As data were collected it became apparent that the scope of the individual surveillance programs varied from utility to utility. This, is some cases, made the data evaluation and interpretation difficult. In order to assure uniform data of high quality in the future, guidelines were developed for a "Standard Boraflex Coupon Surveillance Program". These Guidelines, included as Appendix C to this report, are intended to supplement, not supplant, any test procedures recommended by BISCO or the fuel rack manufacturers. The Guidelines are generally intended for new rack installations where sufficient quantities of Boraflex can be specified for coupons. Some elements of the Guidelines may be applicable to existing programs.

Section 2

TYPICAL NEUTRON ABSORBER CONFIGURATIONS IN SPENT FUEL STORAGE RACKS

SPENT FUEL STORAGE RACK TYPES

High density spent fuel storage racks utilize neutron absorber materials in different ways depending on the type of fuel the racks are intended to receive, fuel rack design and other factors. An overview of the various types of high density fuel racks currently in use has been given previously (4). Accordingly, only those features of fuel rack design important to Boraflex behavior are addressed here. This includes the manner in which the Boraflex is encapsulated and retained within the rack structure.

High density spent fuel storage racks can generally be classified as being of either two types: a "flux trap" design or an "eggcrate" design. For PWR applications, both types are currently used and in some cases both may be used, in the same pool. For BWRs, on the other hand, the designs are exclusively of the "eggcrate" type.

The "flux trap" type of rack is designed to store unirradiated PWR fuel with enrichments generally up to 4.5 w/o U-235. A fuel storage location is formed by using a square tube of stainless steel typically 0.060 to 0.100 in. in thickness with inside dimensions of 8.5 to 9.0 in. as shown in Figure 2-1. The storage cells are typically arranged in a square pitch with center to center spacing of 10.5 to 10.8 in.. Four neutron absorber sheets are located on each side wall of the stainless steel tube and closure plates of stainless steel are provided to capture the sheet. The water gap between storage cells (flux trap) provides an effective means to thermalize neutrons maximizing the effectiveness of the absorber. A lattice of fuel storage cells is created by either connecting the individual cells at the corners or by placing the cells in a rigid framework structure.

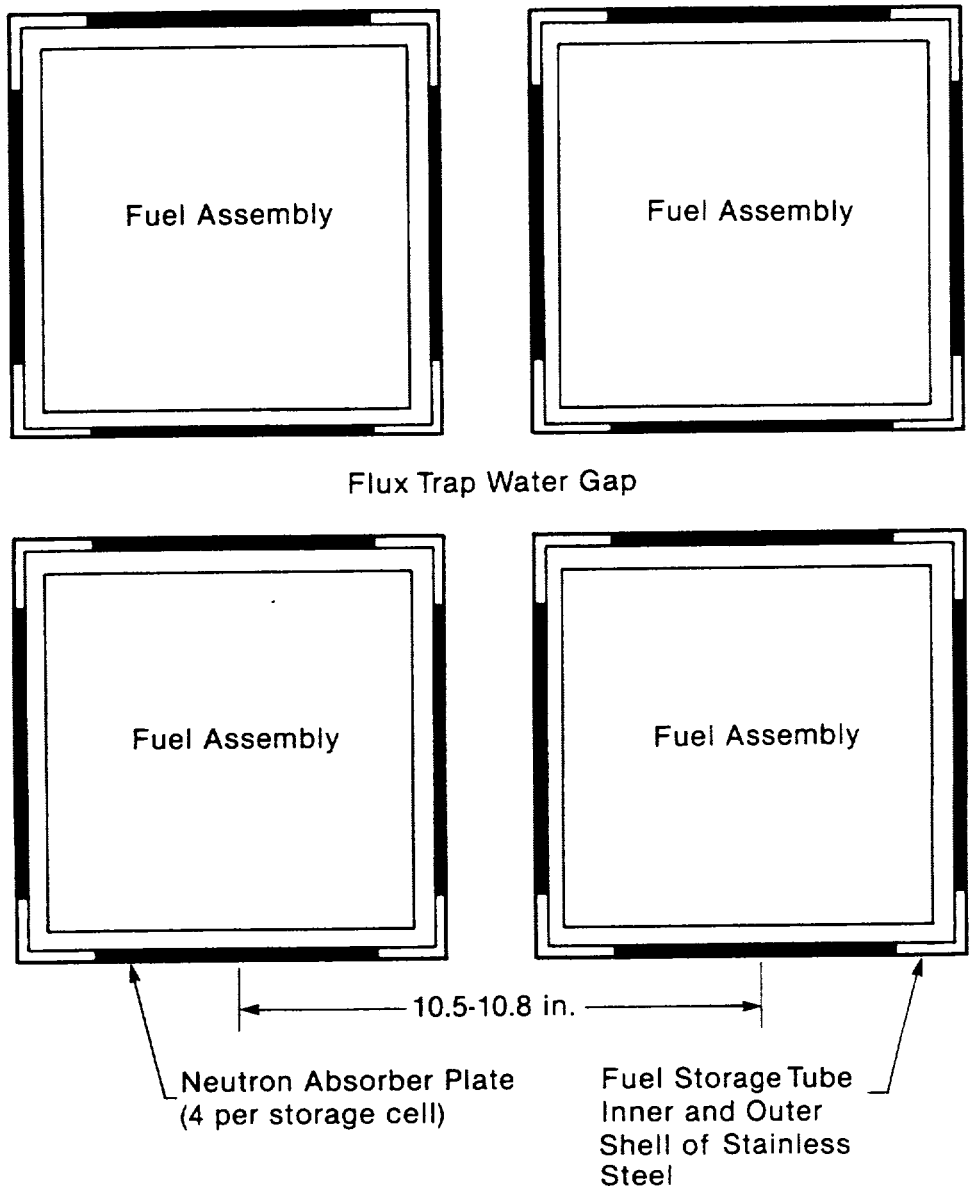

Figure 2-1. Flux Trap Fuel Storage Rack for Unirradiated PWR fuel.

The "eggcrate" type of rack differs from the "flux trap" rack in that the water gap is eliminated and each sheet of neutron absorber material is common to the adjacent cell. Figure 2-2 illustrates a typical "eggcrate" storage array for PWR fuel. Cells are generally arranged on a square pitch with center to center spacing of 9.0 to 9.2 in. for PWR fuel. In determining the reactivity state of the fuel/rack system, credit is taken for fuel burnup. Accordingly, the racks are designed to store irradiated PWR fuel which has accumulated a specified exposure. For BWR fuel types, racks similar to those in Figure 2-2 are used for both unirradiated and irradiated fuel. Typical center to center cell spacing for BWR fuels is 6.0 to 6.5 in..

In both "eggcrate" and "flux trap" designs, the cavity created to encapsulate the Boraflex is vented to the pool water. This allows for an escape path for gases produced when Boraflex is subjected to gamma radiation. This is designed to preclude bulging of the stainless steel closure plates due to pressure buildup of the offgas if the cavity was sealed. Venting therefore allows entry of the pool water and contact with the Boraflex.

BORAFLEX ENCAPSULATION AND RETENTION IN SPENT FUEL STORAGE RACKS

The rack manufacturer receives Boraflex from the supplier pre-cut to the size appropriate for a given design. Typically the material is used in thin (0.040 to 0.11 in. thick) sheets 5.0 to 8.5 in. wide and approximately 12 ft. in length. In the as-produced condition, Boraflex exhibits many properties of an elastomer and as such is not free standing. Means must therefore be provided in the design of the rack to support the material and prevent it from slumping. This is accomplished in a number of ways depending on the rack designer. The methods of Boraflex encapsulation and retention used in the majority of racks currently installed are discussed subsequently.

<u>"Wrapper" Design</u>

A typical wrapper design storage cell is shown in Figure 2-3. The structure of the cell is provided by a thick wall (0.060 to 0.100in.) inner tube of stainless steel with square cross section. The

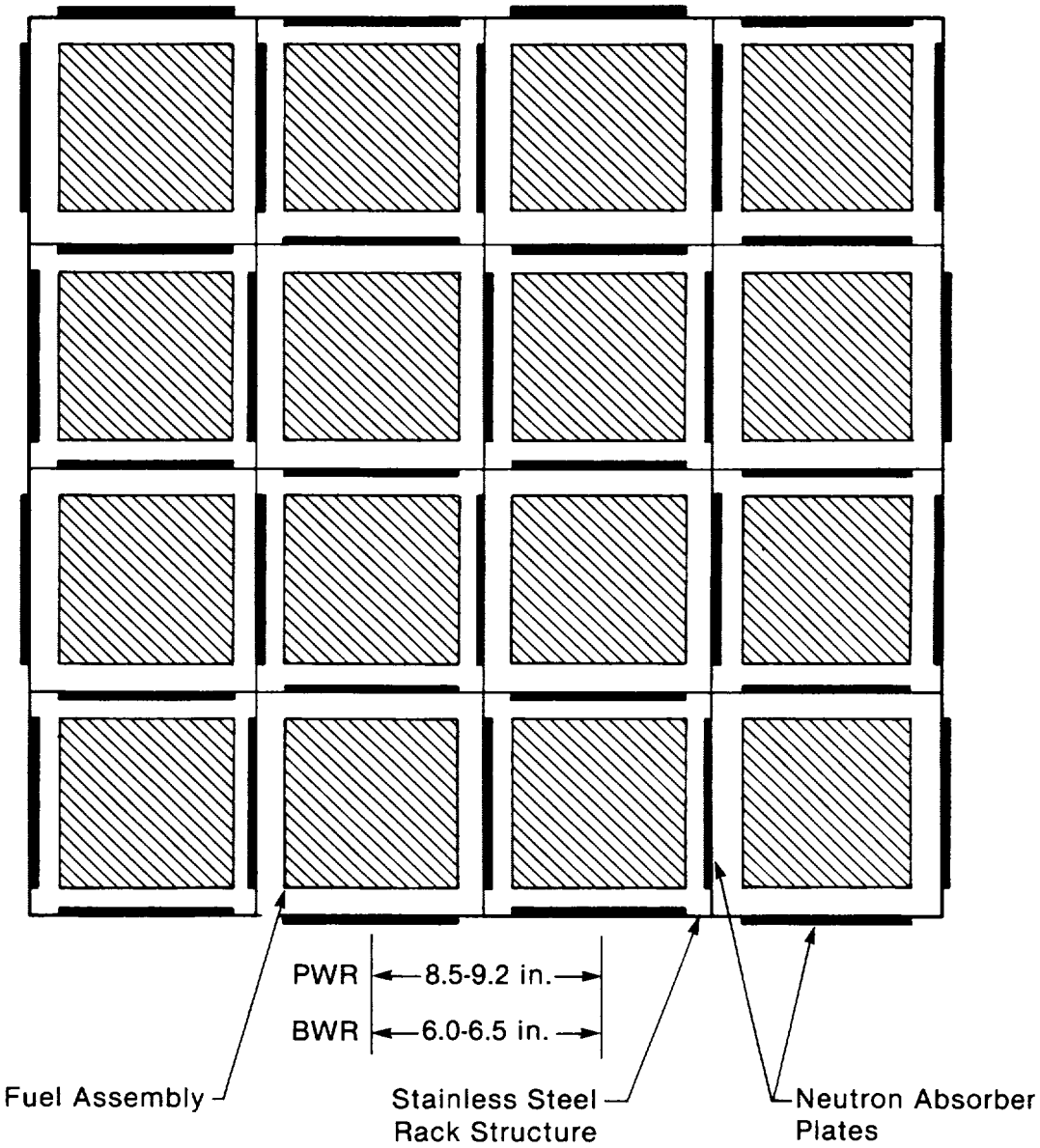

Figure 2-2. Eggcrate Fuel Storage Rack for PWR and BWR Fuel.

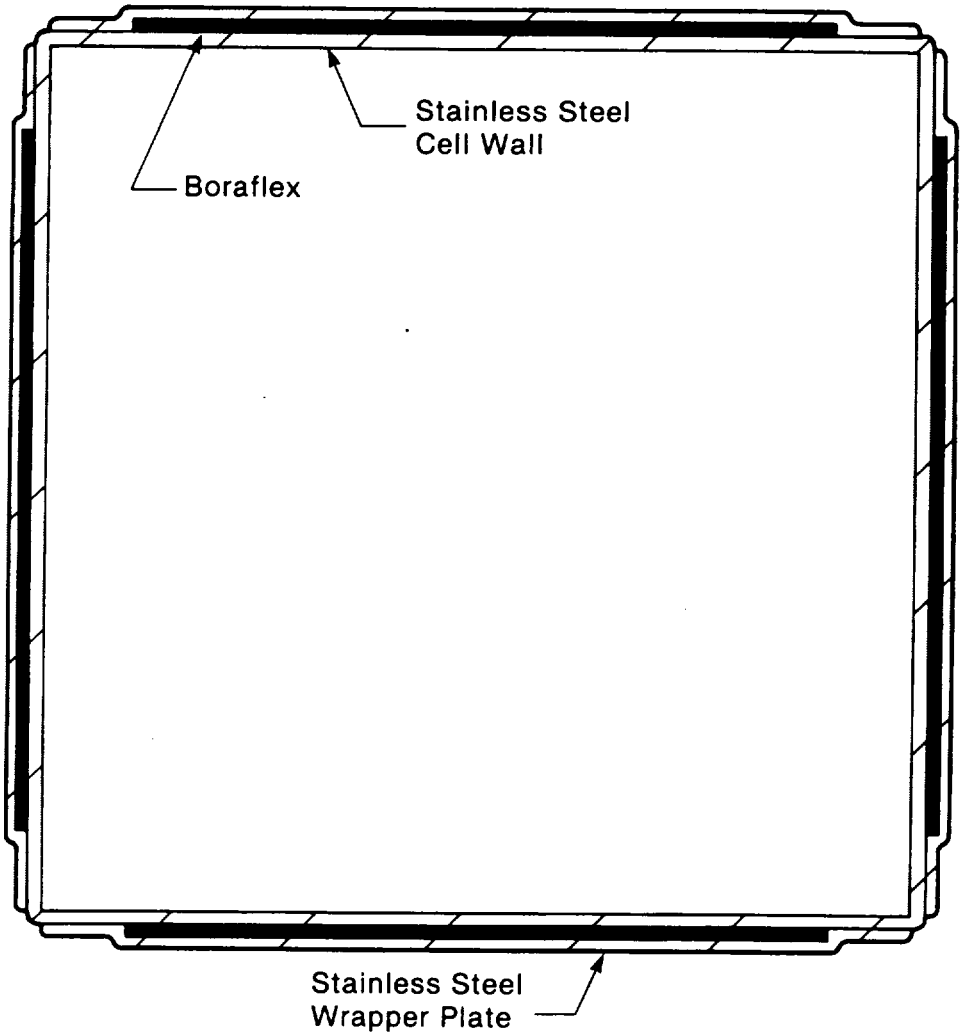

Figure 2-3. Wrapper Design Fuel Storage Cell.

Boraflex sheets are located on each face of the structural tube to correspond generally to the active fuel length. Thin (typically 0.020 in. thick) stainless steel sheet(s) are then place over the Boraflex and spot welded at the corner(s) and along the length of the tube. In some cases manufacturers use an adhesive to hold the Boraflex in place during tube assembly and wrapping.

Another variation of the wrapper design is shown in Figure 2-4. In this case, two L-shaped sheets are pressed firmly over the Boraflex and spot welded to the structural tube at diagonally opposite corners.

"Picture Frame" Design

In the "picture frame" design, an inner, heavy wall stainless steel tube is used to provide structure for the storage cell as in the wrapper design. Instead of using a wrapper, a cavity is formed on the exterior of each side of the cell using stainless steel closure strips tack welded in place. The closure strips are attached on all four sides of the cavity in a "picture frame" fashion as shown in Figure 2-5. The Boraflex is rolled in place and a thinner gage stainless steel closure plate is welded in place.

While the basic element of the Quad Cities racks is a cruciform (not a square tube as shown in Figure 2-5), the picture frame method is used to enclose and encapsulate the Boraflex. During the manufacturing process for these racks, an adhesive (Dow Silicone Sealant No. 999) was used to hold the Boraflex in place during rack assembly.

"Absorber Insert" Design

The "absorber insert" design utilizes removable cartridges to retain the Boraflex sheet in place. The cartridges are designed to slip in between stainless steel storage cells. The cartridges are assembled from a series of U-channels as shown in Figure 2-6. Two V-shaped grooves are rolled into the channels along their entire length to exert a positive force against the Boraflex sheet to hold it firmly in place and prevent slumping.

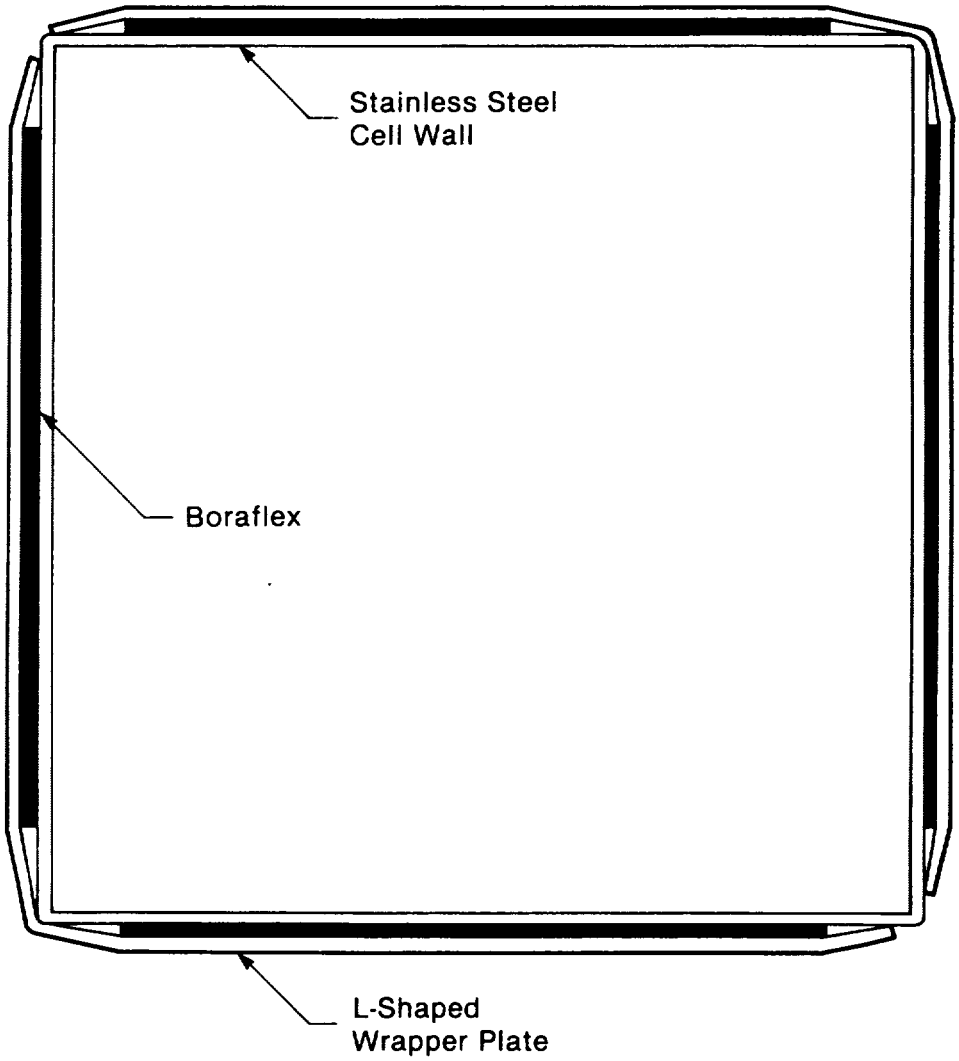

Figure 2-4. Alternative Type of Wrapper Design Fuel Storage Cell.

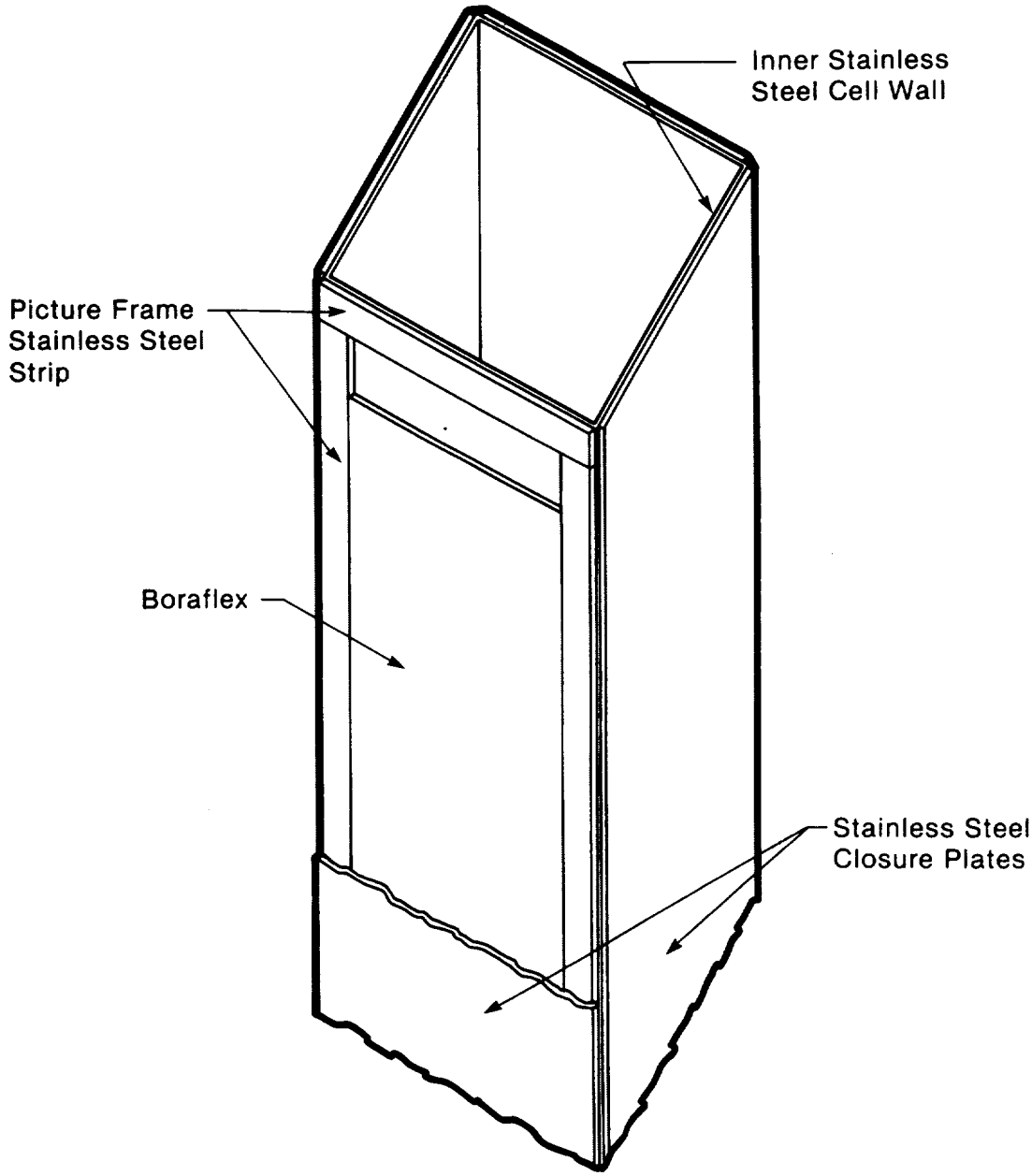

Figure 2-5. Picture Frame Design Fuel Storage Cell.

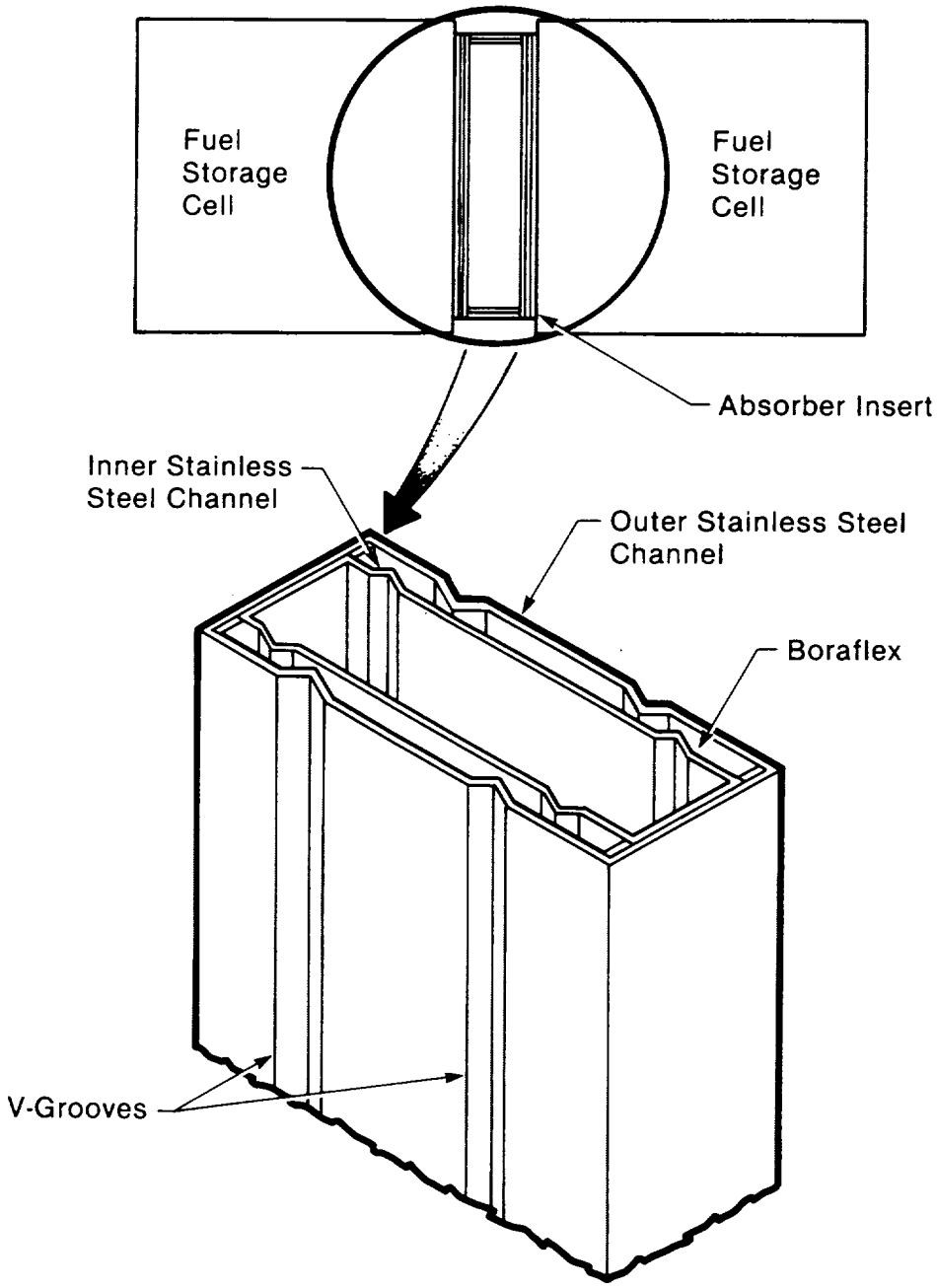

Figure 2-6. Absorber Insert Design Fuel Storage Cell.

The absorber insert design is used in the Point Beach spent fuel storage racks. No adhesives were used to bond the Boraflex to the channel wall (1).

Section 3

REVIEW AND EVALUATION OF DATA FROM UTILITY SURVEILLANCE PROGRAMS

Those U.S. utilities with spent fuel storage racks utilizing Boraflex had been previously identified (4). As of this writing, nine utilities have responded with data contributions solicited under EPRI project RP-2813-4. The data received consist of pre irradiation characterization of small coupons and post irradiation examinations and measurements of the same samples. In one case, two full length absorber insert panels were removed from the racks and examined. These data have also been included in the current evaluation.

In addition, measurements were conducted with neutron radioassay equipment at the Quad Cities and Turkey Point Stations. The former data were previously evaluated under separate contract. A summary of the results of neutron radioassay data are also provided. Table 3-1 contains a compilation of utilities which contributed data to the program.

SCOPE OF UTILITY COUPON PROGRAMS

Based on observations made of utility coupon surveillance data received to date, most utilities with spent fuel racks utilizing Boraflex do have a coupon surveillance program in place, but the specific elements of the programs vary from one utility to another. The programs generally consist of a series of samples prepared from production batches of Boraflex used for the specific racks. The samples are clad or enclosed in metal (generally stainless steel) and range in dimensions from 2 in. x 2 in. to 8 in. x 12 in. A series of coupons are placed in the pool at the time of rack installation, adjacent to individual storage cells designated for discharged fuel. In some programs the coupons receive accelerated gamma exposure by placing freshly discharged fuel next to the coupons after each

Table 3-1

SOURCES OF SURVEILLANCE PROGRAM DATA

Utility	Plant	Data Type
Alabama Power	Farley	coupon
Commonwealth Edison	Quad Cities 1	coupon, neutron radioassay
	Quad Cities 2	coupon
Carolina Power & Light	H.B. Robinson 2	coupon
Duke Power Company	Oconee 1, 2	coupon
Florida Power & Light	Turkey Point	neutron radio-assay
Northeast Utilities	Millstone 2	coupon
Northern States Power	Prairie Island	coupon
Sacramento Municipal Utility District	Rancho Seco	coupon
Wisconsin Electric Power	Point Beach 1, 2	coupon, full pan-els

refueling. The surveillance programs call for the periodic removal of coupons for examination. While the frequency of coupon removal varies from program to program, a typical program would call for removal after 1, 2, 4, 7, 11, 15, 20, 25, and 35 years of service.

During coupon preparation, the Boraflex is generally, but not always, precharacterized with respect to the following attributes:

- Sample weight
- Sample length, width and thickness
- Shore A and/or D hardness
- Neutron attenuation

When the coupons are removed from the pool they are visually examined and generally subjected to measurements similar to those conducted during the precharacterization. In some cases, only nominal as-built dimensions are available and this makes evaluation of dimension changes difficult. With few exceptions, the integrated gamma dose to which the coupon was subjected is not accurately known. In those cases where the dose is known it has been either rigorously calculated or estimated based on the operating history and discharge schedule of fuel placed adjacent to the coupon sample train. Table 3-2 summarizes the scope of each of the utility surveillance programs. Tables 3-3 and 3-4 contain a summary of the pre and post irradiation coupon characterization for each program. The results of coupon inspection are described in the following sections.

RESULTS OF THE UTILITY COUPON PROGRAMS

Visual Examination

Farley. Coupons were removed from the Farley pool after 1 and 2 years of residency. In addition to the 1 year irradiated coupon (01282A), an unirradiated control coupon (03152C) was examined. The irradiated coupon experienced a major increase in hardness and had lost most of

Table 3-2

SCOPE OF COUPON DATA COLLECTED AND EVALUATED

Plant	Coupon ID	Nominal Coupon Size (Inches)	Pool Residence Time (mos.) or Gamma Dose (rads)
Farley	01282A	4x6x.060	12
	03152C*	"	12
	01142E	"	24
Millstone 2	1*	2.75x3x.11	11
	2	"	11
Oconee 1/2	AD16	1(.25)x4.5x.075	68
	AD25		
	AD27		
	AD45		
	AD49		
	AD51		
Point Beach	N1	2x2x.11	$12(4x10^9)$
	N2	"	"
	N3	"	"
	S4	"	$24(1.0x10^{10})$
	S5	"	"
	S6	"	"
	N7	"	$1.44x10^{10}$
	N8	"	"
	N9	"	"
	N10	"	$1.55x10^{10}$
	N11	"	"
	N12	"	"
	N13	"	$1.60x10^{10}$
	Panel*	8x144x.11	84
	Panel	"	$84(1.0x10^{10})$
Prairie Island	05220C/01	8x12X1.25	6
	05200E/04	"	$12(5X10^9)$
Quad Cities 1	05102A	4x4x.070	3
	04302B	"	6
	04272D	"	12
	04302D	"	60
Quad Cities 2	05112C	"	3
	05192A	"	6
	05192C	"	12

--------(CONTINUED)-------

Table 3-2

SCOPE OF COUPON DATA COLLECTED AND EVALUATED
(Continued)

Plant	Coupon ID	Nominal Coupon Size (inches)	Pool Residence Time (mos.) or Gamma Dose (rads)
Rancho Seco	1	2x4x0.085	3
	2	"	"
	3	"	6
	4	"	"
	5	"	12
	6	"	"
H.B. Robinson	MM48A	N/A	6
	MM48B	"	"
	MM48C	"	"

*Unirradiated Controls

Table 3-3

EXTENT OF COUPON SURVEILLANCE PROGRAM MEASUREMENTS

Pre Irradiation Characterization:

Plant	Weight	Dimen-sions	Neutron Attenua-tion	Shore A Hard-ness	Other
Farley		x	x	x	
Millstone 2	x	x	x		
Oconee 1/2					
Point Beach	x	x	N/A	N/A	
Prairie Island	x	x		x	
Quad Cities 1,2	x	x	x	x	Boron content
Rancho Seco	x	x[1]	x	x	
H.B. Robinson			x		

[1] Nominal dimensions only.

Table 3-4

EXTENT OF COUPON SURVEILLANCE PROGRAM MEASUREMENTS

Post Irradiation Characterization:

Plant	Weight	Dimensions	Neutron Attenuation	Shore A / D Hardness	Other
Farley		x	x	x	
Millstone 2	x	x	x	x	
Oconee	x	x	x	x	Modulus of Rupture
Point Beach	x	x	x	x	Full panels inspected. Dose calculated.
Prairie Is.	x	x		x	B-10 content Dose estimated.
Quad Cities 1 and 2	x	x	x	x	Boron content
Rancho Seco	x	x	x	x	
H.B. Robinson			x	x	

its flexibility (5) which is expected based on the BISCO reactor irradiations discussed subsequently. Coupon 03152C was essentially unchanged. Slight discolorations were noted on coupon 01282A; however, the nature of the discolorations were not described in the report. The general appearance of the 2 year coupon (01142E) was similar to that of the 1 year coupon in that the only significant change was an overall increase in hardness and loss of flexibility.

Millstone 2. Two coupons were removed from the Millstone 2 pool after an eleven month residency. One coupon from capsule #1 was unirradiated and was used as a control. The other coupon from capsule #2 had been exposed to gamma radiation from discharged fuel although the integrated dose is not known. It has been reported (6) that the irradiated material has become significantly harder, more fragile and stiffer. Minor dimensional changes and neutron absorbtivity changes were also observed. Changes in Boraflex color are not reported.

Oconee. Two sets of three coupons each were inspected after approximately 5 1/2 years residence in the pool. The samples were configured as tensile specimens and were not precharacterized prior to placement in the pool. It has been reported (7) that all samples had a grey coloration along the edges extending in about one millimeter from the edge. Radioassay measurements showed radiation levels of 1 MR/hr gamma and 3-4 MR/hr beta at a distance of about 1 centimeter. The coupons were reported to be very brittle and cracked easily during handling. Although the gamma dose to which the coupons were subjected was not reported, Shore A hardness measurements indicated they probably received a dose of at least 1×10^9 rads.

Point Beach. The surveillance program at Point Beach has included the periodic removal of coupons starting one year after the fuel racks were installed. The coupon sample train was subjected to accelerated gamma radiation exposure by placing a freshly discharged fuel assembly adjacent to it following each refueling. The latest coupons examined had received a gamma dose in the range of 1.0 to 1.6×10^{10} rads. The examinations reported were conducted by Wisconsin Electric Power Co.

(WEPCO) personnel and an independent laboratory. The results of these examinations have been documented elsewhere (1). The summary reported here is based on Reference 1 and discussion with WEPCO personnel. The major findings include:

- The samples showed degradation in the form of cracks and chipping thought to have resulted from packaging/shipping or unpacking/mechanical damage.
- The samples had changed in color from a shiny black to a greyish color.
- Immersion of samples into clean water darkened the water with a graphite-like particulate material shed from the Boraflex. Successive immersions into clear water darkened the water, but each time to a lesser extent. This in turn lightened the Boraflex to a whitish grey color.
- Several samples showed evidence of thinning in the spent fuel pool environment.
- Radioassay of the coupons indicate the permeation of pool water and containments (primarily Cobalt-60, Cesium-134 and Silver-110.)
- The coupons yielded dust or powder when rubbed.

Since there were significant differences in geometry and encapsulation method of the Boraflex in the coupons and in the fuel racks, two full length panels were removed for inspection. These panels had experienced 6 to 7 years of residence in the pool. The Point Beach racks are of the removable absorber insert design as described in Section 2. One panel had received a high gamma exposure (1×10^{10} rads) and the other no significant exposure. The inspection results have been summarized by WEPCO personnel (1) as follows:

- The unirradiated panel was "brand new" in appearance with the exception of a whitish powder which covered the panel where it was in contact with the stainless steel clad.
- Radioassay of the unirradiated panel showed very little beta/gamma activity indicating little permeation of pool water.
- The irradiated panel showed good overall integrity with no missing pieces, no cracking or other degradation. Some discoloration (greying) was evident along the edges of the panel and appeared as randomly occur-

ing scallops. The largest such discoloration was about 5 inches long and penetrated 0.5 to .75 inches into the panel. The scalloped areas covered approximately 1-2% of the total surface area of the panel. The gray areas yielded a dust or powder much like the coupons when rubbed.

- Radioassay of the irradiated panel indicated water permeation in the nondiscolored areas although less than the coupons. Radiation levels on contact with the gray areas were about seven times those of the nondiscolored areas. This suggested that water may be preferentially permeating the panels at the edges.

- The length of the panel was not measured during the examination so that no definitive conclusions with regard to length changes can be made. The panel width was measured, however, and the shrinkage based on the nominal width including manufacturing tolerances have been computed as described subsequently.

As a result of this inspection, the following observations were offered by WEPCO relative to the progression of changes observed in Boraflex (1):

- When Boraflex is immersed in the spent fuel pool without gamma radiation, it appears to retain its "like new" appearance.

- When gamma radiation is present, the material changes. The changes include color, and from a material of good integrity to one that is brittle and yields a powder when rubbed. Once the Boraflex reaches the grey condition, weight loss, thinning and other changes in physical properties occur.

- The presence of gamma radiation also appears to allow water permeation initially along the edges where the material was cut to size. The flat surface of the panel seems to be more resistant to permeation of the pool water.

- WEPCO believed that the onset of discoloration, permeation and subsequent changes in the material integrity begin at about 10^{10} rads gamma.

Based on the good overall condition of the irradiated panel, after 6-7 years in the Point Beach pool, WEPCO concluded that the Boraflex was expected to retain its serviceability for another 10-20 years.

Discussions with WEPCO personnel (8) have indicated that silica contamination in the spent fuel pool water has been noticed with levels in the range of 3 to 5 ppm measured. Possible sources of silica have been identified as Boraflex and/or a grease used on some underwater tools. An irradiated sample of Boraflex was placed in a beaker of water for an undisclosed period of time at the Point Beach chemistry lab. The water subsequently tested positively for silica. As discussed in Appendix A, Boraflex is believed to contain a significant amount (20 to 25 w/o) of a silica compound.+

Prairie Island. The surveillance program at Prairie Island utilizes large coupons (8" x 12") clad in stainless steel. To date two coupons have been removed and examined, one after six months and one after one year (9). Freshly discharged fuel had been placed next to coupons to accelerate the accumulation of gamma exposure. The gamma dose received by the 1 year coupon has been estimated at 5×10^9 rads. Visual inspections (10,11) showed "waterspotted" areas on the one year coupon which covered more of the coupon than the earlier sample. Review of the photographs of the one year coupon cannot conclusively identify the "water spotting" as being the same type of discoloration as that observed as the Point Beach panel. There are, however, similarities such as scalloped discolorations at the coupon edge and corners.

Quad Cities. Coupon data from the programs at both Quad Cities 1 and 2 have been received and evaluated (12,13,14). Four coupons from the Quad Cities 1 program have been removed to date corresponding to 3, 6, 12 and 60 months pool residence time. Three coupons at 3, 6 and 12 months have been inspected from Quad Cities 2. These coupons have received relatively low gamma exposure with the dose for the 12 month coupon estimated at less than 10^8 rads. According to Commonwealth

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+Private conversations with BISCO indicate the silica content may be less than this estimate although the exact composition of Boraflex has not been provided.

Edison (CECO) personnel, the general appearance of four of the coupons was good although the coupons had lost some of their initial flexibility. Two samples from Quad Cities 2 (coupons 05192A and C) and one sample from Quad Cities 1 (coupon 04302D) showed small blisters over approximately two thirds of their surface area. The blisters ranged in size up to about .125 in. in diameter. Embrittlement was observed in the blistered area as well and it was reported that the material was very easily torn in those areas. Radioassay of a corner of the blistered region indicated permeation of the pool water. The color of these coupons was described as a greyish shade. As discussed in Appendix B, blistering or bubbles in irradiated silicone rubber has been reported in the literature and is believed to be associated with trapped off-gas produced as a result of the radiation-induced crosslinking process.

It is not known why only three of the coupons showed blistering although this may be related to variations in some process variable during the manufacture of these batches of Boraflex. These are the only coupons for which data was collected during this project which showed the formation of blisters.

Rancho Seco. Two coupons each after 3, 6 and 12 months residence time have been removed to date (15). The exposure received by these coupons is not known although freshly discharged fuel has been placed next to the coupon train to accelerate the accumulation of gamma dose. It has been reported (11) that the condition of all coupons was generally the same. The 3 month coupons were found to be only slightly flexible compared to unirradiated specimens. The one year coupons were very hard and brittle. Photographs of the one year coupons showed greying discolorations along one edge to a depth of about 1.5 in..

Robinson. Three coupons from the accelerated surveillance program at H.B. Robinson have been removed after six months pool residence for examination (16,17). These coupons were subjected to gamma radiation from freshly discharged fuel to accelerate the accumulation of gamma dose. The coupon configuration is that of a tensile specimen clad in

stainless steel. Coupon dimensional data was not provided. Neutron attenuation and hardness measurements were made. Visual examination revealed no indication of coupon cracks or other signs of physical deterioration (17). The coupons were hardened but retained significant flexibility.

Shore A/D Hardness

All coupons for which data were received were subject to pre and post irradiation Shore A hardness measurement. In two programs (Robinson and Millstone 2), Shore D hardness was also measured. The pre irradiation Shore A hardness measurements show considerable variability (from 66 to 85 on the scale). It is not known whether this variability is real or whether, in some cases, the measurements were made on coupons too thin to give an accurate result. ASTM D 2240-86 as well as supplier of Shore A durometers recommend that samples be at least 0.25 in. thick and for thinner samples that several layers be stacked to this thickness (18). To test this hypothesis, Shore A measurements were made on successive layers of nominally 0.040 in. Boraflex. The results are shown in Table 3-5.

Since the cumulative gamma dose is not known for many of the coupons, the post irradiation Shore A and D hardness is plotted as a function of pool residence time in Figure 3-1. Referring to the Shore A measurements in Figure 3-1, all coupons registered above 90 on the Shore A scale except those from the Quad Cities program which had received a gamma exposure of less than 10^9 rads. It is therefore probable that these are two classes of coupons in the matrix of samples evaluated in this study, low dose (less than 10^9 rads) and high dose (greater than 10^9 rads and beyond). It should be noted that when the Shore A scale exceeds 90, the manufacturer recommends that a D scale durometer be used (19). The hardness data in Figure 3-1 shows no obvious correlation with pool residence time since many of the samples with relatively short residence time received accelerated gamma radiation exposure.

Table 3-5

SHORE A HARDNESS AS A FUNCTION OF SAMPLE THICKNESS
(UNIRRADIATED BORAFLEX)

Number of Layers	Thickness (in.)	Shore A Hardness	
1	.038	87	+/-2*
2	.078	82	+/-1
3	.117	80	+/-1
4	.156	79	+/-1
5	.195	78	+/-1
6	.234	78	+/-1
7	.274	77 1/2	+/-1

*Estimated repeatability.

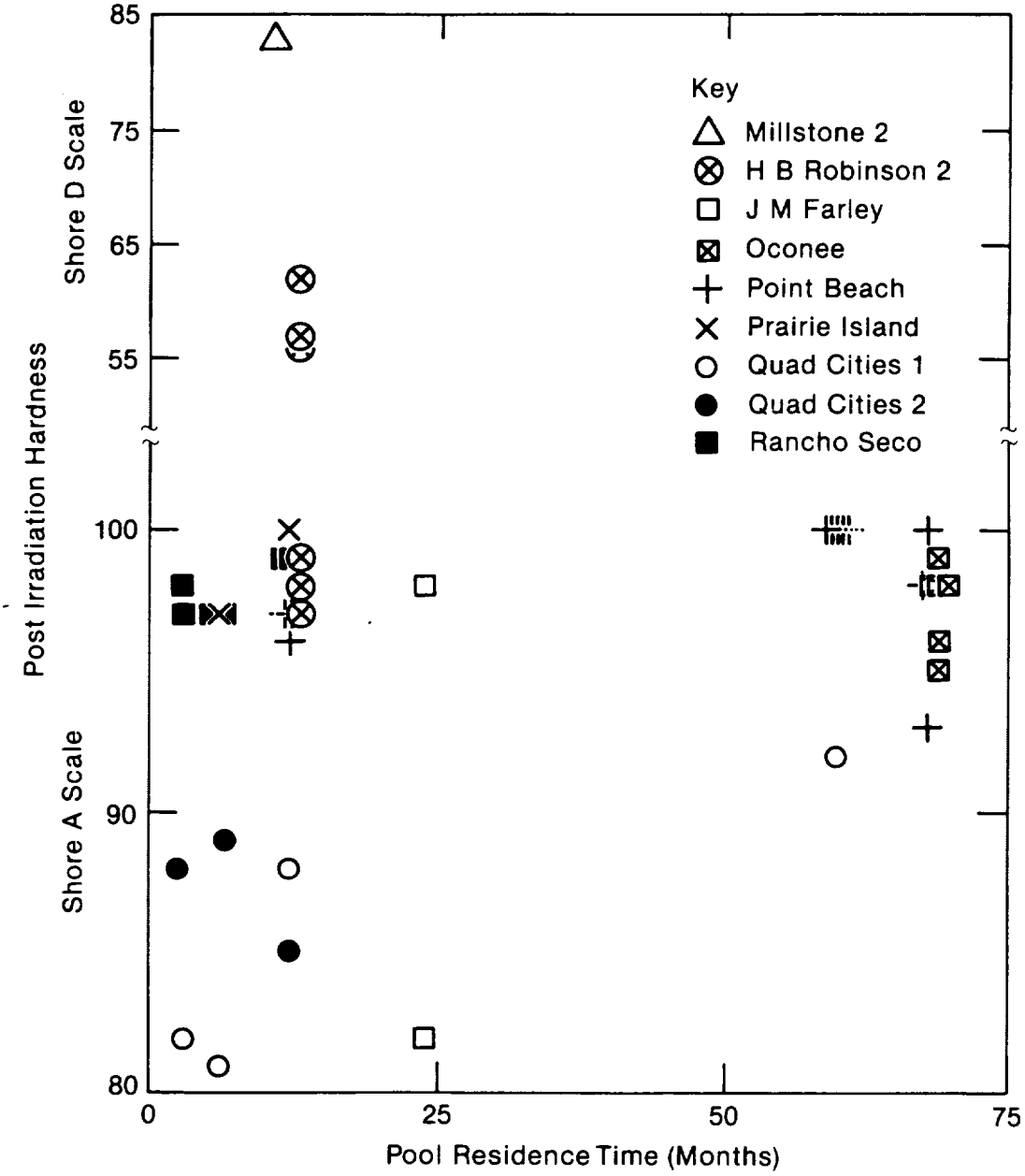


Figure 3-1. Utility Coupon Measurements: Post - Irradiation Shore A and Shore D Hardness.

Dimensional Changes

The percent change in coupon length and width are plotted as a function of pool residence as shown in Figure 3-2. The data included in Figure 3-2 are only for those coupons where pre irradiation measurements are available so that changes in dimensions can be inferred. Furthermore, in cases where coupon degradation due to handling and shipping was significant, the data have been omitted. Accordingly, only coupons N1, N2 and N3 from Point Beach are included (examined after 1 year with a cumulative gamma dose of 4×10^9 rads). The data seems to again fall in two classes: low shrinkage (less than 1.5%) and high shrinkage (2.5 to 3.5%). Of those coupons in the latter class, the Point Beach coupons had received high gamma exposure (4×10^9rads) and the exposure of the 1 year Prairie Island coupon has been estimated at 5×10^9 rads. It is interesting to note that the length change for the 1 year Prairie Island coupon is 3.3% whereas the width change is only 1.0%. This could be indicative of nonuniform or anisotropic shrinkage. On the other hand, both dimensions in the Point Beach coupons changed by approximately the same amount. This introduces the question of variations in the production process of Boraflex, perhaps depending on filler composition, sheet thickness, etc..

Most of the Quad Cities coupons showed less than 1.5% shrinkage in length and width with no preferential shrinkage in either direction. The 5 year Quad Cities 1 coupon, on the other hand, exhibited shrinkage of about 2.4% in length and 1.25% in width. While the dose received by the 6 month Prairie Island coupon and the Farley coupons is not known, hardness measurements indicate that these coupons received a fairly high dose yet shrinkage is limited to 1.5% or less. The 11 month Millstone 2 coupons probably received a fairly high dose based on Shore D hardness measurements but showed very little or no shrinkage in either length or width. Measurements of coupon thickness showed a net increase in this dimension of 2 to 3%. It has been postulated (6) that this increase in coupon thickness may be attributed to water absorption.

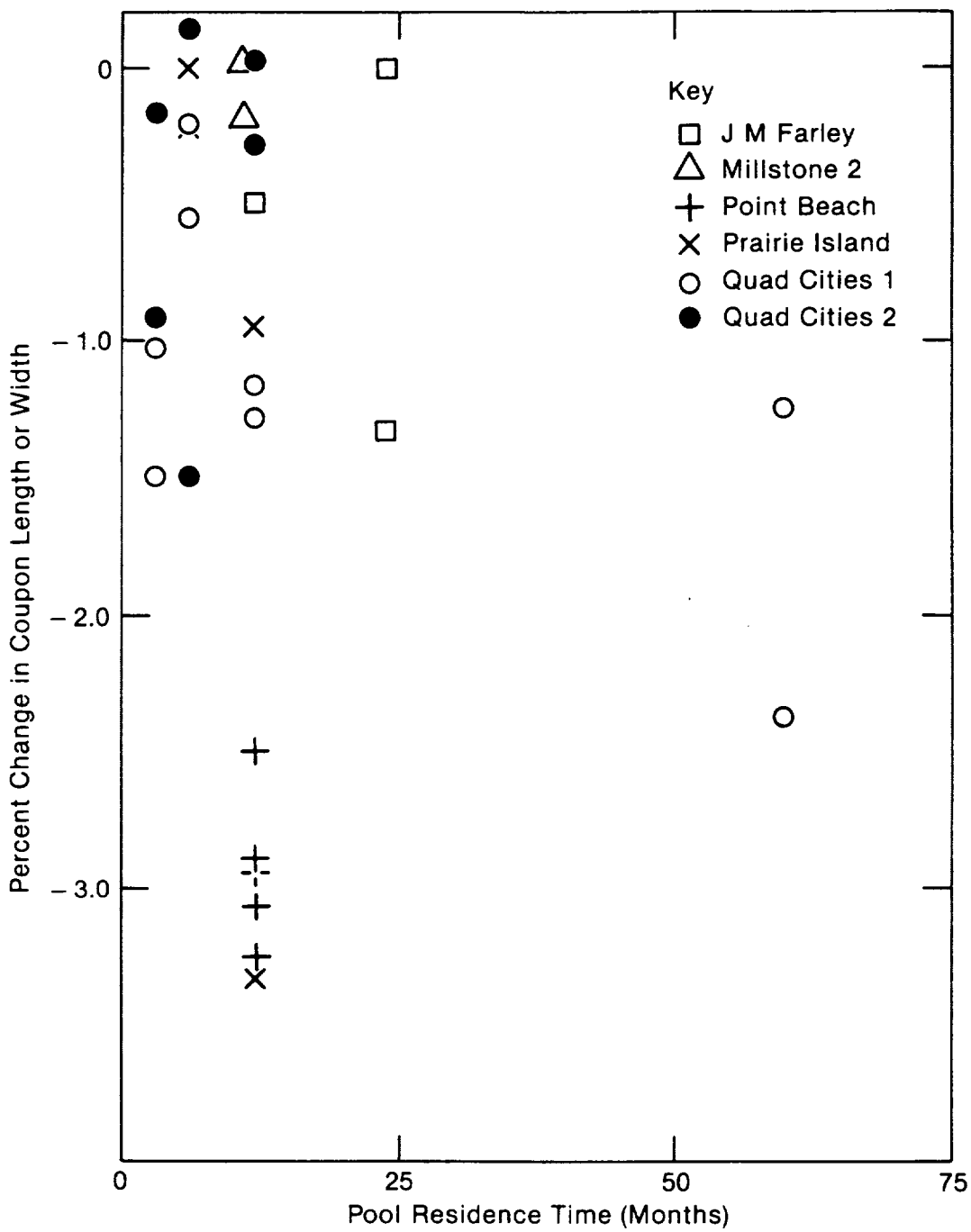


Figure 3-2. Utility Coupon Measurements: Percent Change in Coupon Length or Width versus Pool Residence Time.

For those coupons where the gamma exposure is known, the measured shrinkage is included in a composite Figure in Section 5 along with the BISCO test data and Quad Cities gap data.

Coupon Weight

The percent change in coupon weight is plotted as a function of pool residence time in Figure 3-3. As in the previous case, samples with a piece missing or exhibiting severe deterioration have not been included. While the data shows considerable variability, the general trends are either very little sample weight loss or a weight gain. This may be due to the onset of permeation of the samples by pool water as was observed in the high dose Point Beach coupons and irradiated panel where this was indicated by the absorption of radioactive contaminants. One exception is the Quad Cities 1 five year coupon which showed a 5% loss in coupon weight. This may be due to a missing piece of the coupon although other than the blistering, no such coupon deterioration has been reported (13,14).

Change In Neutron Attenuation

The percent change in neutron attenuation pre and post irradiation versus pool residence time is shown in Figure 3-4. The change in neutron attenuation for most coupons is generally within a band of +/- 2%. The two exceptions are two of the Point Beach coupons which had been in the pool 5-6 years and the six month Rancho Seco coupons. The Point Beach coupon reportedly (1) had significant damage which may have been a contributing factor to the decrease in neutron attenuation. The pre-irradiation attenuation data for the Rancho Seco coupons were made on "representative" control samples of Boraflex (15) and not the actual sample removed from the pool. This may explain the relatively large decrease in neutron attenuating characteristics of these coupons.

To place the neutron attenuation measurements in perspective, the following example is cited. For a neutron absorber material with

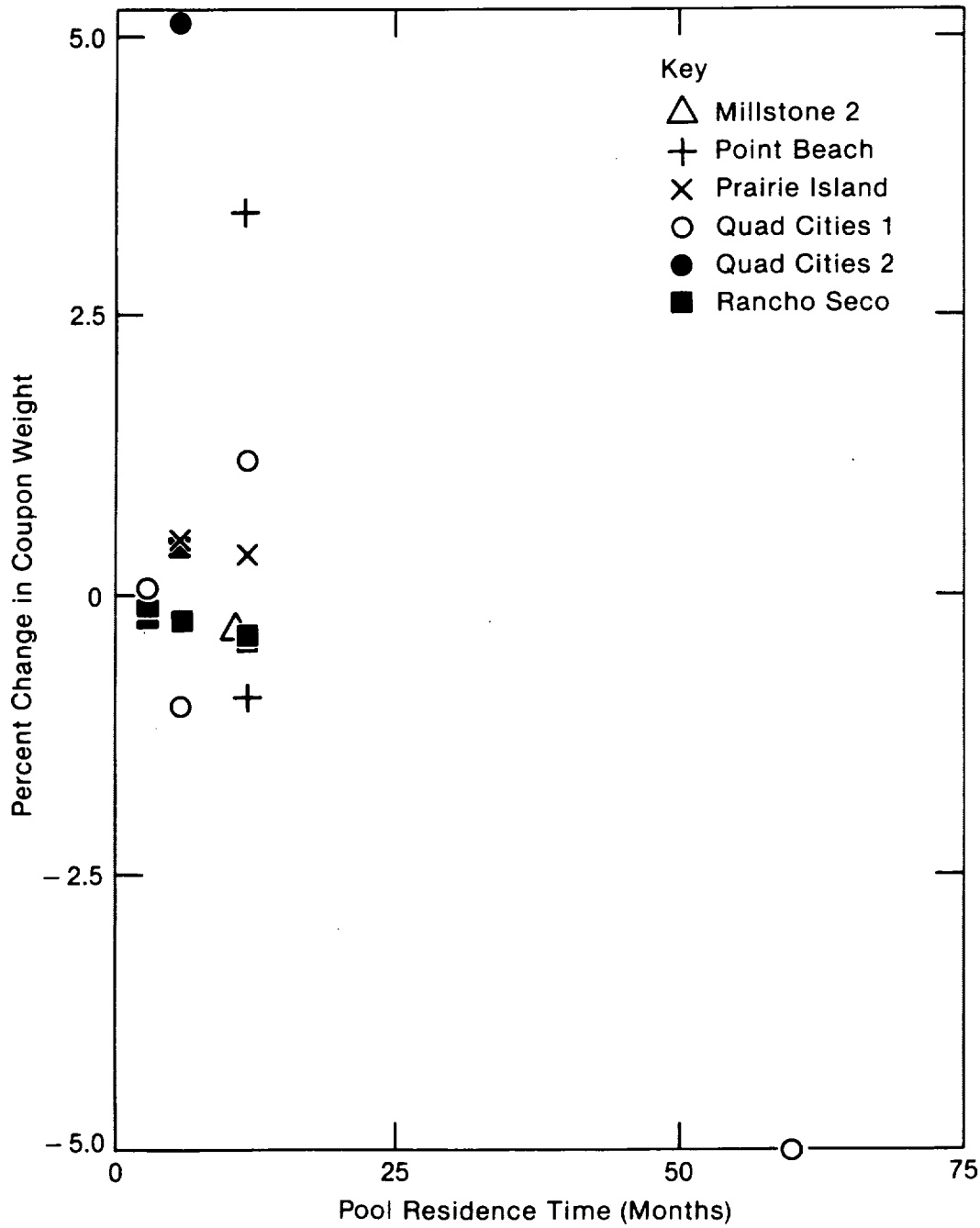


Figure 3-3. Utility Coupon Measurements: Percent Change in Coupon Weight versus Pool Residence Time.

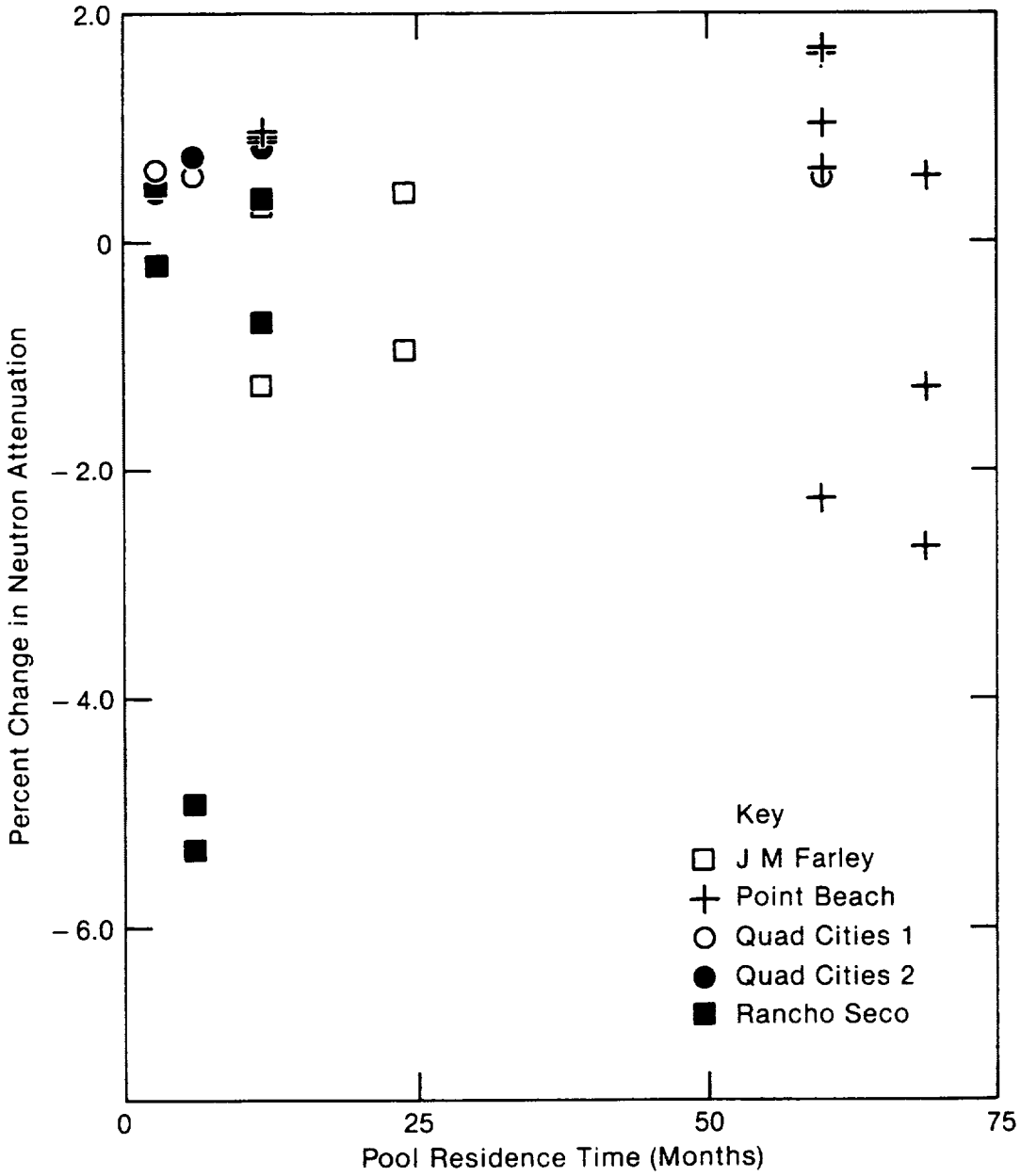


Figure 3-4. Utility Coupon Measurements: Percent Change in Coupon Neutron Attenuation versus Pool Residence Time.

initial Boron-10 areal density of .025 g B-10/cm^2 a "rule of thumb" estimate is that a decrease in neutron attenuation of 1.0% corresponds to a 10% reduction in B-10 areal density. The neutron attenuation measurements are relatively insensitive to small changes in B-10 areal density since at 0.025g B-10/cm^2 the material is "black" to thermal neutrons.

The relatively large variability and changes in neutron attenuation measurements from the coupons programs are probably attributable to factors other than the loss of boron (except perhaps for the 5-6 year Point Beach coupons which had experienced thinning of 25 to 30%). These factors would include, as in the case of Rancho Seco, the use of different pre and post irradiation samples and also differences in the neutron spectrum used in the pre and post irradiation measurements. Differences in the location of the measurements on the specimen could also introduce variability since there are variations in coupon thickness from location to location.

In summary, the data from the utility coupon programs indicate that as expected under gamma irradiation in the pool the Boraflex coupons undergo changes. These changes include shrinkage, a loss of flexibility, embrittlement and an increase in hardness, change in color from shiny black to a whitish-greyish shade, absorption of pool water, and the formation of blisters in some coupons. The major conclusions from the coupon data relative to these changes can be summarized as follows:

- The shrinkage data are quite variable but indicate a maximum shrinkage in any direction of 3 to 4%. Shrinkage may not be uniform in all directions but may be anisotropic.
- Changes in weight exhibit variability. This may be partially attributed to how the various coupons were preconditioned (dried) prior to weighing and also to missing chips in some cases. Radioassay measurements may indicate that permeation of pool water into the Boraflex which might indicate a net increase in coupon weight.
- At relatively low doses (10^9 rads or less) the material looses its initial rubber elasticity. The hardness in-

creases to full scale (Shore A) and the material becomes brittle. At somewhat higher doses, the material changes color from the initial shiny black to whitish grey. The discoloration begins initially on the edges of the coupons and progresses inward with time.

- The variability of some of the neutron attenuation measurements can probably be attributed to the use of different control samples and/or differences in the spectrum of neutrons used in the pre and post irradiation measurements.

QUAD CITIES NEUTRON RADIOASSAY MEASUREMENTS

After the results of the Point Beach coupon and panel inspections were available, Commonwealth Edison initiated a series of neutron radioassay measurements of the Quad Cities spent fuel storage racks. These tests were conducted by National Nuclear Corporation and the data from these tests have been documented elsewhere (2). The data from these tests have been evaluated previously (3) and the test methods and results are summarized below.

Test Methods

Two types of neutron radioassay tests were used at Quad Cities. The first, termed the Standard Test Method, utilizes a Cf^{252} neutron source and four BF-3 proportional detectors which are sensitive to thermal neutrons. The equipment is so designed so that each detector is adjacent to one panel of Boraflex when it is placed in a fuel storage cell.

The BF-3 detectors do not record fast neutrons from the Cf^{252} source but do detect thermal neutrons which have been transmitted through the cell wall, thermalized and scattered back into the cell containing the detectors. If the cell wall contains Boraflex, the back scattered neutrons are significantly attenuated; whereas where gaps exist, the backscattered neutrons undergo significantly less attenuation.

During a measurement, two passes were made in each cell--first from

the top to the bottom and then from the bottom to the top. The count rate is continually recorded and a peak in the count rate is indicative of a discontinuity in the Boraflex absorber. The Standard Tests are considered a "go-no-go" type of measurement but do not provide an accurate indication of the size or axial location of anomalies.

After anomalies in the neutron absorber were indicated in the initial testing campaign, a special test method was developed. This method utilizes a Cf^{252} source and two He-3 proportional detectors and is intended to provide a measure of neutron attenuation in a single panel of Boraflex in a storage cell. The detectors are wrapped in lead (to reduce the potential of gamma interaction) and cadmium to form a one half inch high window in the front of the detector sensitive to thermal neutrons. The source and the detector housing are suspended from the refueling bridge mast. During measurements, the detector and source housing are moved in one half inch increments through a storage cell. The mast position and detector count rate are continuously recorded. By comparing the shape of recorded peaks in the count rate with peaks from measurements on a calibration standard containing gaps of known size, the approximate size and axial elevation of the gaps can be determined.

Results of Test Measurements

In the initial testing campaign using the Standard Test Method, a total of 203 panels containing the Boraflex absorbers in the refueling rack modules were tested. The refueling rack modules are those adjacent to the refueling canal and which received freshly discharged fuel during each of the two refueling outages. These modules had therefore received the highest gamma radiation dose. Of the 203 panels tested, 77 panels showed indication of anomalies or gaps in the Boraflex. In the rack modules which had received a lower dose, a total of 103 panels were tested of which 18 showed indication of anomalies. Although the dose to the rack modules has not been rigorously calculated, the dose in refueling racks has been estimated to be 10^9 rads. Review of the magnitude of count rate peaks recorded

in these measurements conducted by CECO personnel indicate that the average gap size in the refueling rack modules is larger than those in other rack modules which were subjected to a lower gamma radiation dose. Based on those panels determined to have gaps from the standard tests, 28 panels were selected for testing using the special test method. All 28 cells were in the region of the pool containing racks designated as refueling racks.

For the purpose of evaluating the special test data, the following procedure was used. If the data showed indication of a gap in the range of 0.0 in. to 1.0 in., the occurrence is defined as falling into Gap Size Interval 1; gaps in the range of 1.0 in. to 2.0 in. as Gap Size Interval 2; and so on. In a similar manner, each Boraflex panel was divided into 15 axial intervals or bins approximately 10 in.long.

For the 31 gaps detected in the special tests, the average gap size is 1.35 in. +/-0.87 in. (1 sigma). Of the 28 panels tested, three contained two gaps each. Accordingly, the data was reanalyzed assuming a cumulative gap size (sum of two gaps) for those three occurrences. The results of this analysis are shown in Figure 3-5. The average cumulative gap size on this basis is 1.5 in. +/- .85 in. and the maximum gap detected was 4 in..

The axial distribution of gaps is shown in Figure 3-6 in which the number of gaps versus axial interval is plotted. This distribution exhibits several characteristics which should be noted:

- There are no gaps in the first four intervals.
- There appears to be a peak in occurrence around the mid-plane of the cell.
- There appears to be a second peak in occurrence near the top of the cell.

The number of data points in Figure 3-6 is limited; however, the data does suggest that the axial distribution of gaps may be bimodal. In order to test this hypothesis the Student t-test was applied to the

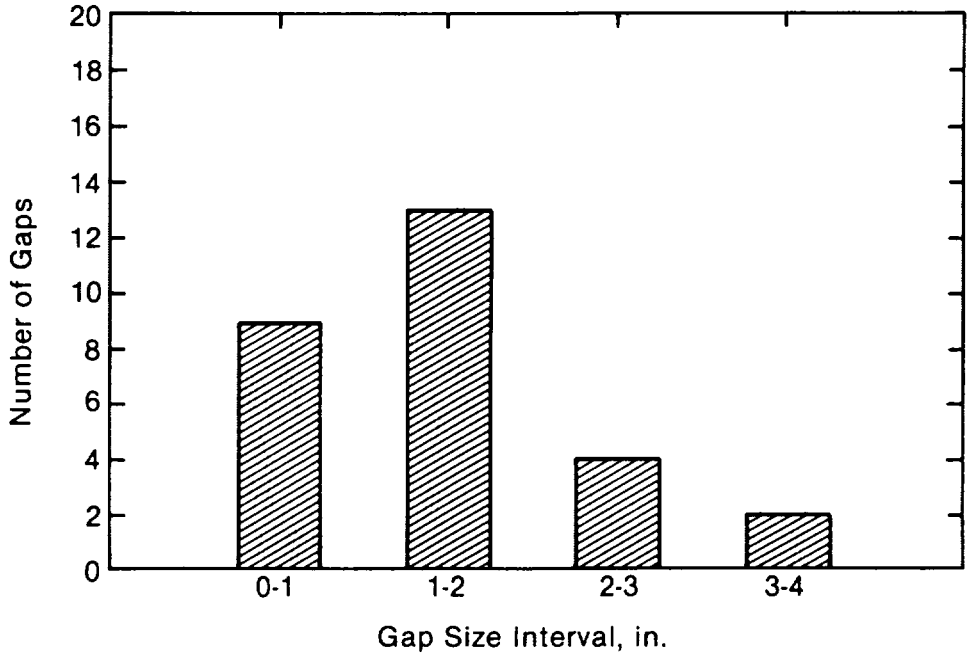


Figure 3-5. Boraflex Gap Size Distribution, NNC Special Test Measurements at Quad Cities.

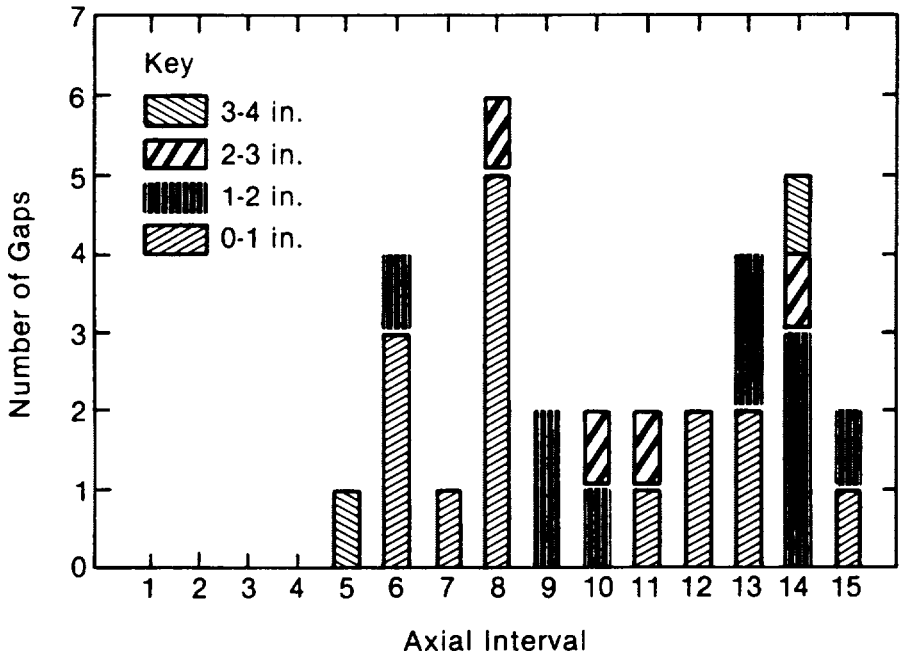


Figure 3-6. Axial Distribution of Gaps, NNC Special Test Measurements at Quad Cities.

data, first under the hypothesis that the distribution is represented by a single population. It is then hypothesized that the axial distribution of gaps is represented by two populations and the Student t-test applied again. These tests indicate that there is a higher level of confidence that the data are represented by two populations than one.

The Chi-squared test was applied to the data to determine whether the data is represented by one population normally distributed. The results of this test indicate there are insufficient data to determine whether the distribution could be normal.

The Chi-squared test was again applied under the hypothesis that the data are randomly distributed in axial intervals 5 through 15 with a mean number of gaps per interval of 2.8. If the distribution is random, the deviation between the actual number of gaps per axial interval and the mean should be represented by a normal distribution. The Chi-squared test indicates that this distribution could be normal and therefore the axial distribution of gaps random. Unfortunately, there are insufficient data to determine whether there is a higher confidence in the data being random or bimodal.

TURKEY POINT NEUTRON RADIOASSAY MEASUREMENTS

Using neutron radioassay equipment similar to that used at Quad Cities for the standard tests, 18 storage cells in the Turkey Point Unit 3 pool were surveyed (20). Of the 18 cells, 8 were in the Region 1 rack modules (see Figure 2-1) and 10 were in the Region 2 modules (see Figure 2-2). A total of 32 full length panels of Boraflex in the Region 1 cells and 22 panels in the Region 2 cells were tested.

Both the Region 1 and 2 storage racks at Turkey Point are of the "wrapper" design described in Section 2. A mastic was used to affix the Boraflex to the wrapper plates prior to storage cell assembly. The details of how the mastic was applied are not available.

During the measurements, gamma radiation background levels from pool contaminents was relatively high thereby limiting somewhat the sensitivity of the measurements. A benchmark cell with gaps of known size was not used to calibrate the equipment as had been done during the Quad Cities special tests. It has been estimated (20) that the minimum gap size detectable with the equipment used at Turkey point was about 1.0 to 1.5 in..

The storage cells selected for radioassay were those which had received the highest cumulative gamma exposure from the discharged fuel assemblies. The gamma dose has been estimated to be 7.8×10^9 rads (20). No detectable gaps were observed in any of the 18 cells surveyed. At this exposure level a maximum cumulative gap size of approximately 6 in. would be expected based on data developed in Section 5 of this report had gap formation occurred. Although the details of how the adhesive was applied are not available, differences in manufacturing methods and potentially the manner in which the mastic was applied may explain why gaps occur in the Quad Cities racks and not in the Turkey Point racks as discussed subsequently.

Section 4

REVIEW AND EVALUATION OF BISCO TEST DATA

EARLY BISCO QUALIFICATION TESTS

As part of a larger program to qualify Boraflex for use in spent fuel storage racks, BISCO sponsored a series of irradiation tests (1977 -- 1980 time frame) at the Ford Reactor at the University of Michigan at Ann Arbor (22). The purpose of these tests was to demonstrate the radiation stability of Boraflex and its suitability for long term service in spent fuel pools. The tests were conducted in a reactor facility where both neutrons and gamma radiation are present to accelerate the accumulation of effective gamma exposure. Accordingly, it must be noted that differences in irradiation environment exist between the test experiments and spent fuel pool environment. In addition, there are probably differences in the gamma spectrum in the test reactor and in the spent fuel pool environment. The results are reported in terms of rads gamma dose but the equivalent dose (when fast neutron and recoil particle damage from neutron alpha reactions in B_4C are considered) is probably much larger and the radiation effects may differ. In terms of total energy deposited, the test irradiation conditions are estimated to result in a dose approximately an order of magnitude greater than that projected for gamma exposure only over the service life of spent fuel racks.

In these tests, small samples of Boraflex (of both 25 and 40 w/o B_4C) approximately 6 in. in length, .25 in. in width and .100 in. in thickness were irradiated in air, distilled water and borated water (2000 ppm) to exposures in the range of 1.6×10^{10} to 1.03×10^{11} rads gamma. The samples were characterized both pre and post irradiation by physical dimensions, sample weight, specific gravity, hardness and tensile strength (data not reported for all samples after irradiation). During irradiation, Boraflex samples in each of the three environments were monitored for gas evolution in terms of total

volume, rate and composition. In addition, one sample was irradiated to a low dose in the spent fuel storage area of the Ford Nuclear Reactor. Additional data on irradiation of Boraflex have been reported in the literature (23,24) and have been included in this review. In a separate test, samples of unirradiated Boraflex were subjected to long term exposure in hot water. These test results have been summarized and evaluated.

Dimensional Changes

The measurements of physical dimensions have demonstrated in most cases a net shrinkage of the samples after irradiation. The data are variable but the general trend is about 2-3% shrinkage in width and up to 8% shrinkage in thickness. The accuracy of these measurements is not known but it is suspected that accurate dimensional measurements on small samples would in general be difficult and especially so in the case of measuring the thickness of very thin samples. This is particularly true in the pre-irradiation state when the material still has the properties of an elastomer.

Since the physical dimension data may not provide a reliable indicator of the total extent of Boraflex shrinkage, the weight and specific gravity data (pre and post irradiation) from References (22), (23) and (24) have been evaluated. Table 4-1 contains a summary of all published data related to weight and specific gravity changes. The specific gravity measurements were made by weighing the sample dry and immersed in water. The true sample volume is then the sample weight times the reciprocal of the specific gravity. This change in sample volume then reflects geometrical changes in length, width and thickness as well as any open porosity which may have developed. The data contained in Table 4-1 have been plotted in Figure 4-1. Review of Figure 4-1 indicates the following:

- There are no data between 2.8×10^8 and 1.5×10^{10} rads.
- It appears that initially all the samples underwent a reduction in true volume. From the data it would appear that at an exposure in the range of 1 to 2

Table 4-1

FRACTIONAL CHANGE IN COUPON WEIGHT, SPECIFIC GRAVITY, TRUE VOLUME AND SPECIFIC VOLUME VERSUS EXPOSURE

				Fractional Change			
Irr. Media	w% B_4C	Data Source	Exposure (rads)	Weight	Specific Gravity	True Volume	Specific Volume
Air	40	(22)	2.81E+08	0.002	0.009	-0.007	-0.009
		(24)	1.50E+10		0.072		-0.067
	25	(22)	1.60E+10		0.048		-0.045
	25	(22)	1.03E+11	-0.024	0.122	-0.130	-0.109
	40	(22)	1.60E+10	-0.025	0.155	-0.156	-0.135
	40	(22)	2.49E+10	0.023	0.219	-0.161	-0.180
	40	(22)	1.03E+11	-0.012	0.077	-0.083	-0.071
Water	+	(23)	5.00E+10		0.189		-0.159
		(24)	1.50E+10		0.122		-0.109
	25	(22)	1.60E+10		-0.005		0.005
	25	(22)	1.03E+11	0.174	0.157	0.015	-0.135
	40	(22)	1.60E+10	0.082	0.229	-0.119	-0.186
	40	(22)	2.49E+10	0.017	0.218	-0.165	-0.179
	40	(22)	1.03E+11	-0.024	0.014	-0.038	-0.014
Borated Water		(24)	1.50E+10		0.106		-0.095
	25	(22)	1.60E+10		0.135		-0.119
	25	(22)	1.03E+11	0.167	0.132	0.031	-0.117
	40	(22)	1.60E+10		0.215		-0.177
	40	(22)	2.49E+10	0.019	0.229	-0.171	-0.186
	40	(22)	1.03E+11	0.154	0.128	0.023	-0.113

+ Boron-10 loading of 0.02 g/cm2

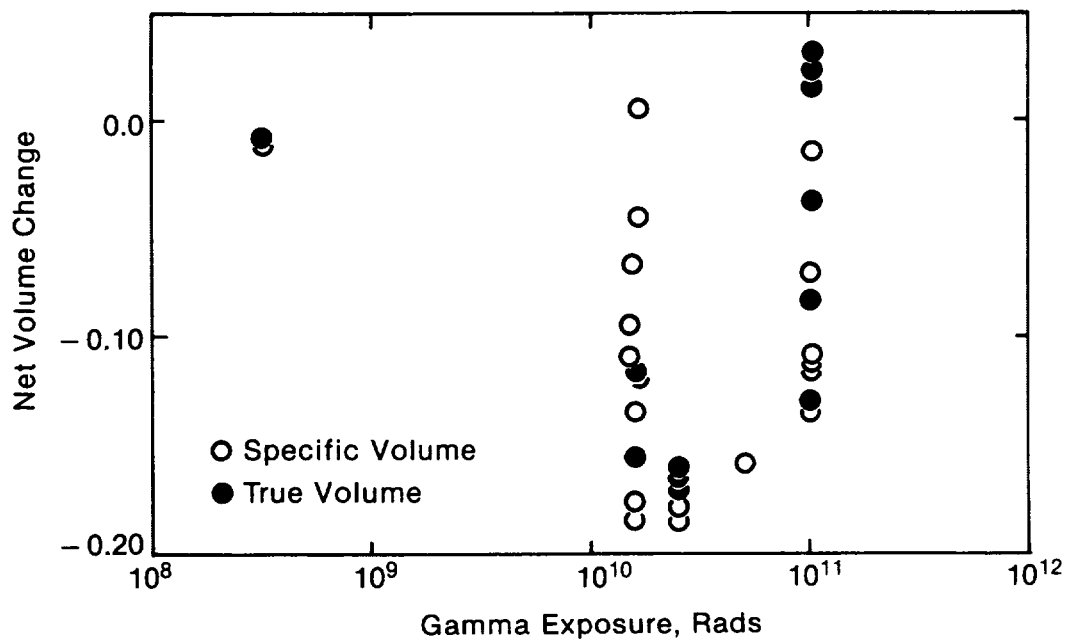


Figure 4-1. Net Change in Specific Volume versus Gamma Exposure. (Source: Irradiation Study of Boraflex Neutron Shielding Materials, 748-10-1 Rev. 1, Brand Industrial Services, Inc., Park Ridge, Illinois, August 1981.)

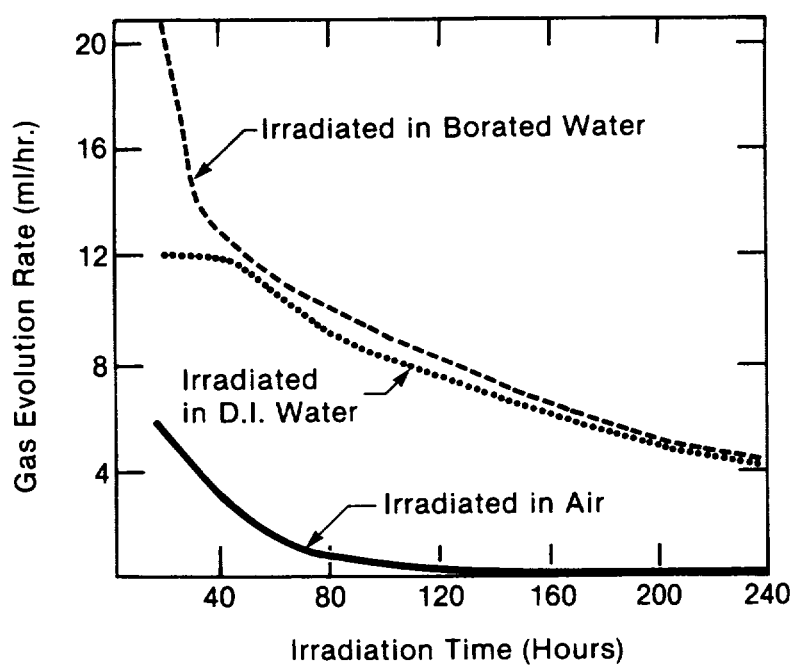


Figure 4-2. Gas Evolution from Boraflex During Radiation Exposure. (Source: Irradiation Study of Boraflex Neutron Shielding Materials, 748-10-1 Rev. 1, Brand Industrial Services, Inc., Park Ridge, Illinois, August 1981.)

$\times 10^{10}$ rads (gamma), the volume reduction ceases and the samples begin to swell. A maximum fractional change in sample volume change of -.171 is observed at 2.49×10^{10} rads.

- The extent of apparent swelling tends to depend on whether the samples were irradiated in air or in water (either distilled or borated). At 1.03×10^{11} rads, the samples which were irradiated in an aqueous environment exhibit the greatest extent of swelling.

Gas Evolution Data

During the irradiation of some of the samples, offgas produced when Boraflex is irradiated was collected and analyzed. The offgas consisted primarily of H_2 with some N_2, O_2 and lesser amounts of CO CO_2 and hydrocarbons as shown in Table 4-2. The source of N_2 is not clear; however, potential sources include air entrained in the samples during manufacture or leakage in the sampling lines. The other offgas products are among those expected for this type of material although their relative compositions differ from measurements by other investigators as discussed subsequently. For the samples irradiated in air at 7×10^7 rads/hour, the gas evolution rate diminished to zero after approximately 150 hours (accumulated dose of 1.0×10^{10} rads) as shown in Figure 4-2. The samples irradiated in distilled and borated water showed continued gas evolution which is believed to be largely due to radiolysis of the water in the reactor environment.

Mechanical Properties

Pre and post irradiation measurements of various mechanical properties of Boraflex have been reported in a number of References (22--25). These measurements include tensile strength, elastic modulus and Shore A hardness for both the unfilled polymers and Boraflex with various compositions of B_4C filler. The results as indicated by these test data can be summarized as follows.

- Tensile strength: The data show considerable variability with some samples showing increases and others showing decreases. This variability may be a result of sample configuration and set during irradiation. In one

Table 4-2

GAS EVOLUTION FROM BORAFLEX DURING REACTOR IRRADIATION

Irradiation Environment	Gas Evolution: Average Gas Generation Rate (ml/g)	(ml/g-h)	Constituent Percentage(%): H_2	O_2	N_2	CO_2	CO	CH_4	C_2H_6
Dry	74	0.4	55	13	25	1	0	1	5
Demin. H_2O (water control)+	206	0.9	57	10	29	3	0.3	0.2	0.1
			(64)	(10)	(26)	(0)	(0)	(0.5)	(0.1)
Bor. H_2O (water control)+	236	1.1	79	5	7	3	1	1	4
			(57)	(40)	(2)	(0)	(0)	(0.4)	(0.5)

+Irradiation capsule filled with only water and no Boraflex.

Source: R. B. Burn and G. Blessing. "Radiation Effects on Neutron Shielding Materials", in Transactions of the American Nuclear Society, vol. 33, suppl. 1, 1979, pp.48-49.

report (25), the tensile strength increased up to 7 x 10^8 rads (pure gamma radiation). It is believed the NS-1 polymer in this report is unfilled Boraflex.

- Elastic modulus: Only one report (25) was identified which presented data for elastic modulus as a function of gamma dose. As shown in Table 4-3, the elastic modulus of the NS-1 polymer increases dramatically with gamma dose.

- Elongation-to-break: Table 4-3 contains the only reported measurements of elongation to break measurements as a function of gamma dose. It is noted that elongation to break decreases rapidly with dose as the material hardens and embrittles.

- Shore A hardness: There are several reported measurements of Shore A hardness as a function of gamma dose. In one report (22) an increase in Shore A hardness from 78 to 89 was observed after irradiation to 2.8 x 10^8 rads in a pure gamma field. In the reactor tests, the hardness data reported were mostly in excess of 90 Shore A with variations depending on the composition of B_4C. Shore A measurements of greater than 90 are not particularly meaningful (19) and a Shore D durometer should be used. The use of a Shore D durometer on irradiated Boraflex may however result in fracture of the sample.

Neutron Attenuation

Neutron attenuation measurements have been reported for pre and post irradiated samples. The purpose of these measurements is to verify the presence of B-10 after irradiation (22-25). Most samples showed very small changes in neutron attentuating properties pre and post irradiation relative to the inherent statistical uncertainties.

Long Term Exposure to Hot Water

Long term out-of-pile testing of unirradiated Boraflex at elevated temperatures and in aqueous solutions has been reported (26). The samples of Boraflex were immersed in borated water (approximately 3000ppm) at 240°F for 6200 hours. The borated water was neutralized with NaOH to a ph of 9.0--9.5. After testing the sample showed an average dimensional decrease along the side of the sample of 0.93% and an increase in weight of 0.24%. Gas evolution from the sample was

Table 4-3

EFFECT OF GAMMA RADIATION ON BISCO NS-1 POLYMER

Dose Megarads	Tensile Strength (PSI)	Elongation %	Elastic Modulus (PSI)
0	510	68	750
16	516	55	938
60	550	40	1375
111	504	38	1326
164	553	23	2404
713	896	3.3	27151

Sample: .1 in. x 1 in. Tensile Bar pulled @ 10 inches/minute.

Source: Boraflex Suitability Report, Revision 1. Park Ridge, Ill.: Brand Industrial Services, May, 1978, 1047-1.

measured with a total of 5.22 cubic inches of gas at STP being generated per square inch of sample surface over the entire test period. Gas evolution diminished with time with 41.3% of all gas evolved during the first quarter of testing and only 8.7% evolved in the last quarter of the test period. The evolved gas was analyzed periodically for composition and showed approximately 20% H, 53% CH_3, 5% CO_2 with the balance comprised of various hydrocarbons. Whether gas evolution implies thermal decomposition at these relatively low temperatures is not clear. Typically, the polysiloxanes are known for service at elevated temperatures (27). The observed gain in sample weight after testing suggests that the samples may be absorbing borated water. In any case, the test is not particularly meaningful since the material tested was unirradiated. As discussed subsequently, the effect of hot water immersion on irradiated Boraflex is probably different than on the unirradiated material.

RECENT BISCO RADIATION TESTING

As a consequence of the gap phenomenon observed at Quad Cities, BISCO initiated a new series of test irradiations in the spring of 1987, the objective of which was to quantify the maximum extent of Boraflex shrinkage (28). Two series of tests were conducted including the irradiation of coupons in a pure gamma spectrum (Co-60) as well as test reactor irradiations in the University of Michigan Ford Nuclear Reactor. In the first test, a series of ten relatively large (2.5 in. x 12 in.) coupons were placed in a Co-60 facility and periodically removed for inspection and characterization. The samples were then returned to the Co-60 facility for subsequent irradiation until they had received a total integrated gamma dose of 1×10^9 rads. The ten samples were precharacterized with respect to dimensions and weight and changes in these attributes were determined after each irradiation interval. After the final irradiation period, Shore A and D hardness were determined.

In the reactor tests, twelve groups of nine small (1.6 in. x 1.6 in.) coupons each were irradiated. At scheduled irradiation intervals, one group of nine samples was removed and characterized. After

characterization the samples were not reinserted for further irradiation but rather another sample group was removed after the next irradiation period. Each sample was precharacterized with respect to dimensions, weight, Shore A and D hardness and neutron attenuation and these attributes were determined after irradiation as well. The last group of nine samples received a cumulative gamma exposure of 1.12 x 10^{11} rads, plus energy deposited by neutrons and recoil particles. The total dose has been estimated to be approximately an order of magnitude greater than the gamma dose alone.

The results of the reactor tests were not particularly conclusive with respect to dimension changes due in part to the small sample size and in part to erosion from the edges of some samples. Accordingly, BISCO has initiated the irradiation of larger samples in a test reactor at the University of Missouri.

Dimensional Changes

Only the changes in sample length and width are considered here. Measurements of sample thickness are considered meaningless owing to the large variability of the data. This is attributed to the measurement of small changes in very thin samples. The percent change in sample length and width from both series of tests are plotted in Figure 4-3. The open symbols in this figure represent changes in coupon length and the closed symbols changes in coupon width. The symbols with error bands are data points from the reactor tests and represent +/- one sigma. The data points without error bands are from the Co-60 irradiations. Owing to the large size of these samples, the standard deviation is much less (typically less than +/- .05% in length and less than +/- .2% in sample width). At each exposure level the indicated change is the average of all nine or ten samples in the group.

Several features of the data presented in Figure 4-3 are worthy of note:

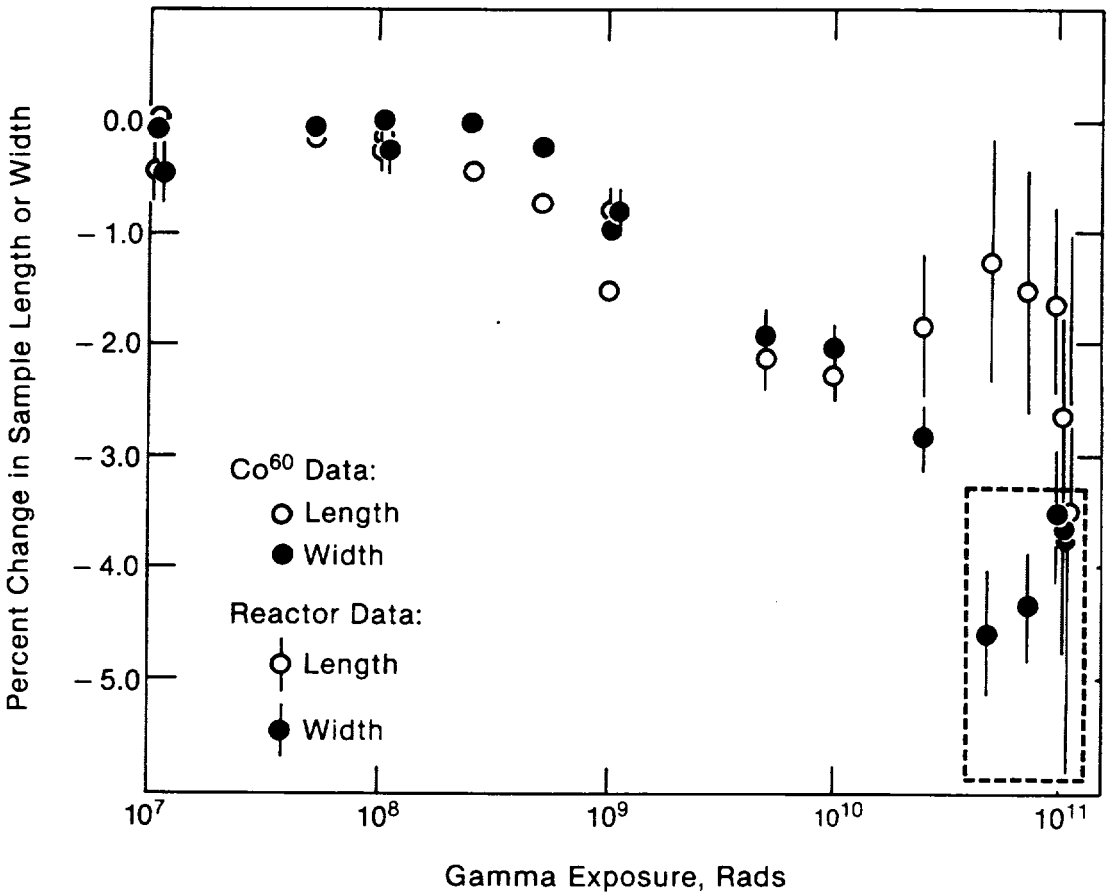


Figure 4-3. Percent Change in Sample Length and Width versus Gamma Exposure. (Source: Irradiation Study of Boratlex Neutron Absorber Interim Test Data, NS-1-050 Interim, Brand Industrial Services, Inc. Park Ridge, Illinois, November 25, 1987.)

- Those samples irradiated in the Co-60 facility exhibit about 50% greater shrinkage in sample length than in sample width. Discussions with BISCO personnel (29) indicate that the samples were cut from sheet material with the length being in the forming direction during the calendaring-like process used to manufacture Boraflex.

- The Co-60 data has been fitted to a linear relation of the form

  $$dL/L = (-1.4156 \times 10^{-9})R - 0.0781$$

  as shown in Figure 4-4. Using all data points except the first at 1×10^7 rads, provides the best fit with a correlation coefficient 99.92%. The first data point has been omitted owing to "end effects". This linear relationship at low doses has been observed in PDMS by others as discussed in Appendix B.

- The reactor data contained in the box in Figure 4-3 at 5×10^{10} rads and beyond may overstate the actual sample shrinkage owing to observed (28) rounding and erosion of the edges of the samples. It has been postulated (28) that alpha particle damage may be responsible for this phenomenon. Water permeation and chemical effects may also be a factor.

- The larger variability in sample length and width changes as well as loss in sample weight discussed subsequently at higher doses tend to support this hypothesis.

- Discussions with BISCO personnel (29) have indicated that data are not available which make it possible to relate either the length or width direction of the reactor samples to a particular manufacturing process variable.

Figure 4-5 contains the average change in sample thickness for each series as a function of gamma dose. The large variability in the measurements make it difficult to infer absolute net changes in thickness. The variability is likely due to trying to measure small dimensional changes in very thin samples.

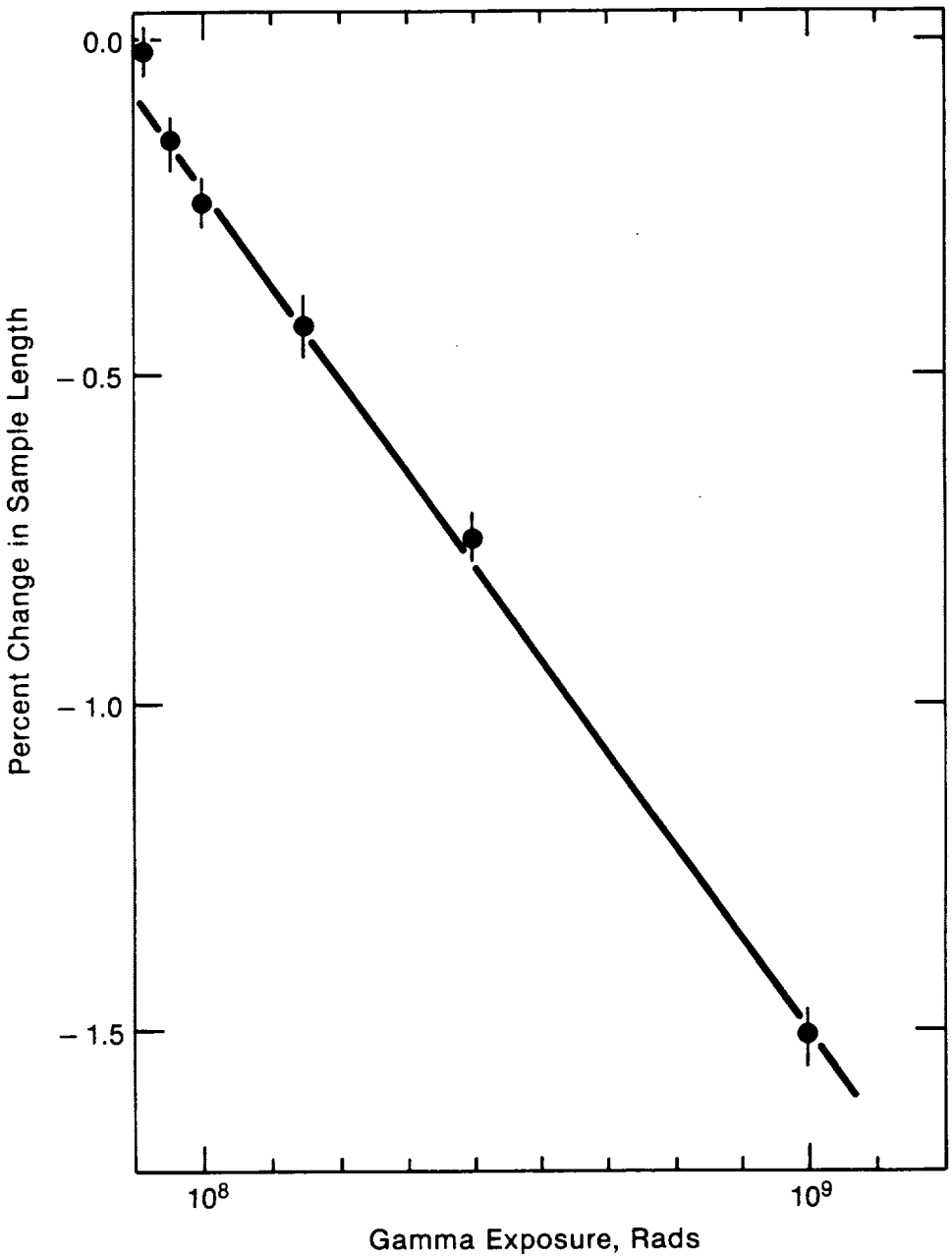


Figure 4-4. Linear Fit of Percent Change in Sample Length versus Gamma Exposure. (Co-60 Irradiations Only).

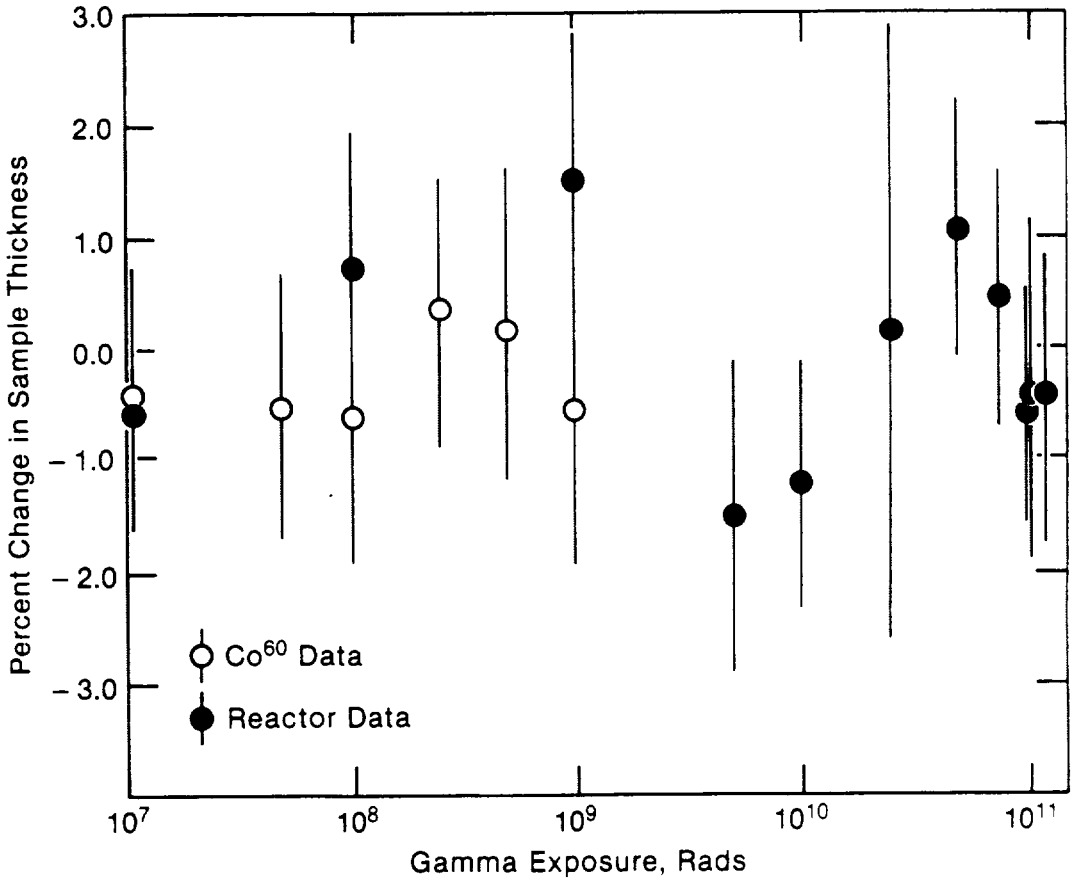


Figure 4-5. Percent Change in Sample Thickness versus Gamma Exposure. (Source: Irradiation Study of Boraflex Neutron Absorber Interim Test Data, NS-1-050, Rev. 1 Interim, Brand Industrial Services, Inc. Park Ridge, Illinois, November 25, 1987.)

Sample Weight Changes

The average weight change in each group of samples is plotted as a function of gamma exposures in Figure 4-6. The open symbols are for the Co-60 samples which were irradiated in air. These samples show a small net gain in weight up to an exposure of 1×10^9 rads. Based on gas evolution associated with gamma induced crosslinking, one might expect a net decrease in sample weight as hydrogen and hydrocarbons are evolved. Other investigators (34) however, have noted that as free radicals are formed in PDMS during irradiation, they may recombine with constituents in air or with water vapor as discussed in Appendix B. This may explain the net increase in sample weight as irradiation continues.

A similar trend is noted in the reactor samples up to 2.5×10^{10} rads. These samples were irradiated in an aqueous environment although the chemistry of the aqueous solution is not known. Beyond 5×10^{10} rads, the trend seems to reverse and at the higher doses the samples show a net decrease in sample weight. As this occurs, the variability of the data increases and it has been postulated (29) that this is due to Boraflex which has been eroded from the edges of the samples. The initial increase in sample weight is believed to be due to water absorption initially beginning at the edges of the samples and permeating inward.

Shore A and D Hardness

The Shore A and D hardness was measured on all reactor samples and on the Co-60 samples after a cumulative exposure of 1×10^9 rads. The data are plotted in Figure 4-7. The Shore A hardness saturates rapidly with a value approaching full scale (100) at 1×10^9 rads. The Shore D hardness tends to saturate beyond exposures of 1×10^{10} rads. However, due to the brittle nature of Boraflex at these exposures, the samples tended to break when subjected to Shore D durometer measurements.

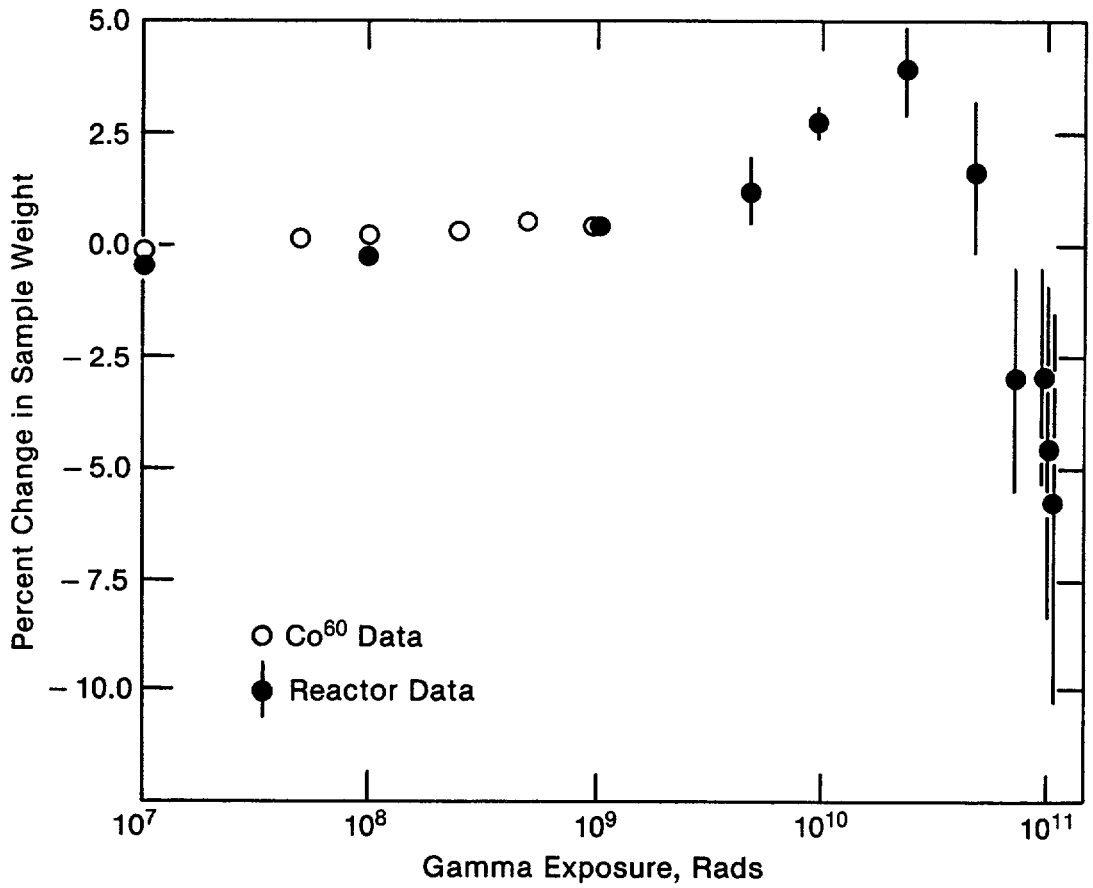


Figure 4-6. Percent Change in Sample Weight versus Gamma Exposure. (Source: Irradiation Study of Boraflex Neutron Absorber Interim Test Data, NS-1-050, Rev. 1 Interim, Brand Industrial Services, Inc. Park Ridge, Illinois, November 25, 1987.)

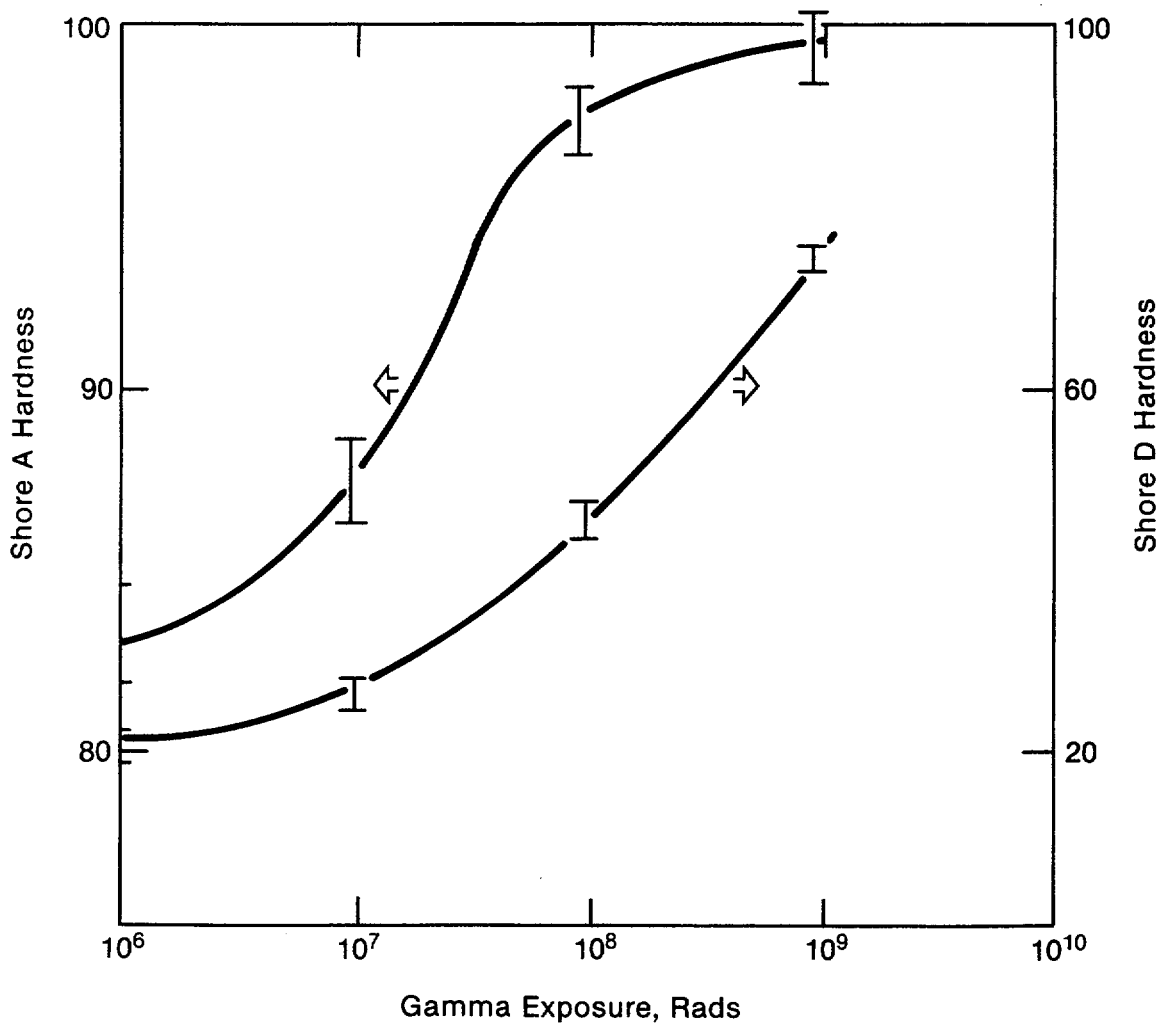


Figure 4-7. Shore A and Shore D Sample Hardness versus Gamma Exposure. (Source: Irradiation Study of Boraflex Neutron Absorber Interim Test Data, NS-1-050, Rev. 1 Interim, Brand Industrial Services, Inc. Park Ridge, Illinois, November 25, 1987.)

Neutron Attenuation

Pre and post irradiation neutron attenuation measurements have been reported for the specimens irradiated in the test reactor. The average pre irradiation attenuation for all samples was 0.979 +/- .002 and 0.0981 +/- .002 after irradiation, thus indicating no change in neutron absorption within the limits of detectability of this type of measuring technique.

Visual Appearance

At cumulative gamma exposures beyond 10^9 rads, Boraflex is reported (28) to have the appearance and feel of a ceramic material. The material is relatively strong in compression but subject to brittle fracture in tension. When fractured, the material breaks into large pieces. At doses of 1×10^{10} and beyond, a fine whitish-grey powder appeared on the surface of many samples. The occurrence of whitish-grey powder was most prevalent on the edges of the samples extending inward for about 1/4 inch. The powder could be wiped off easily and thereby exposed Boraflex of jet black color underneath.

Specific Gravity Measurements

Subsequent to the issuance of Reference (28), the measurement of sample density or specific gravity has been reported (30) for some of the samples irradiated in the test reactor. These data are shown in Figure 4-8. The data indicate a maximum change in specific gravity of about 20% at a gamma exposure of 1×10^{11} rads. Also plotted in Figure 4-8 is the corresponding change in sample specific volume as a function of gamma dose. Changes in true sample volume were not computed since the pre and post irradiation sample weights were not available. The data in Figure 4-8 show considerably less variability than the corresponding earlier data (Figure 4-1) presumedly due to more carefully controlled experimental conditions. Nevertheless, the conclusions seem to be the same; that is, the change in specific volume seems to reach a maximum asymptotic value beyond 1.0×10^{10} rads of about -17%. Contrary to the results from the earlier data, there seems to be no indication of sample swelling at exposures of 1×10^{11} rads.

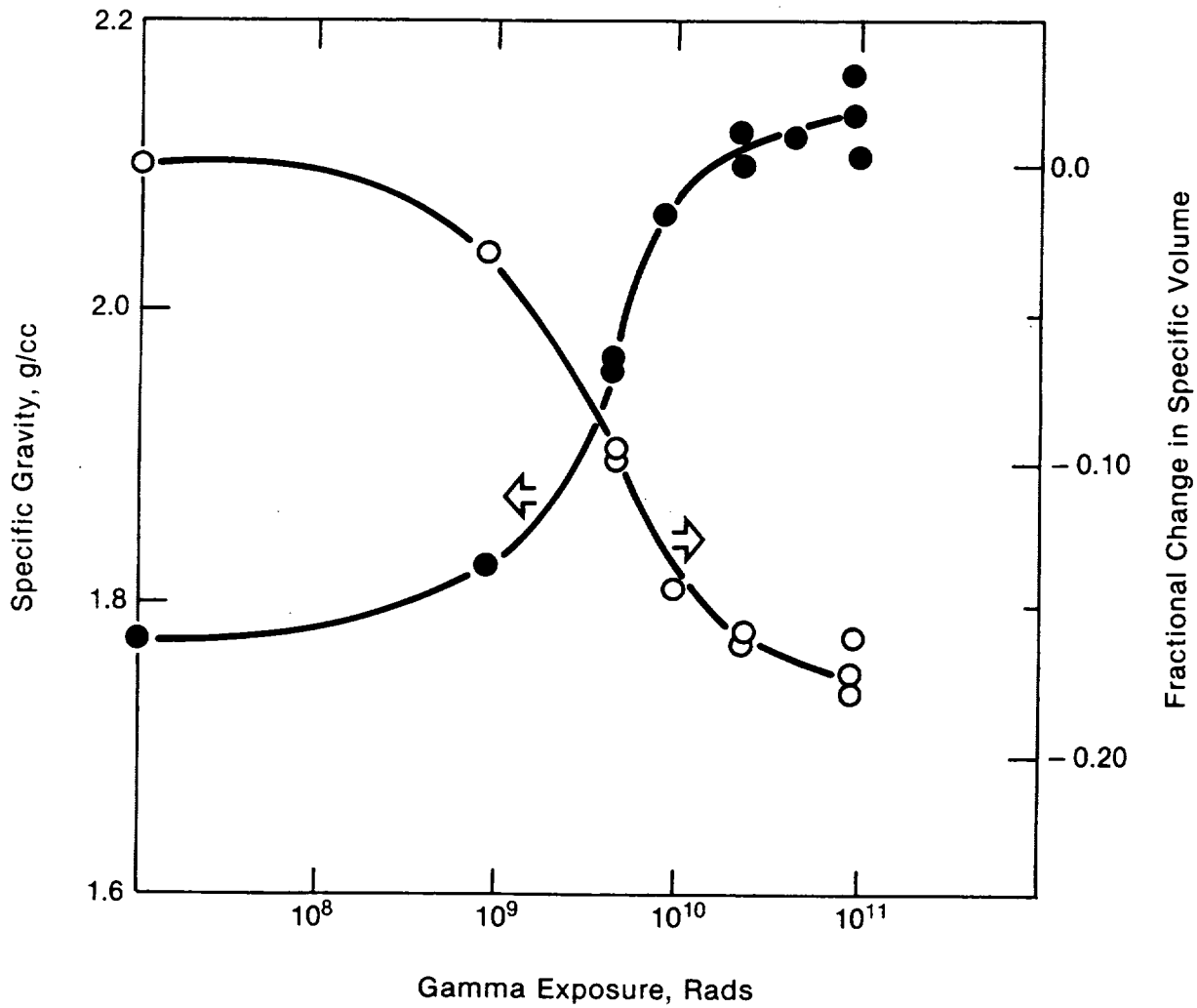


Figure 4-8. Specific Gravity and Specific Volume of Boraflex versus Gamma Exposure. (Source: Reference 30.)

Discussion of Interim Report Conclusions

Preliminary results of the recent BISCO irradiation tests were reported in a BISCO Interim Report in November of 1987 (28). On the basis of the test irradiations, the Interim Report (28) cites some specific conclusions with respect to the behavior of Boraflex in a radiation environment. Certain of those conclusions described in the Interim Report differ somewhat from those in this EPRI study. These include, 1) the definition of those factors that contribute to the determination of total service life, 2) the extent of maximum shrinkage that may occur from irradiation, and 3) the effect of irradiation on the physical and chemical composition of Boraflex.

Relative to the first point, it is acknowledged that the total integrated radiation dose (gamma, alpha, and neutron) to which the reactor samples were subjected is likely to be well in excess of that expected during the 40 year design lifetime of spent fuel storage racks; however, the duration of the tests was only five to six months. The effects of long term exposure of irradiated Boraflex to an aqueous environment cannot be assessed from the available data and therefore ongoing surveillance should be performed to verify performance. Also, because the water chemistry of the test reactor was not reported, it is not known whether it is representative of that normally found in a spent fuel pool. In addition, the details of sample configuration, other than that a "sandwich arrangement" of nine samples, have not been presented and it is therefore uncertain whether all sides, or just the edges of the Boraflex samples, were exposed to the aqueous environment during the test irradiations. Additionally, it is probably not practical to quantitatively project panel width allowance for edge erosion effects from the data presented.

To the second point, the Interim Report concludes that the maximum shrinkage of Boraflex is between 2 to 2 1/2% due to radiation effects.

Data presented in Section 3 of this report and discussed in Section 5 indicates that the maximum linear shrinkage could be more in the range of 3 to 4%. Differences in the radiation environment and spectrum in-reactor versus the spent fuel pool may result in different radiation damage mechanisms and hence the difference in shrinkage.

Relative to the third point, the Interim Report concludes that radiation transforms Boraflex from a filled polymer to a "stable ceramic". The Interim Report contains insufficient data to support this conclusion.

Section 5

DISCUSSION

The previous sections of this report have presented data from the utility surveillance programs and BISCO test irradiations. Additionally, included as Appendix A is a summary of the physical properties and characteristics of Boraflex and other polysiloxane polymers derived from the literature. Appendix B contains a review of the relevant literature on the effects of radiation on polysiloxane polymers. In this section, the data from these various sources are combined and evaluated with the intent of quantifying the combined effects of gamma irradiation and long term exposure to the pool water on Boraflex. Potential factors influencing gap formation and subsequent growth are also discussed.

RADIATION DAMAGE MECHANISMS AND G-VALUES

When Boraflex is exposed to gamma radiation, the material undergoes changes. These changes have been evident in the BISCO test irradiations as well as experiments with materials similar to Boraflex. The radiation induced changes include:

- Evolution of gases including hydrogen, methane and other hydrocarbons
- Physical shrinkage, accompanied by an increase in specific gravity and decrease in specific volume
- Loss of rubberelasticity, increase in hardness and an increase in elastic modulus
- Observed formation of blisters in some specimens believed to be the result of gases which are formed and subsequently trapped in the polymer matrix when exposed to radiation
- Change in surface color from a shiny black to a whitish gray and a tendency of the discolored material to powder

- Permeation of water believed to be the result of the development of open porosity

In addition, there is evidence that indicates environmental factors such as the presence of molecular oxygen, water and other agents may be factors which influence the behavior of this material under irradiation.

The radiation induced changes outlined above are consistent with the radiation damage mechanisms of crosslinking and scissioning as described in Appendix B. At low radiation doses, the evidence suggests that the predominant radiation change mechanism in PDMS is crosslinking. A consequence of crosslinking is the abstraction (release) of $H^{\bullet}$, $CH_3^{\bullet}$ and other radicals and the subsequent formation of crosslink bonds between adjacent polymeric chains. Physically, the crosslinks cause the adjacent chains to be pulled closer together thereby resulting in volume shrinkage and increase in the specific gravity of the material.

As the radiation dose is increased, the number of potential sites for formation of crosslinks is decreased and the translational motion of the polymeric chains become restricted due to a relatively large number of inter-chain ties. Accordingly, crosslinking tends to saturate and the physical changes (shrinkage and increase in density) associated with this damage mechanism approach asymptotic values. At this point the free radicals may continue to be generated without significant formation of crosslink bonds and scissioning is likely to become the predominant radiation damage mechanism. Scissioning is the severing of bonds in the spine of the polymer which results in a reduction in molecular weight and eventual degradation. Evidence has been cited in Appendix B which suggests that the presence of oxygen, water and other agents may favor scissioning over crosslinking.

Gas evolution measurements from samples irradiated in air (see Figure 4-2) indicate that measurable gas evolution ceases at or before a gamma radiation exposure of 1×10^{10} rads, thereby suggesting

crosslinking has saturated at or before this exposure. Since these experiments were conducted in a test reactor and not a pure gamma radiation field, it is useful to estimate the theoretical absorbed gamma dose required before crosslinking saturates. In Figure B-3, the G-value for crosslinking in PDMS is presented as a function of gamma irradiation dose. At low doses, the G-value is about 2.8 and this diminishes to about .65 at a dose of 500 Mrads. The average G-value has been estimated from the data of Delides and Shepherd by extrapolation and integration of G(E) and is in the range of .12 to .20 to doses in excess of 1×10^{10} rads.

In a previous report (3), the total absorbed gamma dose required to crosslink all monomer units in the polymer has been estimated. It has been noted, however, that once crosslinks between chains have been established that restricted translational motion of the chains tends to preclude further crosslinking. For PDMS, the data from Delides and Shepherd (31) indicate that, at saturation, at most only about 14% of the monomer units crosslink.

Using this saturation crosslink density and a range of G-values, it is possible to estimate the dose at which crosslinking in PDMS saturates. We note that:

$$1 \text{ Megarad} = 6.25 \times 10^{19} \text{ ev/g} \qquad (5\text{-}1)$$

and that for a given G value, we can write the number of crosslinks/g induced by 1 Megarad absorbed dose as:

$$1 \text{ Megarad} \text{ ----> } G \times 6.25 \times 10^{17} \text{ crosslinks/g} \qquad (5\text{-}2)$$

Since the molecular weight of the PDMS monomer unit is 74:

$$1 \text{ Megarad} \longrightarrow G \times 4.62 \times 10^{19} \text{ crosslinks/mole} \qquad (5\text{-}3)$$

Since one mole consists of 6.023×10^{23} units, the absorbed dose required to crosslink all monomer units is $(1/G)\ (1.302 \times 10^4)$ Megarads. If f_{max} is the fractional number of monomer units crosslinked at saturation, then the dose to crosslink all possible units is:

$$D_{sat} = (f_{max}/G)\ (1.302 \times 10^4) \text{ Megarads} \qquad (5\text{-}4)$$

Using G-values in the range of .12 to .20 and a value of .14 for f_{max}, it is possible to use Equation 5-4 to provide upper and lower estimates of the absorbed dose to crosslink all potential sites. This exercise provides a dose to crosslink all potential sites of 9×10^9 to 1.5×10^{10} rads.

While it is acknowledged that the polymer matrix in Boraflex may not be identical to the PDMS studied by Delides and Shepherd, it is believed that the estimated dose required for crosslinking to saturate would be approximately the same. It is believed that Boraflex in its as-produced condition has some degree of initial crosslinking. The degree of initial crosslinking is probably induced chemically during the vulcanization process and is indicated by the initial values of Shore A hardness and elastic modulus of the material. Initial crosslinking would tend to reduce f_{max}, the maximum fractional crosslinking density which can be induced by subsequent irradiation.

It has been noted that the Boraflex polymer probably contains radiation stabilizers in the form of free carbon and SiO_2. These stabilizers are believed to prevent crosslinking after abstraction of either $H^{\bullet}$ or $CH_3^{\bullet}$ from the polymer.

Referring to Equation 5-4, it is likely that additives and modifiers which may be present in Boraflex relative to PDMS have the effect of reducing f_{max} as well as the G-value. Accordingly, the net effect may be approximately the same estimated dose to crosslink all possible sites as for PDMS. A saturation dose for crosslinking of about 1×10^{10} rads gamma seems consistent with the gas evolution measurements from the early BISCO test program as well as with specific gravity measurements from the latest BISCO test program.

Changes In Specific Gravity and Specific Volume Versus Dose

The specific gravity measurements from the latest BISCO tests provide a means to estimate the change in specific volume as a function of absorbed gamma dose. This provides not only an estimate of the maximum change in sample specific volume but also the functional dependence of the change in specific volume with dose.

Bopp and Sisman (32) have noted that in crosslinking polymers the decrease in specific volume may be fitted to the equation:

$$dV(R) = dV_{sat} \left(1 - e^{-cR}\right) \qquad (5\text{-}5)$$

where:

R = gamma dose, Rads
$dV(R)$ = fractional change in specific volume
dV_{sat} = asymptotic fractional change in specific volume
c = constant, Rads^{-1}

The latest BISCO measurements of specific volume (reciprocal of specific gravity) versus gamma dose have been fitted to Equation 5-5 with $c = 1.735 \times 10^{-10}\ R^{-1}$ and $dV_{sat} = -.17$. This resulting curve is compared to the data points in Figure 5-1. This comparison

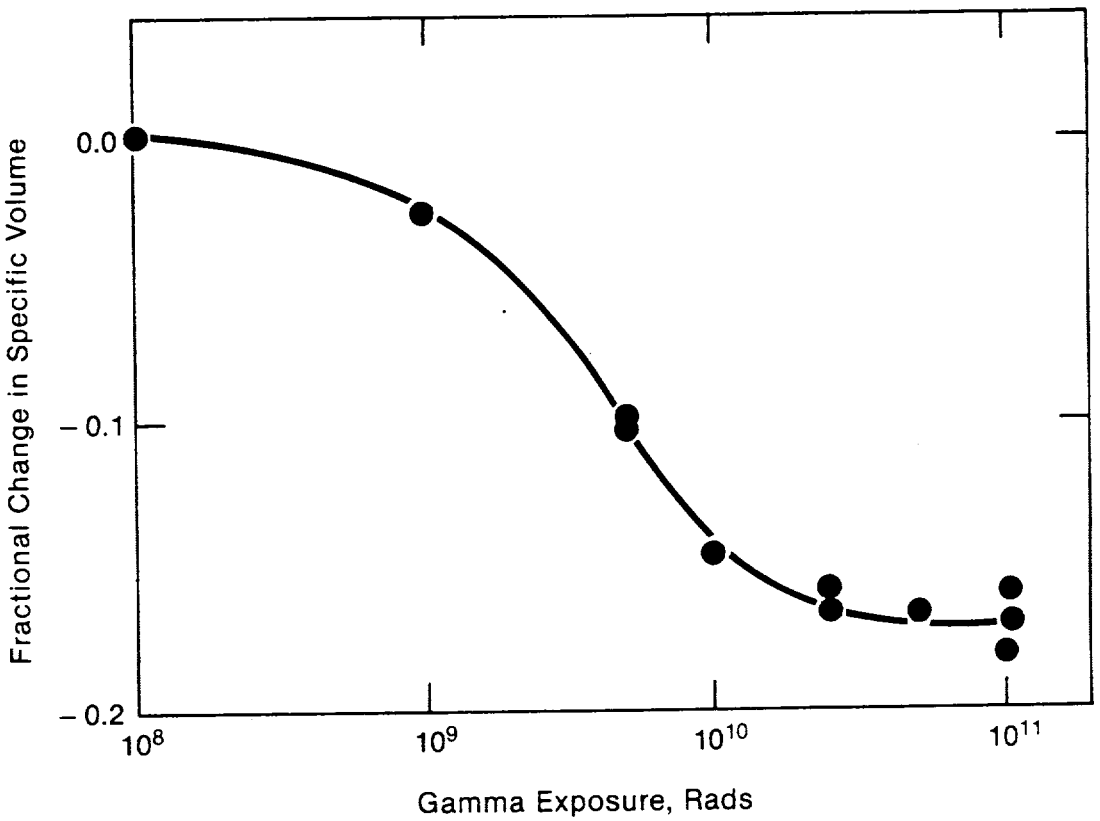


Figure 5-1. Specific Volume Change of Boraflex versus Gamma Exposure from the Latest Bisco Reactor Irradiation Tests.

indicates that the latest BISCO data are well represented by Equation 5-5. In considering the early BISCO data (Figure 4-1), while it does exhibit considerable variability it tends to confirm the maximum magnitude of specific volume change as provided by the latest test data.

It should be noted that this change in specific volume shown in Figure 5-1 reflects changes in the "true" sample volume since the specific gravity measurements on which they are based are via immersion techniques. These volume changes represent changes in envelope dimensions (geometric) or shrinkage of the samples as well as any porosity open to water permeation which may have developed.

Changes In Boraflex Dimensions Versus Dose

Changes in Boraflex dimensions versus gamma exposure can be inferred from a number of data sources. These data sources include the latest BISCO Co-60 and test reactor irradiations, some data from the utility coupon programs (where the dose is known or has been estimated) as well as from the Quad Cities neutron radioassay measurements of gaps. A composite of all data relative to length or width changes in Boraflex collected as part of this study is presented in Figure 5-2.

Perhaps the most precise low dose (up to 10^9 rads) data are from the BISCO Co-60 irradiations. These data indicate an average shrinkage (of ten specimens) in coupon length of 1.506% with a relatively low deviation of +/- 0.043% at the one sigma level. At the same dose the average shrinkage in width is -.957% +/- .191%. Changes in sample thickness are difficult to ascertain owing to the very thin Boraflex specimens. The average measured change in thickness was -.56% with a relatively large deviation of +/- 1.32%. While the method for determining specimen thickness is not reported, it is noted that a 1% change in thickness of a sample with initial thickness of 0.075 in. is only 0.00075 in.. This change is probably less than or equivalent to the precision of the measuring technique.

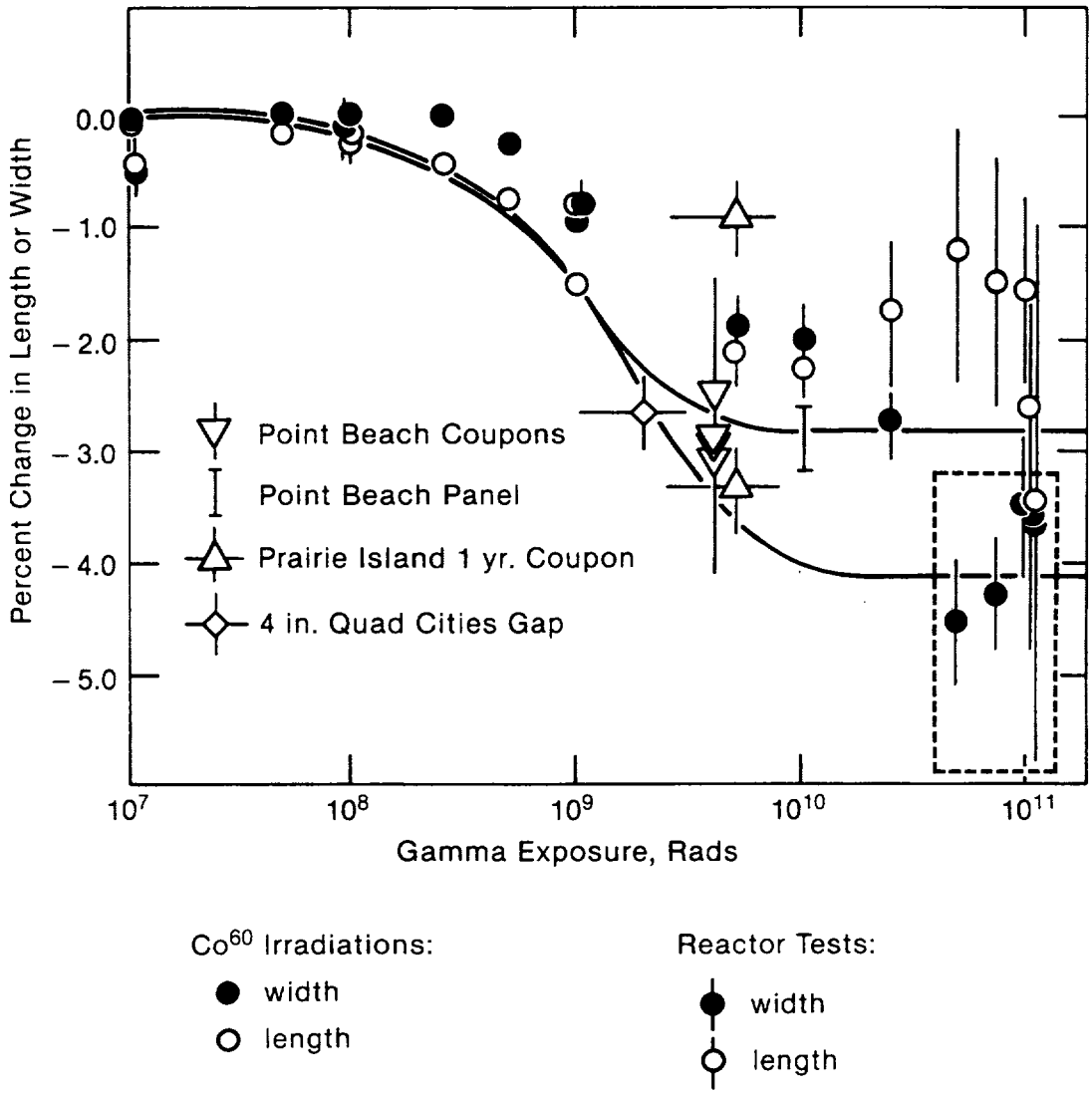


Figure 5-2. Change in Boraflex Length and/or Width versus Gamma Exposure.

In any case, the length and width measurements do provide quantitative data and suggest that the shrinkage may be anisotropic. Discussion with BISCO personnel (29) indicates that the length (long) direction of the samples is parallel to the forming direction applied during the manufacture of Boraflex which may account for the variation in shrinkage rate. These data seem to suggest that the magnitude of shrinkage is 50% greater in length than in width.

The data from the BISCO reactor irradiation program are also plotted in Figure 5-2 and show a greater variability due to the small size of the samples as well as edge erosion effects as discussed in Section 4. The data enclosed in the box represent those coupons where edge erosion may have affected the determination of dimension changes. Because of the large variability of the data, it is not possible to confirm the anisotropic nature of shrinkage as indicated by the Co-60 data. Also, discussion with BISCO personnel (29) indicates that data are not available to relate sample length and/or width to any particular manufacturing parameter. Excluding the data where sample edge effects may influence the measurements, the reactor data suggest a maximum shrinkage in length or width of less than 3% at a dose of up to 1.12×10^{11} rads. Changes in sample thickness cannot be assessed due to the large variability of the measurements.

In addition to the BISCO data, length and width changes from the one year Prairie Island coupon and the one year Point Beach coupons are plotted. It is noted that data for only two of the three Point Beach coupons is plotted since the third was broken during handling. The Point Beach data indicate a maximum shrinkage of -3.10% although the measurement uncertainty is rather large due to the small size of these coupons. The one year Prairie Island coupon was relatively large (8" x 12") and showed a shrinkage in length of -3.33% and about -1% in width. This would again suggest anisotropic shrinkage with length changes being about 3 times greater in this case than width changes. It is possible that the degree of anisotropy may depend on design parameters such as thickness and filler composition.

In addition to the coupon data, the shrinkage corresponding to a 4 in. gap as determined by neutron radioassay measurements at Quad Cities is also plotted. The resolution of the measurement technique was taken as +/-0.5 in. and the uncertainty in the dose estimate is +/-50%. A 4 in. gap corresponds to a shrinkage of 2.6% in length.

The data presented in Figure 5-2 provide a means for projecting changes in Boraflex dimensions as a function of gamma dose. As was previously demonstrated, Equation 5-5 provides an accurate means of representing observed changes in sample specific volume as a function of absorbed gamma dose. It is therefore not unreasonable to assume changes in sample length can be represented by an equation of similar form:

$$dl/l = (dl/l_{sat})\ (1-e^{-CR}) \qquad (5\text{-}6)$$

where:

R = gamma dose, rads
C = constant, $rads^{-1}$
dl/l_{sat} = asymptotic value of shrinkage

The constant C, in this case, is not necessarily the same as in Equation 5-5 since Equation 5-6 represents the change in envelope dimension and Equation 5-5 the change in specific volume which includes porosity effects.

In order to develop estimates of C and dl/l_{sat}, the previously estimated doses for crosslinking (and hence shrinkage) to saturate are used. In addition, the average sample length change at a gamma dose of 1×10^9 rads from the BISCO Co-60 irradiations is used. It was noted that the gamma dose required for crosslinking to saturate was estimated to be between 9×10^9 and 1.5×10^{10} rads. If we use the

conditions:

$$dl/l = -1.506\% \ @ \ 1 \times 10^{9} \text{ rads} \quad (5\text{-}7a)$$

$$(dl/l)/(dl/l_{sat}) = .999 \ @ \ 9 \times 10^{9} \text{ rads} \quad (5\text{-}7b)$$

we obtain the following upper estimate of changes in Boraflex length versus gamma dose:

$$dl/l = (-2.8\%) \ (1 - \exp(-7.67 \times 10^{-10})R) \quad (5\text{-}8)$$

If the conditions:

$$dl/l = -1.506\% \ @ \ R = 1 \times 10^{9} \text{ rads} \quad (5\text{-}9a)$$

$$(dl/l)/(dl/l_{sat}) = .999 \ @ \ R = 1.5 \times 10^{10} \text{ rads} \quad (5\text{-}9b)$$

are used, than the following lower estimate equation is obtained:

$$dl/l = (-4.1\%) \ (1 - \exp(-4.61 \times 10^{-10})R) \quad (5\text{-}10)$$

These upper and lower estimate curves are plotted in Figure 5-2 to provide an estimate of the range of length/width changes projected for Boraflex as a function of gamma dose. It is noted that the curves fit almost exactly the Co-60 data and bound within experimental uncertainty the coupon and gap data. The exceptions are the data enclosed in the box in Figure 5-2 where it has been noted that erosion effects may overstate the extent of shrinkage. In summary, the data in Figure 5-2 would indicate:

- Some samples showed more shrinkage in one direction than in the other.

- The maximum shrinkage in either direction saturates at approximately 1×10^{10} rads and is in the range of 3-4%.

Changes in Specific Volume Versus Geometric Volume

The data from the BISCO specific gravity measurements indicate a maximum change in specific volume of about -17%. The data based on geometric measurement of coupon length and width measurements can be used to estimate the change in geometric volume of the coupons for comparison to the specific volume change. In order to estimate the change in geometric volume, the upper and lower estimate curves in Figure 5-2 for length change versus gamma dose have been used. Using the Co-60 data at 1×10^9 rads, an average sample volume change of -3.0 % is computed with a maximum of -3.9% and minimum of -2.1% at the one sigma level. The relatively large range in maximum and minimum volume is introduced by the large uncertainty in the thickness measurements.

Of the 3.0% average volume change, about one half (1.5%) is attributed to shrinkage in the length direction of the coupons. This provides a basis for converting length changes into volume changes. Figure 5-3 contains a plot of change in volume versus gamma exposure. The change in specific volume indicative of true volume changes is plotted as well as the upper and lower estimate geometric volume change derived from the corresponding length change curves in Figure 5-2. The lower estimate curve minus 1 sigma and the upper estimate curve plus 1 sigma are also plotted.

The measured geometric volume changes from the BISCO test irradiations as well as the utility coupon data are also plotted. The geometric volume change corresponding to a 4 in. Quad Cities gap measurement has been computed assuming volume change is equivalent to two times the length change. It is noted that the geometric volume changes are generally bound by the upper estimate curve plus 1 sigma and the lower estimate curve. The maximum geometric volume change as projected by the lower estimate curve is about -8.5% which compares with -17.0% maximum change in true sample volume. The difference between the two

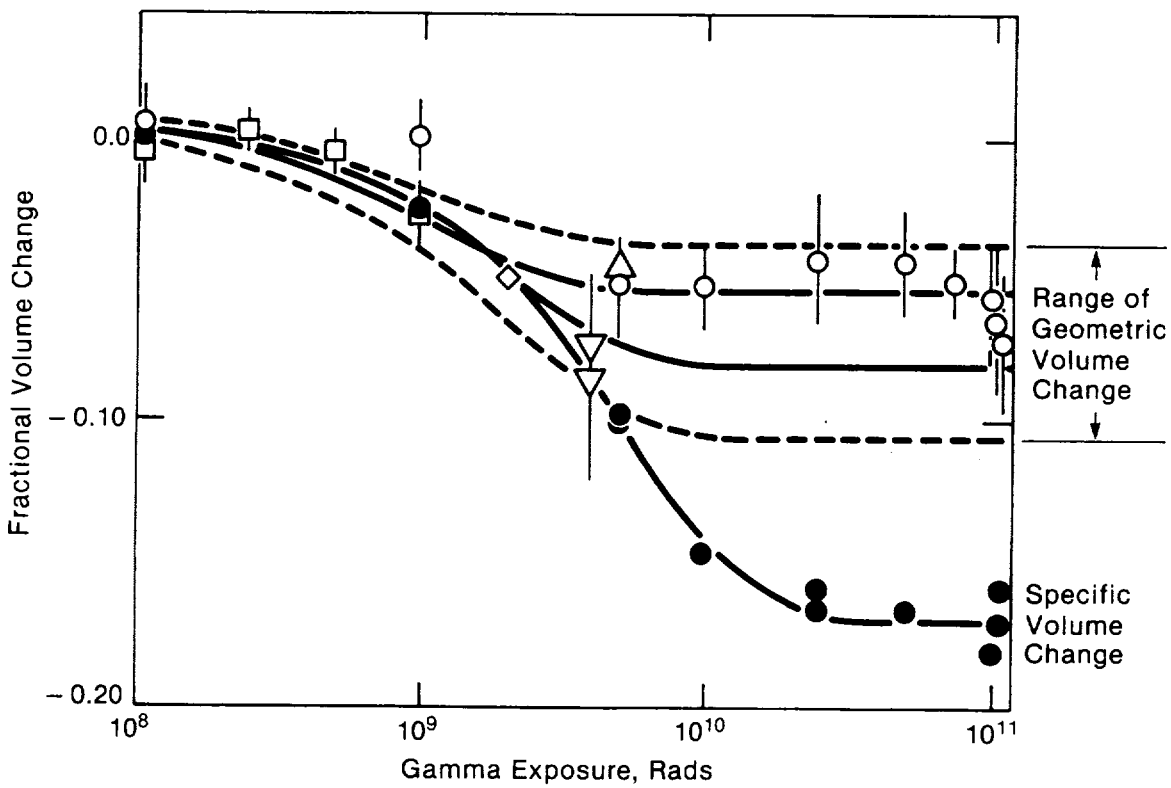


Figure 5-3. Change in Boraflex Geometric and Specific Volume versus Gamma Exposure.

values is believed to be open porosity which is inherent in the immersion measurement of volume.

It is noted that at 1×10^9 rads both the specific and geometric volume changes are the same and at higher doses they begin to diverge. The difference between the true volume change and the geometric value change can provide an estimate of the development of open porosity as a function of gamma dose. Figure 5-4 provides an estimate of the range in open porosity versus gamma dose based on the bounding curves of geometric volume changes in Figure 5-3.

While no measurements of open porosity have been reported to confirm these estimates, the visual appearance of both irradiated and unirradiated Boraflex qualitatively confirms the existence of open porosity, the edge surface appearing to contain a significant number of voids (see Figure 5-10). The radioassay measurements of the unirradiated and irradiated panels examined at Point Beach further suggest a radiation induced mechanism whereby water permeation is accelerated relative to the unirradiated material.

The development of surface crazing, or microcracks, in the material may be related to either chain scissioning or internal stresses attributed to other radiation mechanisms. Chain scissioning and internal stresses are potential effects which could result in the formation of porosity. Erosion of B_4C and other filler particles from the surface of the Boraflex is another such mechanism which would contribute to the formation of porosity. As discussed subsequently, the cut edge of unirradiated Boraflex contains significant initial porosity as confirmed by scanning election microscopy.

Gap Formation and Gap Growth

An essential factor determining whether Boraflex sheet will develop gaps appears to be the existence of a mechanism for restraint of the sheet. In the Point Beach fuel racks, the sheets of Boraflex are held

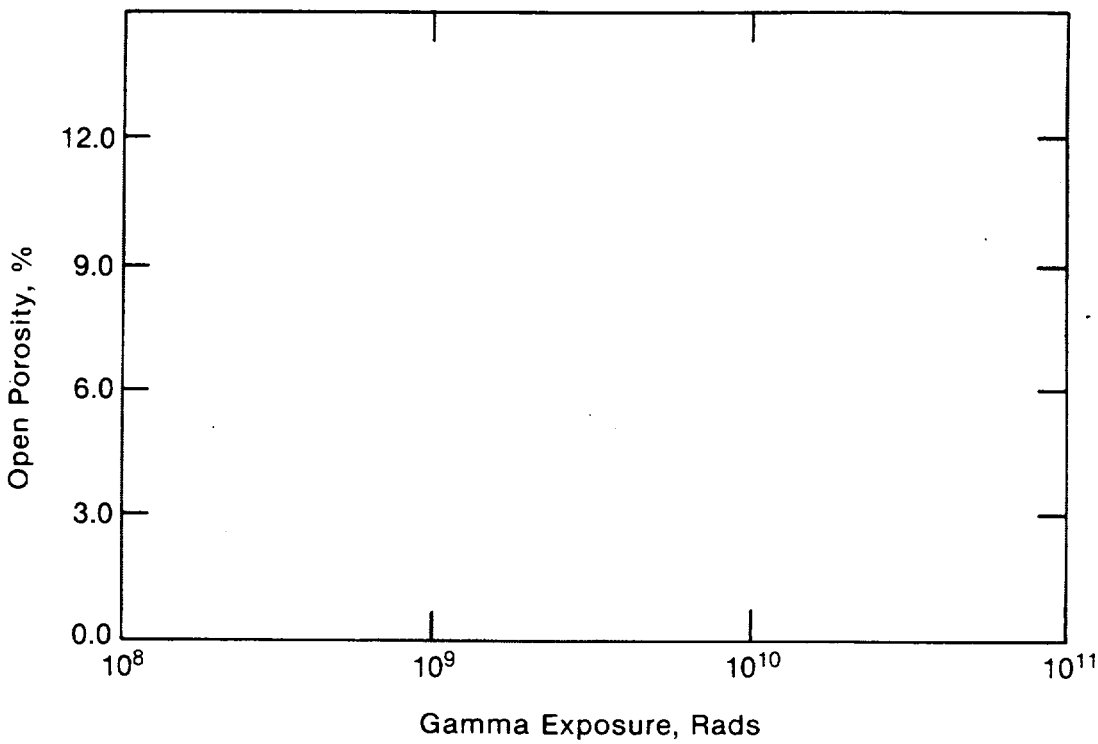


Figure 5-4. Estimated Range of Boraflex Open Porosity versus Gamma Exposure.

in place between a pair of V-shaped grooves (see Figure 2-6) in the stainless steel sheathing. When these sheets were removed for examination, they were intact. Presumably, as the Boraflex sheet was subjected to radiation-induced shrinkage, the frictional restraint provided by the V grooves was not sufficient to result in local stresses to cause the material to tear.

In other rack designs, restraint provided either through the use of adhesives or by mechanical means appears to be sufficient to cause the formation of tears or gaps. In the Quad Cities racks it has been noted that the Boraflex sheet is held in place with an adhesive (Dow Silicone Sealant No. 999) during manufacture. The design drawings for these racks have been reviewed and there appears to be no additional means for mechanical restraint. It has been postulated by BISCO (30), however, that distortions in the stainless steel enclosure introduced during the welding process may be sufficient to cause substantial restraint.

Since the condition of the Dow Sealant, in particular its adhesion properties as a function of gamma dose are not known, uncertainty exists with respect to the manner and degree of Boraflex restraint in the Quad Cities racks. Nevertheless, it is useful to postulate three bounding scenarios which include:

- The adhesive bond provided by the Dow sealant completely breaks down at low doses of gamma exposure.
- The bond between the Boraflex and stainless steel is "perfect", that is completely uniform, and the mechanical properties of the Boraflex are uniform along its entire length.
- The bond is intact at the ends of the Boraflex sheet (i.e., region expected to receive the lowest dose) and has failed or partially failed in the central region.

In the first scenario, since the bond is postulated to have failed along the entire length of Boraflex, the sheet is unrestrained and would be expected to shrink in a stress free condition as irradiation proceeds. A net shrinkage would occur but tearing of the sheet and

subsequent gap formation would not be expected.

If the bond were "perfect", as in the second scenario, high local stresses would develop in the sheet as the material tries to shrink and one might expect the material to tear at many locations forming many small gaps along the length of the sheet.

In the third scenario, with the Boraflex sheet restrained at the ends, and as the material shrinks, the greatest accumulation of local stresses would be expected in the central position of the sheet. Therefore, the sheet may preferentially tear in the central region. This scenario seems to be supported at least partially by the Quad Cities gap measurements of gap occurrence versus axial elevation (see Figure 3-6).

Assuming a mechanism of restraint, whether it is provided by the adhesive or by mechanical means, it is useful to estimate the accumulation of stresses as a function of gamma exposure relative to the tensile stress of Boraflex. In Section 4 it was shown that Boraflex shrinkage from the latest BISCO Co-60 irradiations could be well represented as a linear function of dose up to an exposure of 1×10^9 rads (see Figure 5-5 for resulting strain versus dose). Data were presented in Section 4 (Table 4-3) from early BISCO test irradiations with the "NS-1" polymer (believed to be unfilled Boraflex) which provided an estimate of changes in elastic modulus as a function of exposure to 7×10^8 rads. The data presented in Table 4-3 have been fitted as a linear function of dose as shown in Figure 5-6 over one decade (1×10^8 to 1×10^9 rads). The work of Bueche (33) described in Appendix B has indicated that the elastic modulus of PDMS can be represented as a linear function of exposure over such ranges.

If the strain induced in a restrained panel of Boraflex as it tries to shrink is a linear function of dose and the elastic modulus increase as a linear function of dose, the product, the stress, will increase as the square of the dose. To estimate the buildup of stresses in a

restrained panel of Boraflex, the elastic modulus and strain as a function of exposure shown in Figure 5-5 and 5-6 are used. Figure 5-7 shows the results of that calculation and indicates that over one decade in dose, stresses approaching 600 psi are estimated.

The tensile strength of unirradiated Boraflex has been reported in Appendix A as being 200 psi which is somewhat less than for the unfilled NS-1 polymer reported in Table 4-3 (510 psi). Over the range in exposure studied, the tensile strength of the NS-1 polymer increases to 896 psi (or about 75%). If it is assumed that the tensile strength of Boraflex increases in a similar manner, say to 350 psi, over this exposure interval it can be seen that the estimated stress is of the same magnitude as the tensile stress.

The presence of chemical agents such as water, free oxygen and other agents may reduce the stress to tear relative to what would be in air or vacuum. In summary, these estimates tend to confirm the buildup of stresses in a restrained panel of Boraflex to levels sufficient to cause tears.

Once a tear occurs, the growth of the resulting gap can be estimated using the shrinkage data contained in Figure 5-2. In Figure 5-8, the cumulative gap in terms of percent of the initial Boraflex panel length is plotted as a function of gamma exposure. For a given fuel rack design, the maximum cumulative gap size (percent) in this Figure is multiplied by the length of the Boraflex panel to obtain the cumulative gap size in inches. Should more than one gap form in a panel, the sum of the individual gaps would be equal to the cumulative gap size. Figure 5-8 indicates for a Boraflex panel 144" long, the range in cumulative gap size would be between 4 in. and 6 in.

Water Permeation and Coupon Weight Changes

It has been noted that gamma radiation seems to change Boraflex in such a manner as to make it susceptible to some degree of water

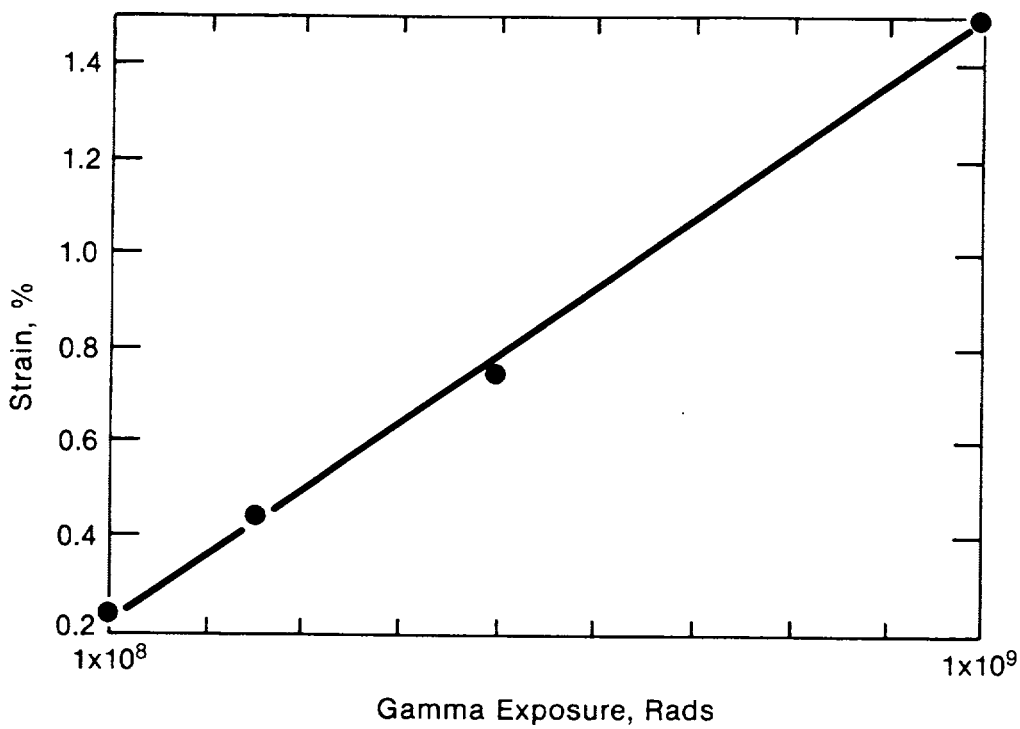


Figure 5-5. Shrinkage Induced Strain in a Restrained Panel of Boraflex Over the Exposure Range of 1×10^8 to 1×10^9 Rads.

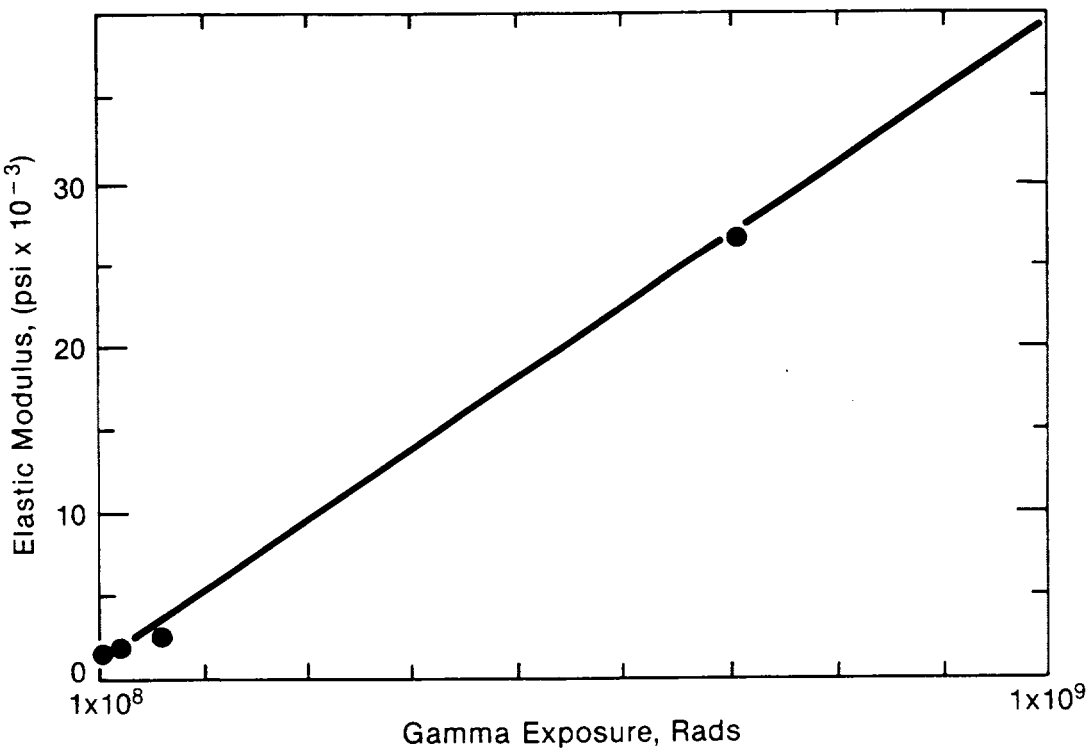


Figure 5-6. Elastic Modulus of the NS-1 Polymer Over the Exposure Range of 1×10^8 to 1×10^9 Rads.

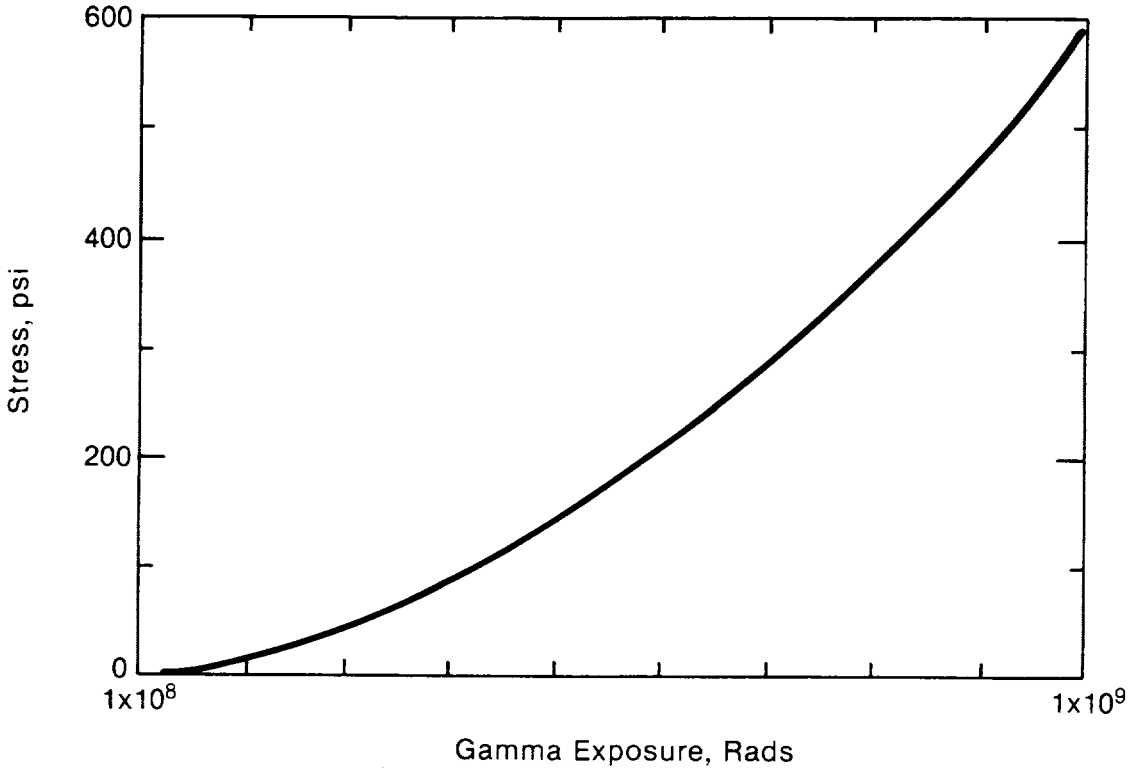


Figure 5-7. Estimated Stress in a Restrained Panel of Boraflex Over the Exposure Range of 1×10^8 to 1×10^9 Rads.

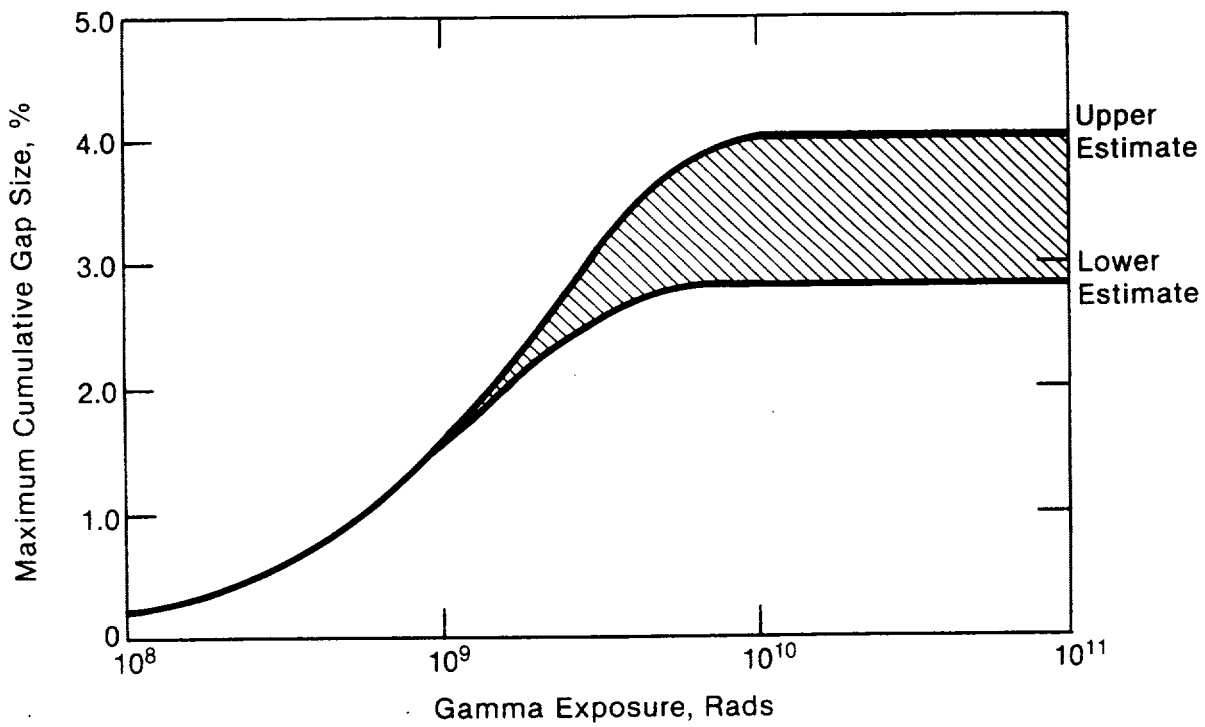
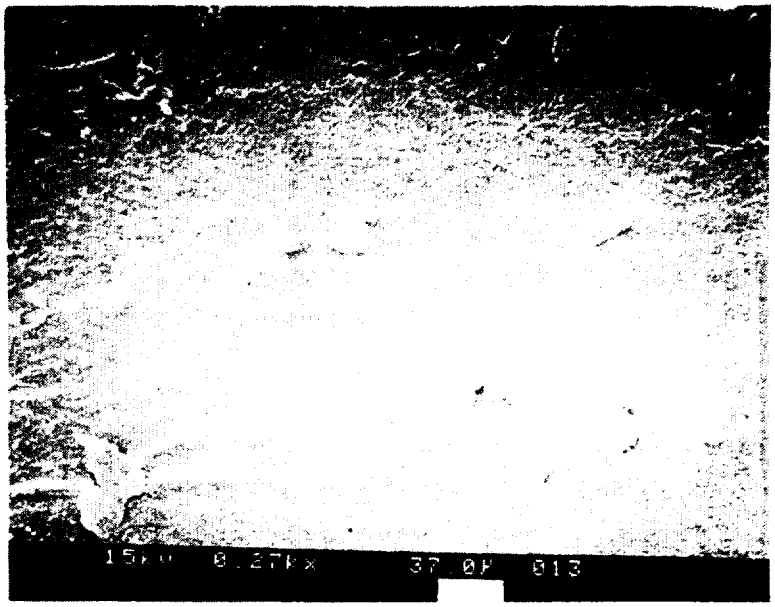


Figure 5-8. Maximum Cumulative Gap Size as a Percentage of Initial Boraflex Panel Length versus Exposure.

permeation. This has been suggested by radioassay measurements of the irradiated and unirradiated panels inspected at Point Beach. Similar measurements of the Quad Cities coupons for pool contaminants tend to confirm this finding. The irradiated Point Beach panel as well as surveillance coupons further indicate that water permeation starts at the edges where the panel/coupon has been cut to size after manufacture and progresses inward. Edge erosion has also been noted in the latest BISCO reactor irradiation and was attributed to thermal neutron radiation damage (28). Water permeation from the cut edge of the coupons could have also been a factor based on the as-manufactured condition of the edge as described subsequently.

In order to determine whether there are differences between the flat, "shiny" surface of Boraflex and the edge where it has been cut to size, mounts of both surfaces were prepared from fuel rack grade Boraflex for scanning electron microscopy (sem). Figure 5-9 shows the scanning electron micrograph of the flat, "shiny" surface of Boraflex at magnifications of 270X and 2800X. The surface appears relatively smooth, probably characteristic of the polymer matrix with minor imperfections including "ripples" and some scattered "debris" on the surface. The former may be an image of similar imperfections in the carrier sheet used during the forming process. The latter could be filler particles which have not been completely sealed by the polymer. In general, the flat surface appears more or less completely "sealed" by the polymer matrix.

Figure 5-10 shows the cut edge of the same specimen of Boraflex at 280X and 2800X magnification. In contrast to the flat surface, the cut edge contains relatively deep voids (compared to the flat surface) and what appears to be exposed particles of filler material. Some of the voids or pores may have been caused by filler particles which were extracted from the polymer matrix during the cutting process. The pores shown in Figure 5-10 are probably deeper than they appear in the micrograph since sem tends to "flatten" the depth of field. A comparison of Figures 5-9 and 5-10 confirms that there are distinct differences in surface morphology (flat versus cut edge) which could make the cut edge more susceptible to the onset of water permeation.



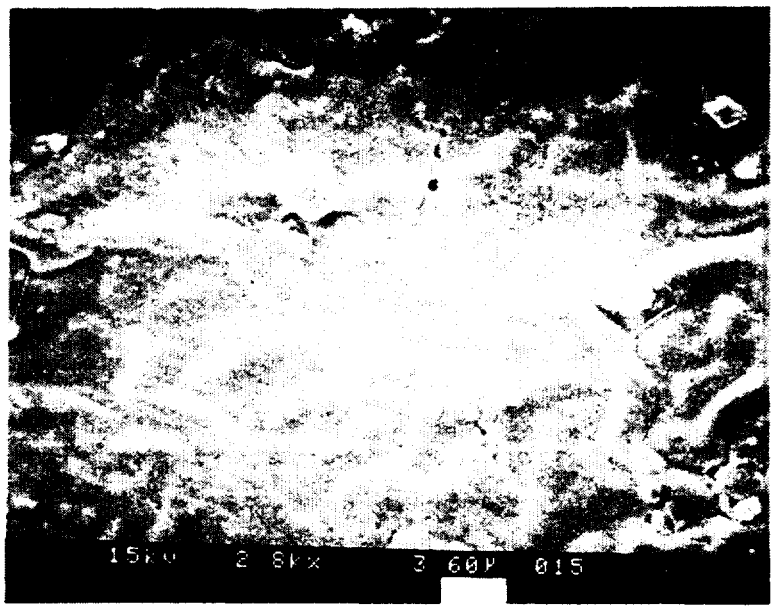


Figure 5-9. Scanning Electron Microscopy of the Flat Surface of Boraflex at 270x and 2800x Magnification.

Figure 5-10. Scanning Electron Microscopy of the Cut Edge of Boraflex at 280x and 2800x Magnification.

The increase in sample weight in the latest BISCO reactor irradiations (see Figure 4-6) up to a gamma dose of 2.5×10^{10} rads is further indication of water permeation. Beyond this exposure the samples show a weight decrease which has been attributed to edge erosion (28). At exposures of 10^9 rads and less, sample weight gain is less than .5% and increases to 3 to 4% at 2.5×10^{10} rads. This result is generally consistent with the postulated development of open porosity discussed previously.

It is interesting to note that samples irradiated in air in the Co-60 tests show a similar increase in weight up to an exposure of 1×10^9 rads. If crosslinking were the only mechanism at play, one would expect a decrease in sample weight due to the generation and evolution of $H^{\bullet}$ and hydrocarbon radicals. It was noted in Appendix B that the presence of molecular oxygen and perhaps moisture (humidity) in the air combine with free radicals remaining in the polymer. This offers one potential explanation for the apparent increase in sample weight measured in Co-60 tests conducted in air. It is noted that such chemical effects may continue after the polymer is removed from the radiation field as long as free radicals are present.

Test Reactor versus Spent Fuel Pool Radiation Conditions

In order to accumulate integrated gamma exposures in a reasonable time frame, BISCO conducted test reactor irradiations. It has been noted that significant differences between the test reactor radiation spectrum and that in the spent fuel pool exist with the total energy deposited in the test reactor being significantly greater than the fuel pool for the same gamma exposure. In the test reactor, fast neutron radiation as well as recoil alpha and Li particles from thermal neutron reactions with Boron-10 (in the B_4C filler) are present and are not factors in the pure gamma spectrum of the spent fuel pool.

A rough estimate of the effect of fast neutron and recoil particles can be made. The experimental data of Kline and Jacobs (34,35) has

been used to estimate the energy deposited by fast neutrons. Corrections to the neutron scattering cross sections have been applied to account for differences between Boraflex and the polymers studied. The estimated energy deposited by recoil particles from neutron induced reaction in Boron-10 depends on a number of variables including the thermal flux depression factor in the samples, boron carbide particle size and test reactor spectrum. Since the exact sample configuration and boron carbide particle size distributions are not known, only an order of magnitude estimate is possible.

Nevertheless, such an estimate indicates that the combined effect of fast neutron and recoil particle energy deposition is at least an order of magnitude greater than the gamma dose alone. That is to say, for a gamma exposure of 1×10^{11} rads in the reactor, the total exposure is probably in excess of 1×10^{12} rads. Of this additional exposure, this estimate suggests approximately one third is attributable to fast neutrons and two thirds to recoil particles.

Boraflex Service Life

The ultimate service life of Boraflex will be determined by the ability of the polymer matrix to perform its intended function--to retain the boron carbide filler material. That ability is likely to be influenced by not only the integrated gamma dose received during the service life (estimated (30) to be in the range of 2.5×10^{10} to 3×10^{11} rads) but also by the effects of long term exposure to the aqueous pool environment. It is noted that in the BISCO reactor tests the samples were subjected to perhaps an order of magnitude greater dose (when fast neutron and recoil particle energy deposition is considered) than that expected during the service lifetime in a pool. The test irradiation environment is therefore conservative relative to the integrated gamma exposure projected over forty years in a spent fuel pool. However, the tests were relatively short in duration (five to six months) and therefore do not provide complete data of the long term effect of environmental factors such as pool water chemistry, temperature, etc.. Accordingly, while there has been no data available to this study which would suggest the onset of a rapid or

gross degradation mechanism leading to the loss of boron carbide from Boraflex, it appears prudent to continue adequate surveillance programs to monitor the long term performance on a plant by plant basis.

Factors which may influence the service life of Boraflex include:

- Integrated gamma dose
- Pool water chemistry
- Pool water temperature
- Rack design specific conditions such as the potential for local flow around the Boraflex
- Boraflex thickness
- Boron carbide and other filler composition in the Boraflex

With regard to the first four factors, information is presented in Appendix B which indicates that the environment (i.e., presence of molecular oxygen, water, etc.) can have an influence on the behavior of materials, such as Boraflex, under irradiation. These effects may be long term in developing since the rate at which agents in the pool water enter Boraflex is likely to be a diffusion governed mechanism. As such, pool temperature, the presence of open porosity (believed to be a function of gamma dose), and the availability of chemical agents (potential for local flow around the Boraflex) may all be important factors. Furthermore, there is some indication from the Point Beach coupon train that local flow can cause erosion from the surface of irradiated Boraflex (1).

The initial thickness of the Boraflex sheets is likely to be a factor which influences service life. Boraflex is used in spent fuel racks over a range of thickness from 0.040 in. to in excess of 0.100 in.. If, as has been suggested, water permeation and chemical effects are important, then they may have a lesser effect (on a percentage of Boraflex volume basis) on thick sheets than on thin sheets for the same exposure conditions.

In addition, the volume percentage polymer versus volume percentage of filler (i.e., boron carbide loading) may also effect service life. For Boraflex with high boron carbide loadings, the volume percent of polymer is less and there is physically less matrix to retain the boron carbide.

In summary, the data currently available, and in particular that for the Point Beach panel which had been exposed to the pool environment for 6-7 years, has demonstrated that Boraflex has performed its intended function of retaining the boron carbide filler material for this period of time. However, since this period of experience is relatively short relative to the design service life of 30 to 40 years, caution must be exercised in projecting the ultimate allowable service life and it is recommended that the performance of Boraflex be monitored, verified and documented. From the available data there are no indications that combined exposure to gamma radiation and the pool aqueous environment result in the onset of rapid or gross degradation of the polymer matrix that would cause the loss of boron carbide. Factors have been identified which are likely to affect service life and some of these will vary from plant to plant. Accordingly, a formal surveillance program at each plant appears a prudent course to verify the continued serviceability of the Boraflex.

Section 6

CONCLUSIONS AND RECOMMENDATIONS

When Boraflex is subjected to a gamma radiation field it undergoes changes as been evidenced by data from the BISCO test irradiations, utility surveillance programs and from other sources identified in the literature. The data from these sources has been evaluated as part of this project and the observed changes in physical characteristics of Boraflex are what would be expected for this class of polymers based on reports identified in the literature. In summary, evidence of radiation induced changes include:

- Evolution of gases including hydrogen and hydrocarbons
- Physical shrinkage accompanied by an increase in specific gravity and decrease in specific volume
- Loss of rubberelasticity, increase in hardness and an increase in elastic modulus
- Observed formation of blisters in some specimens
- Change in surface color from shiny black to a whitish grey and a tendency of the discolored material to powder
- Permeation of water believed to be the result of development of open porosity

The first four of the above are consistent with the radiation damage mechanism of crosslinking as described in Appendix B. The color change and formation of porosity may be a result of scissioning and/or chemical effects attributed to the aqueous service environment.

Physical shrinkage seems to vary from sample to sample--perhaps a result of manufacturing variables such as sheet thickness and filler content. Some samples have shown greater degrees of anisotropic shrinkage than others (i.e., more shrinkage in one direction than in

another) and this may again be due to manufacturing variables. The maximum shrinkage in either direction seems to be limited to 3-4%. These estimates provide a basis for projecting a maximum cumulative gap size for a given rack design should a particular design be subject to gap formation.

While neutron radioassay measurements detected the presence of gaps in the Quad Cities racks (2), inspection of a full length panel from Point Beach (1) and neutron radioassay measurements at Turkey Point (20) indicate that gaps have not formed in these rack designs. A key factor determining whether a particular rack design is susceptible to gap formation appears to be the manner in which the Boraflex sheets are restrained in the rack structure. In a tightly restrained panel of Boraflex, stresses approaching the tensile stress of the material over a relatively small increment of exposure (10^8 to 10^9 rads) have been estimated, thus suggesting a mechanism for gap formation.

The recent test reactor irradiations sponsored by BISCO have subjected samples of Boraflex to integrated radiation doses well in excess of those expected during the 30 to 40 year service life of fuel storage racks. The gamma dose alone in these tests was approximately equal to that expected during the normal service life of the racks. The energy deposited by fast neutron and recoil particles results in an equivalent dose estimated to be an order of magnitude greater than the gamma dose alone. These tests indicate no loss of Boron-10, as determined by neutron attenuation measurements, but slight edge erosicn of the Boraflex in some samples. The latter has been attributed to thermal neutron/recoil particle effects (28) although the presence of water cannot be discounted as a contributing factor.

In summary, the BISCO test irradiations demonstrate integrity of the Boraflex to radiation doses well in excess of those expected for the material in spent fuel racks. It has been noted, however, that while the tests were conducted in an aqueous environment, the duration of these tests was only on the order of five to six months. Accordingly, material integrity under the combined effects of gamma radiation and

long term exposure (30 to 40 years) to the aqueous pool environment remains undemonstrated. Data available to this study would indicate no mechanism to suggest a rapid or gross degradation of Boraflex that would result in the loss of boron carbide.

Evidence from the literature has been presented which suggests that the presence of chemical agents including air, molecular oxygen and water can influence the behavior of polydimethylsiloxanes and other materials similar to Boraflex. The rate at which these agents penetrate the Boraflex is likely to be a diffusion governed mechanism. Differences between the true volume of irradiated Boraflex samples and the geometric volume as determined by dimensional measurements suggest a radiation induced mechanism which produces open porosity in the Boraflex. This is further supported by the penetration of radioactive pool contaminents from the pool water in the irradiated Point Beach panel relative to the unirradiated panel. The development of open porosity would be expected to accelerate the permeation of pool water into the Boraflex.

Because of these factors, the ultimate long term service life of Boraflex subjected to gamma radiation concurrent with long term exposure to the pool aqueous environment is somewhat uncertain from the data currently available. Owing to the nature of the material and the mechanisms at play, demonstration will probably await long term exposure in the spent fuel environment. Accordingly, continued surveillance of Boraflex currently in place in spent fuel racks around the country would seem to provide the best source for developing these long term data.

As a result of these conclusions , the following recommendations have been developed with the intent of improving the quality of data generated in the future relative to the performance of Boraflex in spent fuel racks:

- The irradiated panel examined at Point Beach has received an exposure estimated to be 1×10^{10} rads accumulated over a period of approximately 7 years in the spent

fuel pool. Consideration should be given to the preparation of large coupons from this material for reinsertion into a spent fuel pool. Characterization of the coupons should be as recommended in Appendix C where possible. Some coupons should be exposed to further irradiation in the pool and others only to pool water without further irradiation.

- Consideration should be given to establishing lead PWR and BWR surveillance programs with surveillance coupons prepared and monitored per the guidelines outlined in Appendix C. For these programs some additional characterization and measurements may be desirable.

- In lieu of further sample irradiations in test reactors, consideration should be given to an accelerated exposure program in a utility spent fuel pool. This may be conducted as part of the lead programs described above.

- Determine whether some physical property of Boraflex can be correlated with gamma exposure to serve as a dosimeter measurement of integrated dose. Alternatively, develop methodology to rapidly and with reasonable degree of accuracy calculate the integrated gamma exposure of surveillance coupons.

- Continue to collect and evaluate data from utility surveillance programs as they become available. These data can be used to supplement the data collected as part of this study and to further verify the estimates of Boraflex performance.

- For utility coupon programs initiated in the future, the manufacturer's recommended surveillance procedures should be supplemented with those outlined in Appendix C.

The following recommendations are made relative to the design and manufacturing of new spent fuel racks which utilize Boraflex:

- No means of mechanical or adhesive restraint should be used so that the material can undergo shrinkage in a stress free condition thereby precluding the potential for gap formation.

- Oversize panels should be provided to compensate for the effect of shrinkage on the reactivity of the fuel/rack system.

Section 7

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APPENDIX A

PROPERTIES AND CHARACTERISTICS OF POLYSILOXANE POLYMERS

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Appendix A

PROPERTIES AND CHARACTERISTICS OF POLYSILOXANE POLYMERS

GENERAL MOLECULAR STRUCTURE OF POLYSILOXANES

Polymers are large molecules, typically long chains comprised of rather simple units repeated many times. Generally, they have a distribution of molecular weights described mathematically by various "averages". In the solid state, they can be amorphous or crystalline or a combination of both. The amorphous regions soften over a range of temperatures, as in "glass" transition, whereas the crystalline regions, if present, have a more clearly defined melting "point" which characterizes them.

Most polymers have carbon in the backbone of the chain with side groups which distinguish one polymer from another, but the chain can also include other atoms such as N, O, and Si. The polysiloxane polymers, along with a relatively few other polymers have an inorganic backbone chain. In the polysiloxane case, this is characterized by:

```
      A           A           A
      |           |           |
  -   Si  -  O  -  Si  -  O  -  Si  -
      |           |           |
      B           B           B
```

Where A and B are typically hydrocarbon side groups. The most common silicone polymer has a "repeat unit" where the form of A and B is CH_3 and is commonly referred to as silicone rubber. In the literature, silicone rubber is also referred to as polydimethyl siloxane (PDMS) and dimethyl polysiloxane. Other common types include a phenyl or vinyl group for A and/or B.

These silicone classes of polymers are characterized by a temperature service range which is very large compared to many other polymers (A-1). The Si-O backbone is degraded or oxidized only slowly at about 400°C or higher and typical service temperatures extend up to 300°C. At the same time these polymers are flexible at temperatures as low as -100°C, a property which is probably partly due to the flexible oxygen linkage and limited crystallinity. Without significant crosslinking between chains, the polymer chains can range in size and form from oils to viscous liquids to elastic solids. Although the formulation of Boraflex is proprietary, the general form is a polysiloxane polymer believed to be similar to polydimethyl siloxane.

CHARACTERISTICS OF ELASTOMERS

Generally the description of an ideal elastomer is (A-2):

- It should be rapidly stretchable to very high elongations (up to 500% or more).
- It should possess comparatively high tensile strength when fully stretched, i.e., the tensile restoring force continues to increase as the elongation increases to high extension.
- It should snap back (rapidly) when the stress is released.
- It should retract completely with no permanent set.

When the above behavior is observed, certain molecular and environmental conditions usually exist. They are (A-2):

- The material is a polymer.
- The material is amorphous.
- The temperature is above T_g, the glass transition temperature.
- The material is lightly crosslinked.

It will become apparent later that many of the above are notable in the case of Boraflex, and that changes in Boraflex properties in the service environment may be correlated with the descriptions and conditions of effects reported in the literature.

The rubberelasticity of polymers is provided by stretching and rearranging the chains under stress, where the system is in a very flexible state. Return to the shape of the original state is provided by points which act as ties between chains and these, in principle, can be crystalline regions, chain entanglements, or, most commonly, crosslink bonds between chains. Crosslinks are typically made by chemical actions sometimes called "curing" or "vulcanization"; but, as will be noted later, nuclear irradiation can also yield crosslinks.

For slight crosslinking or a small number of tie points, the chain length between crosslinks is large and the elongation that can be obtained under stress is very large, perhaps 1000% or more. However, the rubberelastic modulus is correspondingly low because the system is inherently not very rigid. If the crosslinking density is increased, the system becomes more rigid. The modulus rises, but the elongation which is possible decreases. Concurrent with increased crosslinking, shrinkage typically occurs probably because the chains are brought closer together and the free volume decreases.

As in the case of polymers in general, rubber elastic materials are considerably affected by fillers and additives. It is very common to add fillers as a method to change the properties. In other cases, the filler is needed to make the elastomer useful in a special way, and, as a result of the filler and the service environment, the physical properties, etc., change very noticeably. Such is the case with Boraflex where B_4C is the filler used to provide reactivity control, and, in turn, the filler tends to affect the elastomer's properties.

BORAFLEX ELASTOMER

Boraflex is reported (A-3) to be a primarily methylated polysiloxane elastomer filled with finely divided boron carbide powder, B_4C, (100 to 400 mesh). The polymer is believed to be very similar to dimethyl polysiloxane as reported in the literature, but it is assumed that variations in the structure, possibly at the methylated site, might be present. For example, Reference (A-1) cites the addition of phenyl

groups, in the amount of 0.1 to 0.6 mole present, for methyl groups to increase both the vulcanization rate and the initial crosslink density. Phenyl groups are sometimes substituted to improve low temperature performance, to enhance radiation resistance and to lower resilience. Carbon and silica fillers have been added to these polymers which have been vulcanized with radiation (A-4). It has been reported (A-5) that carbon and silica are present in Boraflex for the purpose of increasing radiation resistance of the material.

Polysiloxane polymers are generally reinforced with silica fillers (A-1). The use of silica can increase the tensile strength of such polymers from 50 psi for the nonreinforced polymer to 1500 psi for the reinforced material. Fumed and/or precipitated silica is generally used and consists of SiO_2 with a number of hydroxyl groups on the surface of the filler aggregate. It has been postulated (A-1) that the increased tensile strength results from hydrogen bonding and/or van der Waals forces between the hydroxyl radials on the filler and oxygen atoms in the spine of the polymer.

The PDMS polymer is basically the matrix for the composite Boraflex (A-3), with the B_4C serving as a filler with a large neutron thermal absorption cross section. It is because of the B-10 isotope in the naturally occurring boron that it is useful in nuclear fuel storage racks for providing the required reactivity control. The polymer is manufactured by Dow Corning for BISCO and has been referred to as NS-1 polymer (A-5). Boraflex can be manufactured with ranges of B_4C content (percentages) and dimensions (thickness). Reference (A-3) cites a typical composition a for spent fuel storage applications as noted in Table A-1. The B_4C powder can very in size from 100 to 400 mesh depending on the B-10 loading of the composite (A-5). Presumably, a finer mesh powder is used at the higher B-10 loadings to assure complete encapsulation of all or most of the B_4C particles. According to reference (A-5), "The NS-1 polymer acts to provide a waterproof coating for the majority of the boron carbide in the matrix, thus reducing any chance of water contact."

Based on the elemental compositions cited in Table A-1, it is possible to estimate the weight percent polymer matrix and filler in the composite Boraflex material. Such an estimate yields 35-40 w/o polymer, 40 w/o B_4C and 20-25 w/o silica with perhaps a small quantity of carbon. Accordingly, in the composite material a little more than one third (on a weight percent basis) is comprised of the matrix and a little less than two thirds filler.

In addition to the constituents identified in Table A-1, it is likely that Boraflex contains small quantities of other materials. Because of its form (elastomer versus oil or gel) the polymer matrix in Boraflex is likely to contain some initial degree of crosslinking. This is can be accomplished chemically in PDMS during the manufacturing process by the use of vulcanizing agents such as peroxides (A-1) and platinum believed to be used in the case of Boraflex. As discussed subsequently, the presence of such residual catalysts can influence the nature of radiation damage.

As-produced Boraflex with a B-10 loading of 0.020 gm B-10/cm^2 and 2.5 mm thickness exhibits the properties shown in Table A-2 (A-3). It is to be noted that elastomers in particular and polymers in general are typically affected to a large extent by fillers. The properties summarized in Table A-2 would be expected to depend upon the nature of the filler, the filler properties, the filler size, the service and environment in which it is used, etc. . In addition to the changes in the polymer matrix with service, the filler properties and bonding might also change, particularly if the environment includes nuclear radiation.

Table A-1

TYPICAL BORAFLEX ELEMENTAL COMPOSITION (%)

Element	Composition
Boron	31.5 w/o
Carbon	19.0
Silicon	24.5
Oxygen	22.0
Hydrogen	3.0
TOTAL:	100.0 (100%)

Source: Boraflex Neutron Shielding Material Product Performance Data, Park Ridge, IL, August 25, 1981, N-38, 748-30-2.

Table A-2

BORAFLEX PROPERTIES

Property	Amount
Modulus of Elasticity	1000 psi
Tensile Strength	200 psi
Specific Gravity	1.7 g/cc
Hardness	75 Shore A
Temperature Stability	200 °C *

*Note: minimum without variable distortion
Source: Boraflex Neutron Shielding Material Product Performance Data, Park Ridge, IL, August 25, 1981, N-38, 748-30-2.

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APPENDIX B

RADIATION EFFECTS IN POLYSILOXANE POLYMERS

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Appendix B

RADIATION EFFECTS IN POLYSILOXANE POLYMERS

It has been noted in Section 4 that data are not available relative to the long term performance of Boraflex under simultaneous exposure to gamma radiation and the aqueous spent fuel pool environment. Accordingly, the published literature of radiation studies with the PDMS polymer has been reviewed. The intent of this review is to document the relevant literature and to provide an understanding of:

- The predominant radiation damage mechanisms in PDMS
- The effect of radiation damage on the physical properties of PDMS
- The effect of environment (i.e., presence of air, oxygen, water, etc.) on the physical properties of irradiated PDMS

A search of the literature has indicated that the effects of ionizing radiation on the polysiloxane polymers, and in particular PDMS, have been studied experimentally quite extensively starting in the 1950's. While the data reported are, in many cases, for relatively low dose experiments (up to 5×10^8 rads) as compared to the integrated dose expected during the design service life of Boraflex, the experiments were conducted under various yet carefully controlled conditions. Thus, the effect of radiation and service environment can be examined either independently or in combination. The following Appendix of this report contains a summary of the published literature relative to experimental studies of radiation effects in the PDMS polymer.

GENERAL EFFECTS IN POLYMERS

When a polymer is subject to a radiation field, changes in the atomic/molecular structure occur (B-1). Radiation can result in the severing of atomic bonds and subsequent formation of new bonds

(crosslinking) between atoms in adjacent polymeric chains as will be described in detail subsequently. Radiation may also result in another mechanism, referred to as scissioning, in which radiation causes the severance of atomic bonds in the main chain of the polymer but crosslinking does not occur.

The relative rate (per unit of energy absorbed) at which a particular process occurs is characterized by a "G-value". A "G value" is a description of the number of events of a given type that occur when 100 eV of energy is deposited. For example, G(scission) = 2 implies that two scission events (two atomic bonds are severed) occur for each 100 eV absorbed. For crosslinking of polymer molecule repeat units, which are already incorporated in molecular chains, G(XLU) can be defined as the number of polymer repeat units which have been crosslinked to others for each 100 eV of energy deposited by a radiation field. G(XL) refers to the number of crosslinks formed and is one half of G(XLU) since two units are involved in one crosslink.

It has been noted (B-1,B-2) that polymers can be classified into two groups according to which radiation damage mechanism is predominant:

- Crosslinking polymers have chains linked following irradiation. This leads to higher molecular weight and/or branching, and eventually to formation of an insoluble network.
- Scissioning polymers have chains which are broken during exposure to radiation. This results in a decrease in the average molecular weight of the polymer.

Both processes can occur simultaneously in many polymers, and the classification of polymer type depends on the predominant process. Table B-1 presents some examples. It is believed that crosslinking is the predominant mechanism in dimethyl polysiloxane at low doses of radiation exposure in vacuum (B-1,B-2). The experimental evidence (B-2) suggests that at high dose levels, crosslinking tends to saturate and scissioning may be the predominant mechanism.

Table B-1

SOME EXAMPLES OF POLYMER CLASSIFICATION

Crosslinking Types	Degrading Types
Polystyrene	Polymethyl methacrylate
Polyethylene	Polyvinylchloride
Polypropylene	Polytetrafluoroethylene
Nylon	Poly-alpha-methylstyrene
Natural Rubber	Polyisobutylene
Polydimethylsiloxane	
Polyesters	

Source: Adapted from A. Chapiro, Radiation Chemistry of Polymeric Systems, New York: Interscience Publishers, Inc., 1962.

Table B-2

COMPOSITION (IN PERCENT) OF EVOLVED GASES FROM POLYSILOXANE POLYMERS DURING IRRADIATION

Polymer	H_2	CH_4	C_2H_6	C_6H_6	Investigator
Dimethylsiloxane	41	47	12	--	Charlesby
Octamethylcyclotretrasiloxane	34	60.5	4.5	--	Warwich
Octamethylcyclotretrasiloxane	27	57	16	--	Kantor
Dimethylsiloxane	31	47	22	--	St. Pierre et.al.
Methylphenylsiloxane	31	28	8	--	Prober

Source: Adapted from A. Chapiro, Radiation Chemistry of Polymeric Systems, New York: Interscience Publishers, Inc., 1962.

Presence of molecular oxygen and other chemical agents tends to encourage scission as compared to crosslinking in many polymers. Oxygen is believed to combine with radicals formed in the polymer due to chain scission or evolution (abstraction) of hydrogen or other gases. In order for oxygen to have a significant effect, there must be an adequate supply and oxygen must diffuse into the polymer at a rate comparable to its rate of reaction within the polymer. The effect of irradiation environment on PDMS is discussed subsequently.

EFFECTS IN POLYSILOXANES: A REVIEW OF THE LITERATURE

Crosslinking and G-Values

Polysiloxanes were among some of the first polymers studied by Sissman and Bopp (B-3,B-4) and others (B-1) with regard to determining the behavior of physical properties of materials subjected to nuclear radiation. In the 1950's and 1960's they were further studied by a number of investigators (B-5--B-11), a primary goal of this work being to develop information about the crosslinking process.

As in the case of Boraflex, a characteristic of the radiolysis of the organic silicone polymers investigated is that gases are evolved during radiation. In a summary of data from several sources (B-12) it has been noted that when silicones are irradiated in the absence of O_2 (in vacuum), the evolved gases contain 30 to 40% hydrogen. A large fraction of the gas is methane, and in addition, ethane, etc., is present in appreciable amounts. Irradiation of polymethylphenylsiloxane and octamethylcyclotetrasiloxane yields gases which differ from those of PDMS. The composition of evolved gases from these various polysiloxanes is shown in Table B-2.

These results lead to the conclusion that both C-H and Si-C bonds were fractured leading to the formation of hydrogen atoms and methyl and phenyl radicals. Accordingly, it has been noted (B-12) that at least two primary radiation events must be assumed to take place as shown in Figure B-1. Subsequently, two primary crosslink bonds may be formed

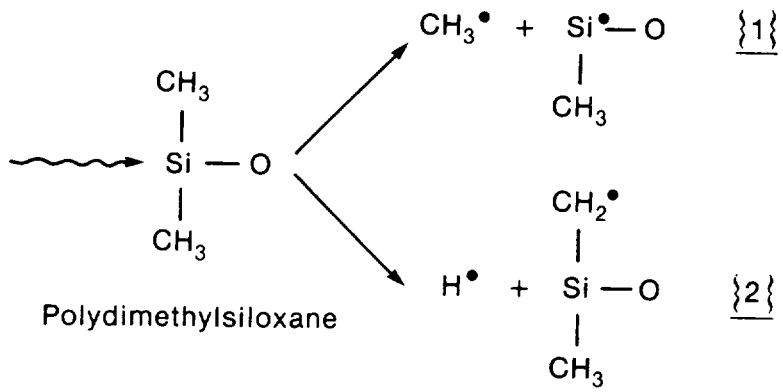

Figure B-1. Primary Gamma-induced Radiation Events in Polydimethylsiloxane.

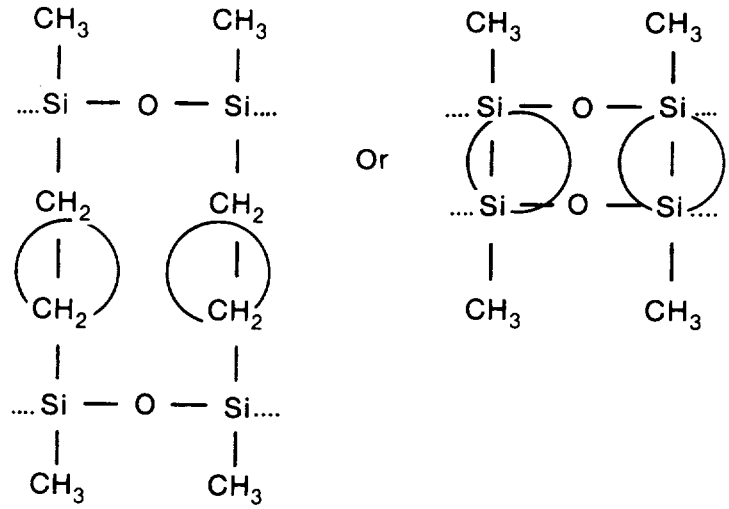

Figure B-2. Subsequent Crosslink Bond Formation.

as shown in Figure B-2.

Several early studies have been reported in which the G-value for crosslinking was determined experimentally (B-5,B-7,B-8,B-13,B-14). In this work, the behavior of PDMS at low radiation doses was investigated over a range of molecular weight from liquids to gels to elastomers. Delides and Shepherd in a somewhat more recent publication (B-15) have noted that this early work could be summarized as follows:

- For PDMS, the degree of crosslinking is proportional to the radiation dose, at least up to a reasonably high dose.
- The degree of crosslinking is independent of the molecular weight.
- The degree of crosslinking depends primarily on the dose received and is independent of both the type and intensity of radiation.
- Some discrepancies remained. For instance, G(XL) varied from 1.6 to 4.5 (B-7,B-16,B-17).

Delides and Shepherd (B-15,B-18) subsequently investigated gamma irradiated PDMS as a function of dose up to 500 Mrad and found:

- The crosslink density dependence on dose was linear to about 160 Mrad and exponential for higher doses, tending to a constant value for extremely high doses. (See Figure B-3).
- For doses less than 160 Mrad, they estimated a G(XL) of 2.8 +/- 0.3 which was in good agreement with some of the other earlier work.
- At 500 Mrad, they estimate G(XL) = 0.6 to 0.7 and ascribe the decrease from the value of 2.8 to hindrance of translational motion of the polymer chains due to crosslinks. They also note that there is a decrease in the number of monomer units available to produce radicals.
- Evolved gas measurements also suggest a saturation effect as the doses become very large.
- It has been noted that the presence of oxygen is known to alter the results. Also, gases produced during irradiation can be trapped in the polymer and must be removed for accurate analysis. Gases in crosslinked spe-

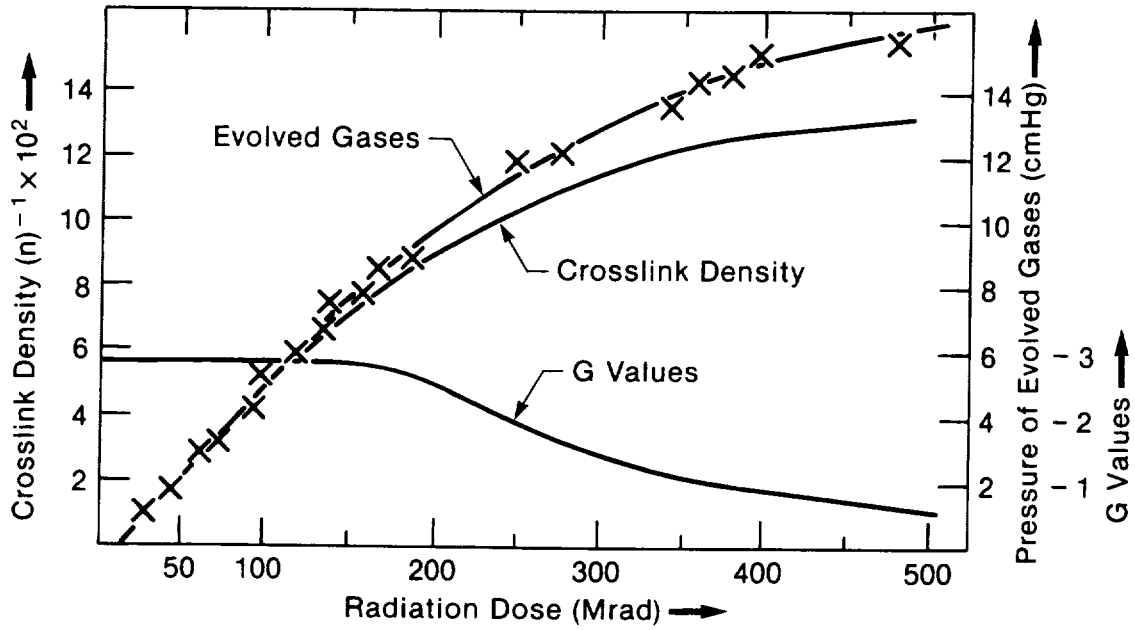

Figure B-3. Crosslink Density, Evolved Gases and G-Values versus Gamma Radiation Exposure for PDMS. (Source: C. G. Delides and I. W. Sheperd. "Dose Effects in the Crosslinking of Irradiated Polysiloxane", Radiation Physics and Chemistry, vol. 10, 1977, pp. 379-385.)

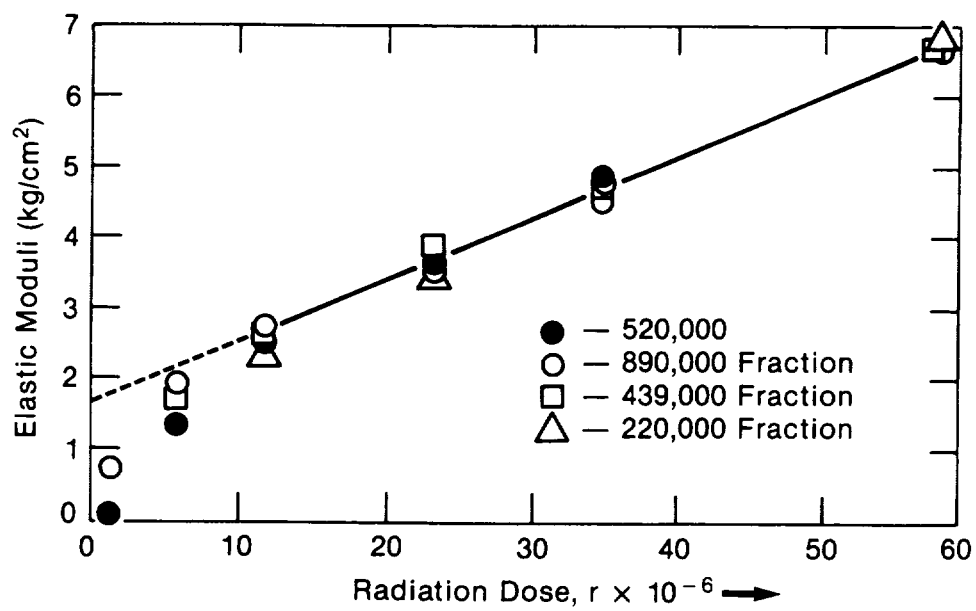

Figure B-4. Elastic Moduli of PDMS versus Electron Radiation Dose. (Source: A. M. Bueche. "An Investigation of the Theory of Rubber Elasticity Using Irradiated Polydimethylsiloxanes", Journal of Polymer Science, vol. 19, 1956, pp. 297-306.

cimens have been observed to produce bubbles in the polymer (B-18).

A summary of the G values for crosslinking, G(XL), has been presented by Chapiro (B-12) which includes work of a number of investigators. Table B-3 summarizes the G-values for crosslinking as determined by various techniques and with various radiation sources for PDMS and other similar materials.

Referring again to G values, Charlesby (B-1) points out that G(XL) varies with temperature and cites the example of G(XL) = 2.6 at -78°C up to G(XL) + 4.7 at + 150°C. Others (B-17) have observed the same effect in PDMS and in the copolymer dimethyldiphenyl polysiloxane.

Effect of Radiation on the Properties of Polysiloxanes

As exposure to radiation changes the molecular structure and composition of polysiloxanes, the physical properties of these materials also change. Of interest in the current study is the effect of radiation on the following properties:

- Specific Volume
- Hardness
- Elongation to break
- Tensile Strength
- Elastic Modulus

A summary of the available literature relative to those properties with radiation exposure is discussed subsequently.

Specific volume, or alternatively, density, of polymers changes with irradiation as summarized by Charlesby (B-1). In the case of crosslinking polymers, the distance between chains is shortened by the crosslinking bond. For instance, in polyethylene which crosslinks and which has been studied in some detail, the specific volume at 160°C decreases from about 1.29 cc/gm at 0 dose to 1.135 cc/gm at about 750

Table B-3

SUMMARY OF G(XL) FOR VARIOUS POLYSILOXANES

Description	G(XL)	Reference*
Polydimethylsiloxane:		
infusibility	3.4	(B-14)
gel-point determination	2.8	(B-14)
elastic modulus	3.1	(B-14)
swelling & elastic modulus	2.4--2.7	(B-5,B-7)
M_n by cryoscopy	2.5	(B-8,B-25)
gel-point determination	2.2--2.5	Barnes, et. al.
gel-point determination:		
in vacuo	2.8	Okamura
in air	2.5	Okamura
gel-point determination:		
in vacuo	2.1	Davison
in air	1.1	Davison
Octamethylcyclotetrasiloxane:		
determination of dimer	2.0	Kantor
Polymethylphenylsiloxane:		
M_n by cryoscopy	0.8	Prober

*For reference with no number, refer to Chapiro (B-12) , p. 480.

Mrad gamma equivalent. This is a decrease of about 12%. The rate of decrease is larger at lower doses. The contraction in dimensions is attributed to the formation of crosslinks between carbon atoms which results in a decrease in the intermolecular distance from about 4A to 1.54A at the crosslink site.

Since polysiloxanes have been shown to crosslink, it is to be expected that the specific volume in this case will also decrease with dose, rather rapidly at low dose with an ultimate saturation as the density of crosslinks becomes greater. Decreases in dimensions with dose in which a shrinkage of 8 to 9% in thickness in a polysiloxane film irradiated by 10-15 Kev electrons has been noted (B-19). Lateral shrinkage was negligible, possibly because of adherence to a rigid substrate. Subsequent heat treatment caused further changes in dimensions. Roberts (B-19) also investigated the changes in sensitivity to irradiation in some polysiloxanes by changing the organic groups. When phenyl groups were substituted for methyl groups, a dose 6 times greater was required to achieve the same radiation-induced change in physical property.

The effect of irradiation on the mechanical properties of polysiloxanes has been studied quite extensively (B-5,B-6,B-7, B-8,B-20). In early studies, Harrington (B-9,B-10) investigated the effects of Co-60 radiation on a wide range of the commercially available elastomers. In particular, he studied a series of Dow Corning elastomers (manufacturer of base Boraflex polymer used by BISCO) which included dimethylpolysiloxane and various copolymers including methyl/vinyl, methyl/phenyl and methyl/vinyl/phenyl. Both filled and unfilled polymers were included in the matrix of test specimens studied.

The change in hardness, elongation to break, tensile strength and color of the Dow Silastic materials as a function of increasing gamma dose can be summarized as follows:

- Hardness: Shore A hardness increases with dose.

- Elongation to break: Decreases significantly with dose.
- Tensile strength: Initially most specimens show an increase in tensile strength at low dose. Subsequently, some showed further increase while others showed a decrease over the range of doses studied.
- Embrittlement: At higher doses, all specimens broke when subjected to a 180° bend test.
- Color changes: Some samples showed color changes when subjected to gamma radiation.

The above observed material changes with gamma radiation exposure tend to confirm and verify the behavior observed with Boraflex as described in Sections 3 and 4.

Elastic moduli of polysiloxanes tend to increase linearly with dose as a determined by a number of investigators (B-5,B-7,B-14). In the case of Bueche's work (B-7), the dose range was 60 Mrad (electron irradiation), with deviations from linearity only at low doses where end effects apply as shown in Figure B-4. These results are associated with, or complimentary to, mechanical property studies of irradiated filled-polymers where the crosslinking causes changes in tensile strength, Shore A hardness and elongation-to-break as discussed previously.

Environmental Effects

As noted previously, the environment, namely the presence of molecular oxygen as well as other agents, (water vapor, peroxides, etc.) is an important element which may influence the behavior of polysiloxanes in a radiation field. In addition to chemical agents, temperature may be an important factor. It should be noted that irradiated polysiloxanes are very different materials from unirradiated polysiloxane in that the former contain many free radicals. It is believed that many, if not most, of the polymers as defined as crosslinking types in Table B-1 would undergo degradations if sufficient free access of oxygen were provided (B-2). In order for oxygen to have a significant effect, it must diffuse into the polymer at a rate comparable to its

rate of reaction in the polymer. If diffusion is slow relative to the rate of radical formation, then the effects of oxygen are likely to be confined initially to the surfaces and edges of the polymer. As oxygen diffusion proceeds, the effects of oxygen would progress inward from the surface. The rate of oxygen diffusion into the polymer would be expected to be a function of temperature, increasing as the temperature increases.

The primary reaction of oxygen is thought to be (B-2):

$$R^{\bullet} + O_2 \longrightarrow RO_2^{\bullet}$$

where the radical $R^{\bullet}$ has been formed by a chain scission or abstraction of a hydrogen atom. These investigators did not determine whether oxygen effects the rate of polymer degradation by accelerating scissioning or by retarding crosslinking (B-2).

Other agents have also been observed to accelerate chain scissioning in silicone rubber. Osthoff, Bueche and Grubb (B-21)) have shown that some of these agents are water, carbon dioxide, alkaline polymerization catalysts and peroxide residues (introduced during the vulcanization process). These investigators studied the effect of chemical stress relaxation in stressed samples of PDMS. Samples of PDMS were initially elongated and the load (grams) required to maintain constant elongation as a function of time was measured. Experiments were conducted in various atmospheres and temperatures. Figure B-5 illustrates the effect of dry N_2, N_2 + water vapor, air and dry CO_2 on the load required to maintain constant elongation. The introduction of water vapor at 50 hours causes a rapid decrease in the required load. It was postulated (B-21) that this rapid decay in stress in the presence of water vapor involves a scission of the siloxane bond with the subsequent formation of silanols:

$$-\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}} + H_2O \longrightarrow 2-\overset{|}{\underset{|}{SiOH}}$$

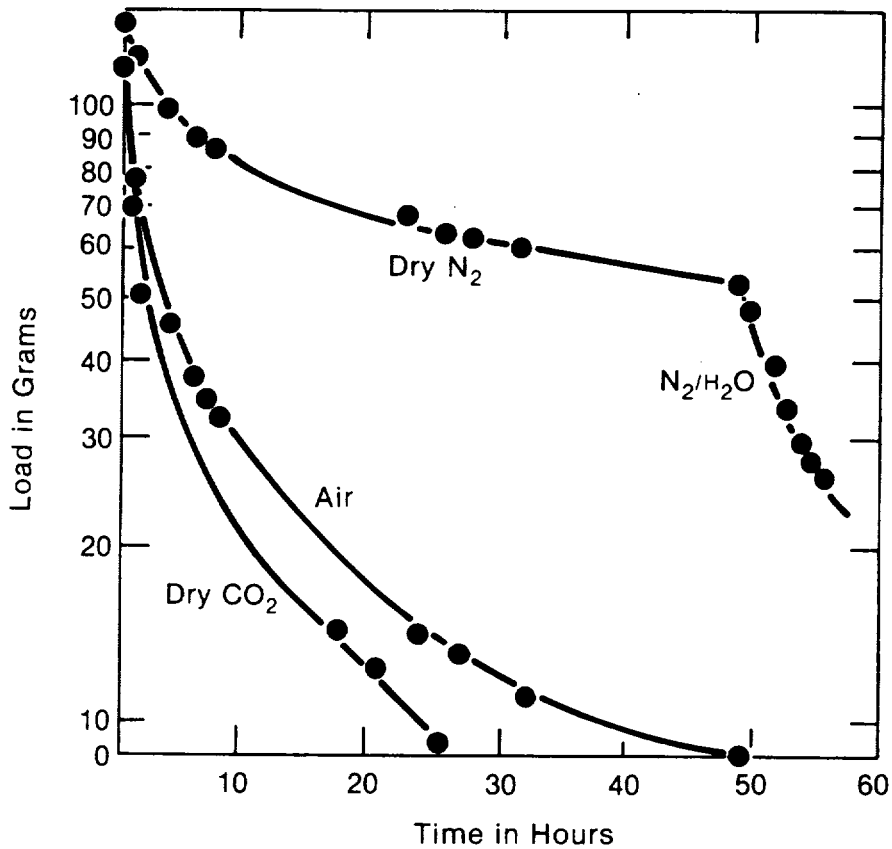

Figure B-5. Effect of Water, Air and Carbon Dioxide on Stress Relaxation of PDMS at 130° C. (Source: R. C. Osthoff, A. M. Bueche and W. T. Grubb. "Chemical Stress-Relaxation of Polydimethylsiloxane Elastomers", Journal American Chemical Society, vol. 76, 1954, pp. 4659-4663.)

Figure B-5 also indicated that air and dry CO_2 can also accelerate stress relaxation in PDMS. Contrary to the previous study cited, pure dry oxygen was found to have no effect (stress relaxation curve was the same as for dry N_2). Similar effects have been observed in other irradiated polymers (B-22--B-24). In these cases the effect has been termed oxidative scission.

The effect of residual agents from chemical vulcanization was also studied. The stress relaxation of PDMS crosslinked with 1.65% benzoyl peroxide and by 800 kev electron radiation are compared in Figure B-6. The presence of water vapor appears to have a strong influence on stress decay in the chemically crosslinked material but no effect in the sample crosslinked with radiation. The crosslink density for the two samples is not given. If the crosslink density of the irradiated sample were significantly greater than the chemically crosslinked sample, the effect of chemical stress relaxation might not be evident due to a large number of tie points between chains.

The effect of air on silicone and other elastomers irradiated under stressed conditions was studied by Harrington (B-9). In these experiments, tensile samples of silicone rubber and other materials were restrained at the ends and were subjected to gamma radiation. Some samples were irradiated in air and others in vacuum. The samples irradiated in air to a dose of 5×10^7 roentgen developed cracks and in some cases the samples broke. The companion samples irradiated in vacuum did not have cracks. It was postulated (B-9) that ozone formed by the radiolysis of air was the prime agent causing the cracks in the stressed elastomers.

This mechanism for crack initiation appears analogous to stress corrosion cracking which can occur in some alloys. For example, oxygen attack of stainless steel at the grain boundaries can cause crack initiation and growth at stress levels well below the tensile strength of the material. The effect of radiation environment on stressed Boraflex and mechanisms of gap formation is discussed in Section 5 of this report.

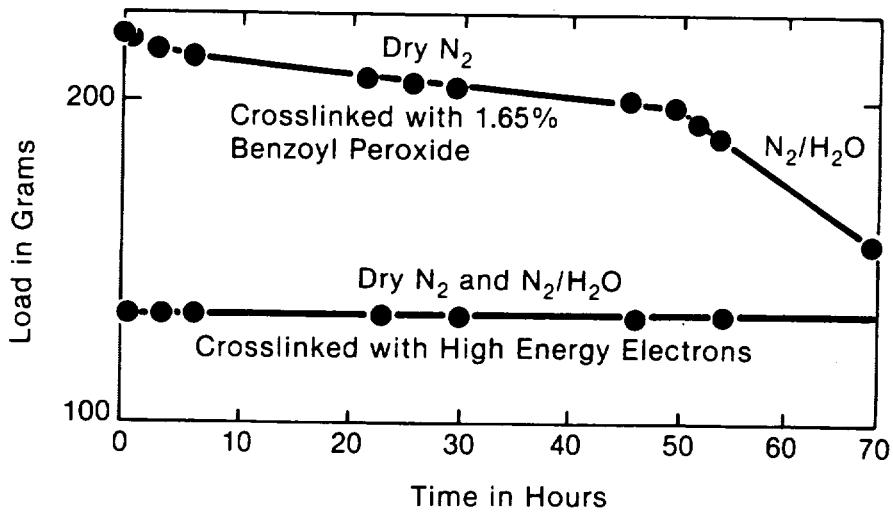

Figure B-6. Stress-Relaxation of PDMS Crosslinked with Benzoyl Peroxide and Electron Radiation. (Source: R. C. Osthoff, A. M. Bueche and W. T. Grubb. "Chemical Stress-Relaxation of Polydimethylsiloxane Elastomers", Journal American Chemical Society, vol. 76, 1954, pp. 4659-4663.)

Environmental effects in elastomers may continue for some period after they are removed from the radiation field since ions and electrons created as a result of the radiation persist for considerable periods (B-2). It has been noted that gamma radiation causes the creation of a variety of free radicals in the polymer. The diffusion of chemical agents into the polymer and the combining with free radicals would be expected to continue after the gamma field is removed.

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APPENDIX C

GUIDELINES FOR A STANDARD BORAFLEX COUPON SURVEILLANCE PROGRAM

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Appendix C

GUIDELINES FOR A STANDARD BORAFLEX COUPON SURVEILLANCE PROGRAM

Notice

The following are intended to be used as guidelines in establishing Boraflex Coupon Surveillance Programs for individual fuel rack installations. As such, they are not intended to supplant elements of programs recommended by the manufacturer of either the fuel storage racks or Boraflex. The intent, rather, is to serve as a supplement to tests and procedures as recommended by the Boraflex or fuel rack supplier. Accordingly, only specific elements of the Guidelines may be selected for implementation at a particular facility.

1.0 PURPOSE AND SCOPE

These guidelines have been developed to provide the utility with a basis for specifying recommended elements of a Boraflex Coupon Program. While these guidelines are intended principally for plants initiating new surveillance programs, there may be elements which can be used to benefit existing programs. The guidelines have as their objectives a standardized coupon surveillance program which will:

- Provide data in sufficient quantity and of sufficient quality (pre and post irradiation characteristics) to yield accurate and meaningful information on the performance of Boraflex in the spent fuel pool environment.
- Provide coupon data which can be readily extrapolated to tracking and projecting the performance of Boraflex in the spent fuel racks.
- Provide industry-wide data which is uniform in quality and accuracy.
- Be applicable to both PWR and BWR pools with racks utilizing Boraflex for criticality control.

To meet these objectives the following sections of this document address methods for coupon material selection, coupon configuration and quantity, frequency of surveillance and methods for pre and post irradiation of characterization of specific physical attributes.

Various ASTM Standards for the measurement of the specific physical attributes have been referenced that may be useful in developing techniques for obtaining coupon data of uniform quality and sufficient accuracy. In some cases the ASTM Standards will not be practical to apply exactly as prescribed and may require adaptation to Boraflex. However, the standards can be useful in understanding the intent of the measurement and the sensitivity to measurement variables. Since the spent fuel pool water condition may be an important element in the overall service life of this material, recommendations for monitoring pool water chemistry and temperature are also provided.

2.0 SURVEILLANCE PROGRAM OVERVIEW

While a coupon program consisting of many large coupons scheduled for frequent inspection can provide useful data, it is recognized that certain limitations exist with respect to coupon size, number and frequency of surveillance. For this reason the program outlined here utilizes two types or sets of coupons. The first type consists of coupons characterized with respect to certain physical attributes which can be readily examined in the station chemistry laboratory. These coupons, termed the standard coupons, are designed for periodic removal, inspection and, if feasible, are reinserted in the pool for subsequent exposure. The recommended inspections and measurements are nondestructive and have been selected to provide an indication of the general condition of Boraflex and any indication of gross or unusual degradation. The standard coupons are scheduled for frequent inspection, typically on a schedule dependent on refuelings. It is recognized that in certain situations that reinsertion of coupons may prove impractical and each reactor program will have to be adjusted as necessary to meet any local constraints.

The second type or set of coupons will be precharacterized with respect to the same set of physical attributes as the standard coupons but will be scheduled for more extensive post irradiation examination. These coupons, termed the special coupon set, will probably have to be sent to an independent laboratory for the post irradiation

examination. Since the post irradiation tests of the special coupons may involve certain destructive testing, these coupons are not scheduled for reinsertion in the pool. The frequency for removal and inspection of coupons from the special set is less frequent than for the standard coupons, typically once every five years.

3.0 COUPON PREPARATION

3.1 Scope

This section provides recommendations for sampling production lots of Boraflex and coupon material selection. Coupon configuration and methods of encapsulation are also addressed.

3.2 Coupon Selection

3.2.1 Standard Coupons.

Approximately 20 samples to serve as standard coupons should be selected. For the purposes of selection, the production lots from which the coupons are selected should be randomly identified and no two samples should be taken from the same production lot. Coupon material from the same production lot should be selected randomly consistent with BISCO's quality assurance procedures. In addition, one archive sample should be randomly selected from each production lot and retained. Each coupon and sample should be identified as to the production lot from which it was taken and assigned a unique identification number. Serialization documentation for full traceability from raw material to installed position in the fuel racks should be retained. Material certification of isotopic specifications and chemical compositions for each production lot should be retained.

3.2.2 Special Coupons.

Approximately 10 coupons and archive samples should be selected as in paragraph 3.2.1 to serve as special coupons. Each coupon should be

clearly identified as to its production lot and assigned a unique identification number. Documentation and certification specified under 3.2.1 also applies.

3.3 Coupon Size and Orientation

Coupons should be of certain minimum dimensions according to the dimensions of Boraflex used in the spent fuel storage racks. Coupon width should be equal to the nominal width of the Boraflex sheet used in the fuel racks. Coupon length should be approximately twice its width.

A small hole should be punched in one corner of the coupon. The hole will serve to orient the coupon and also serve as a convenient means to suspend the coupons for specific gravity measurements. The short edge of the coupon nearest the hole is considered the top of the coupon. The long edge nearest the hole is considered the right edge. With the coupon oriented so that the hole is in its upper right hand corner, the facing surface is considered the front of the coupon; the opposite surface, the back of the coupon. The edges of the coupon cut during manufacture should be identified and recorded. The edges which have been cut during coupon preparation should be similarly identified and recorded.

3.4 Coupon Encapsulation

Each coupon should be encapsulated in a clad material identical to that used to capture and retain the Boraflex in the spent fuel storage racks. For many applications, this material is stainless steel. Vent holes should be provided to allow the escape of offgas produced when Boraflex is irradiated. The vent holes should allow the pool water to enter the capsule and contact the Boraflex. The size and location of vents should be selected so as to simulate, as closely as possible, the water exchange rate between the interior of the capsule and the pool as well as local flow conditions which prevail in the spent fuel storage racks. Since different means for venting are used in various

fuel rack designs, each will have to be evaluated separately.

Means should be provided to open or close the capsule (for the purposes of Boraflex removal) without causing damage to the coupon. Such means may include, but need not be limited to, mechanical fasteners such as machine screws. Welding and crimping are to be avoided since these would generally require cutting the clad and the potential for mechanical damage to the Boraflex.

Each coupon should be placed in a capsule oriented such that the top edge of the Boraflex corresponds to the top edge of the capsule with the small hole located in a position corresponding to the upper right hand corner. When the capsules are suspended in the pool, the top edge of each Boraflex coupon should be oriented toward the pool surface. One flat surface of each capsule cladding should be clearly marked with the unique coupon identification number. The marking should be accomplished by stamping, etching or welding in letters and/or numerals at least 1/2" high.

3.5 Coupon Installation

The set of standard coupons and set of special coupons should be affixed to separate trains for placement in different locations in the spent fuel pool. The maximum length of the trains should be restricted to approximately one half of the active fuel length of fuel stored in the pool. The elevation of the coupon trains in the pool should be selected so that the midplane of the trains corresponds to the midplane of the active fuel stored adjacent to the trains. This is to assure that all coupons in a given train receive uniform gamma exposure.

The rack location of the coupon train containing the standard coupons should be selected so that freshly discharged fuel is stored on all four adjacent sides of the train after each refueling outage. In this manner, the standard coupons will receive accelerated gamma exposure

relative to the average exposure of the storage racks.

The rack location for the special coupons should be selected so that gamma exposure is accumulated at a rate corresponding to that of an average storage cell in the racks.

Specific requirements for the coupon train will vary from pool to pool and the specific design details should be developed by the utility and coupon supplier. Similarly, refueling procedures vary from utility to utility so that the details of coupon train placement must be developed on a site specific basis.

3.6 Related Documents

3.6.1 ASTM Standards.

- D 1898-68 Practice for Sampling of Plastics

4.0 SURVEILLANCE FREQUENCY

4.1 Scope

This section provides guidelines for establishing schedules for coupon removal and surveillance. One schedule is recommended for the standard coupon set and another, less frequent schedule, for the special coupons. Provision is made for more frequent sampling and more detailed examination of the standard coupons should indication of unusual Boraflex degradation be observed. The recommended surveillance frequencies are based on the assumption that the standard coupons will be subjected to accelerated gamma exposure from freshly discharged fuel assemblies after each refueling outage. This will assure that the coupons will lead the average rack exposure by a substantial margin.

4.2 Standard Coupons

The schedule for removal of the standard coupons should be keyed to the cumulative gamma exposure received by the coupons. Since the gamma exposure is to be accelerated by placing freshly discharged fuel adjacent to the coupons after each refueling, the following schedule is recommended. After initial coupon placement, a minimum of one standard coupon should be removed just prior to the next refueling outage. Coupon removal should be repeated in a similar manner just prior to the next two refueling outages. Thereafter, the frequency for coupon removal and inspection should be just prior to every other refueling. After inspection per Sections 5 and 6, the coupons are to be reassembled and returned to the spent fuel pool.

4.3 Special Coupons

One coupon each should be removed and tested every five years following coupon installation. The special coupons are not to be returned to the pool.

4.4 Variations in Sampling Frequency

Should inspections of standard coupons indicate unusual degradation of the Boraflex, increased sampling frequency and inspection should be considered. For these purposes, unusual degradation of the Boraflex is defined as any observable or measurable change in the condition of the material which would result in loss of the boron carbide. Examples of such changes include:

- Excessive thinning of the material particularly along the edges.
- Changes in coupon length or width in excess of those expected from normal shrinkage of Boraflex.
- A significant reduction in coupon weight.
- Softening of the Boraflex.
- Blistering, cracking or spalling of the surface of the coupon.

In such case, the standard coupon should be inspected as per the testing requirements for the special coupons. Results of these tests and measurements should be compared to the Acceptance Criteria, guidelines for which are provided in Section 7.0.

5.0 TESTS FOR STANDARD AND SPECIAL COUPONS

All coupons should be precharacterized with respect to those physical and chemical attributes specified in Sections 6.3 through 6.9, exclusive of 6.7. After removal from the pool, the standard coupons are to be characterized with respect to those attributes outlined in Sections 6.3 through 6.7. The special coupons are to be subjected to testing per Sections 6.3 through 6.9.

6.0 COUPON CHARACTERIZATION

6.1 Scope

This section provides guidelines as to which physical and chemical attributes are to be characterized pre and post irradiation. Appropriate ASTM Standards have been cited which provide some guidance in developing measurement procedures. Because the properties of irradiated Boraflex may differ from the materials addressed by the Standards, the procedures may require adaptation for application to irradiated Boraflex.

6.2 Coupon Conditioning

For precharacterization of as-produced Boraflex, the coupon should be conditioned at standard laboratory temperature and standard laboratory atmosphere. The purpose of sample conditioning is to bring the material into equilibrium with normal average room conditions and to obtain reproducible measurement results.

For coupons which have been exposed to the spent fuel pool water, the coupons should free of surface moisture and conditioned at standard laboratory temperature in a desiccator for 48 hours. The coupon should be then conditioned to the laboratory atmosphere.

6.3 Visual Inspection

The general overall appearance of the coupon should be noted and recorded. Noticeable qualitative changes in surfaces, outline and general appearance should be recorded. These changes include color, surface irregularities, edge erosion, cracks, etc.. Changes should also be noted as they occur, especially those which alter the shape so that intended dimensions are no longer significant. A color photograph, of sufficient resolution to distinguish areas of different color and shades, should be taken and retained.

6.4 Dimensions

Coupon thickness should be determined. The thickness of each coupon should be determined at nine locations as shown in Figure C-1. Coupon length and width should be determined at three locations each as shown in Figure C-2. Measurements of length and width should be made using a method providing an overall reproducibility of +/- 0.50% or less. Care must be exercised in measuring to account for edge erosion that may have developed in the coupons.

6.5 Coupon Weight

Coupon weight should be determined using an instrument capable of weighing accurately to 0.1% of the coupon weight. Coupons which have been exposed to the pool water should be weighed before and after conditioning. The pre and post conditioning weight should be recorded.

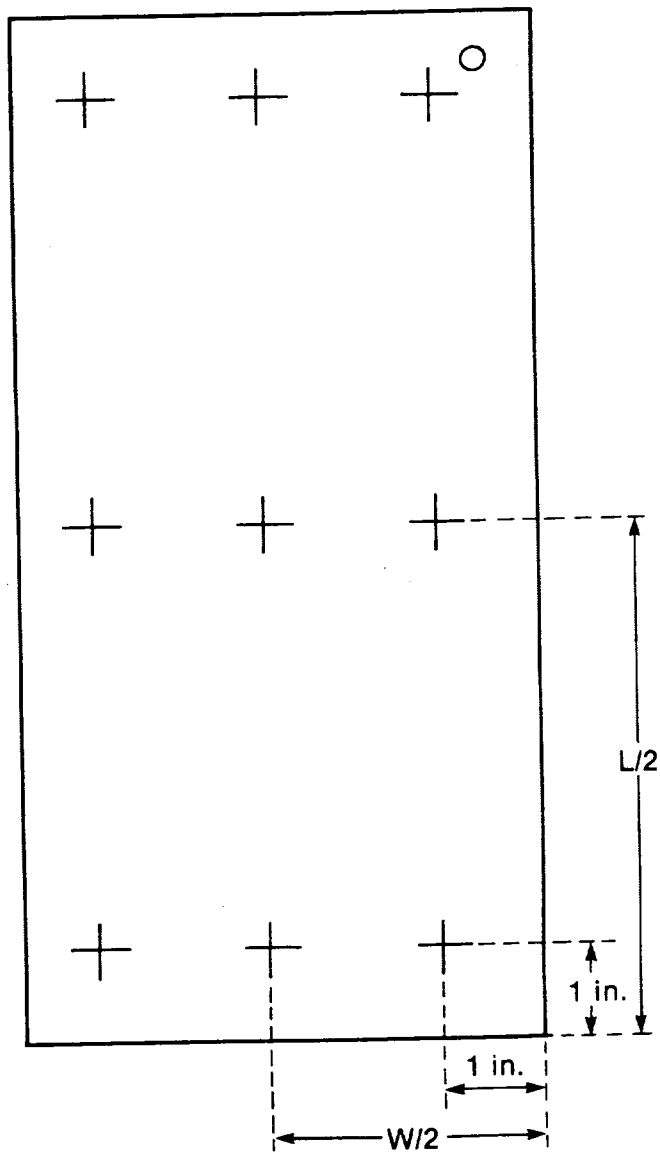

Figure C-1. Locations for Coupon Thickness Measurements.

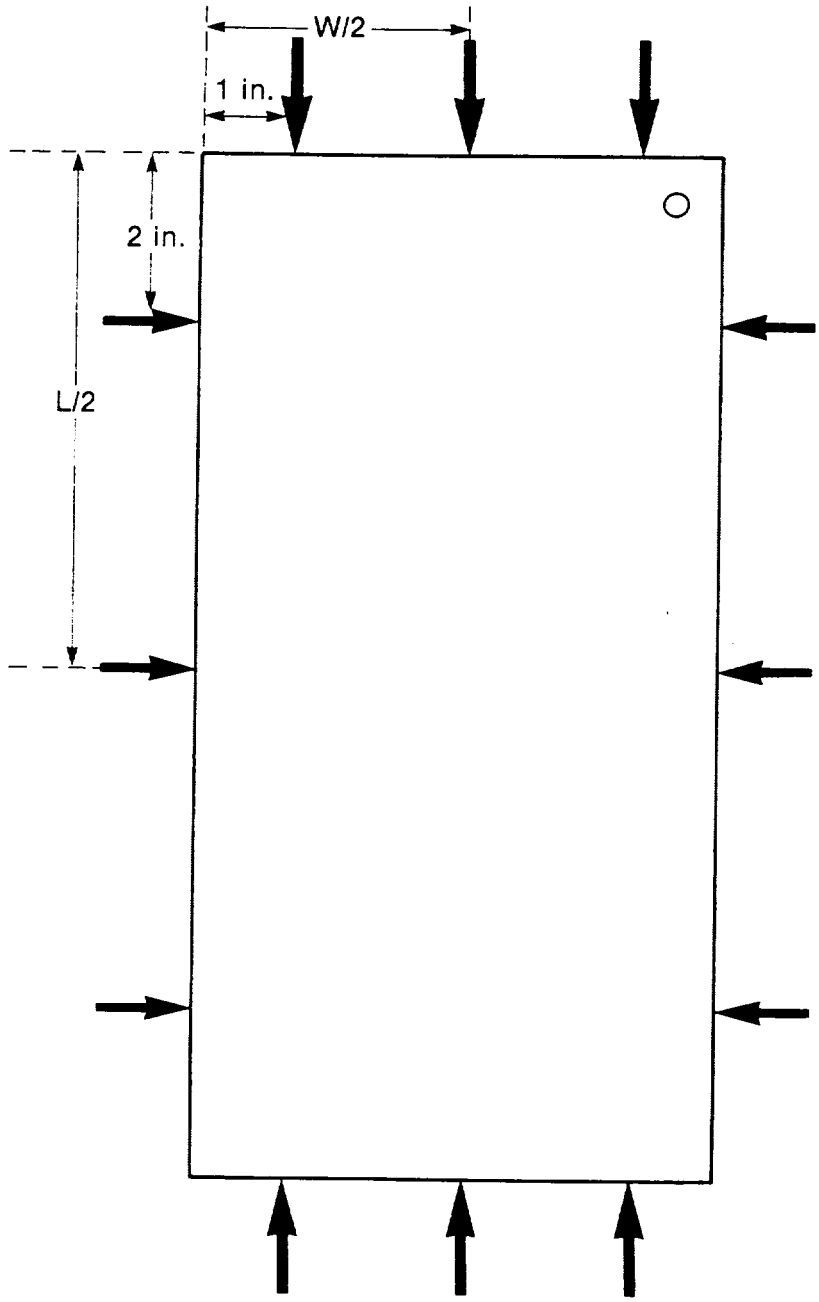

Figure C-2. Locations for Coupon Length and Width Measurements.

6.6 Shore A Hardness

Shore A hardness should be determined using a Type A durometer. Shore A measurements are to be taken at the locations as shown in Figure C-3. Shore D hardness measurements are not advisable since the use of a Shore D durometer may result in destruction of the coupon. The Shore A measurements are intended to provide a rough estimate of the gamma exposure and to detect any gross softening of the material. Coupons of sufficient thickness or layers of sufficient thickness, as described in Section 3.0 of this report, should be used.

6.7 Radioassay

In order to provide an indication of the extent of water permeation into the coupons, radioassay of the surface of the coupon for beta and gamma radiation should be performed. Radioassay should be performed with a suitable detector having a window sensitive to beta and gamma radiation and of dimensions not larger than one sixth the width of the coupon. Measurements of the activity on contact with the coupon are to be made midway between the top and bottom edges as follows:

- On the right and left edges of the coupon.
- One quarter of the distance in from the right and left edges.
- Midway between the right and left edges.

The beta and gamma activities (Mr/hr) as well as the gross activity as a function of detector location are to be recorded and retained.

6.8 Specific Gravity and Coupon Volume by Immersion (special coupons only)

Specific gravity and coupon volume by immersion should be determined by a displacement method. For the purposes of computing the volume of the coupon by immersion, the volume should be defined as the reciprocal of the density multiplied by the sample weight.

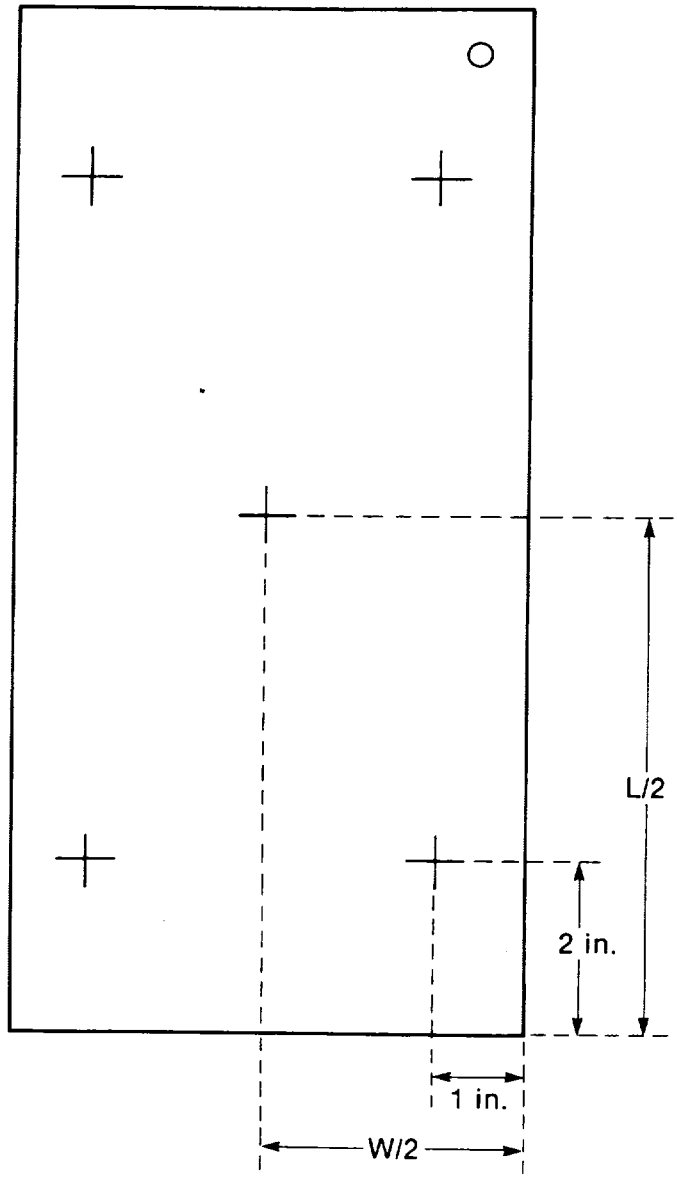

Figure C-3. Locations for Shore A Hardness Measurements.

6.9 Boron Determination (special coupons only)

Boron verification measurements should be made via neutron attenuation measurements. The purpose of the neutron attenuation measurements is to verify the uniformity of B-10 loading at several locations on the coupon. Neutron attenuation measurements should be taken at three locations as shown in Figure C-4 and compared with measurements taken on a control coupon. If a significant decrease in neutron attenuation is measured relative to the control coupon, boron determination via chemical analysis should be completed. At the location having the lowest measured neutron attenuation characteristics, a sample of suitable size should be removed from the coupon. The sample should be subjected to analyses for filler composition (B_4C) and total boron content. The B-10 loading in grams, B-10/cm^2, should be computed and compared with the Acceptance Criteria in Section 7.0.

6.10 Related Documents

6.10.1 ASTM Standards.

While there are no ASTM Standards specifically for Boraflex, there exist several Standards for the general class of materials, plastics and rubber. A list of related Standards which can provide some guidance in developing specific procedures for inspecting and testing Boraflex coupons includes:

- D 1349-87 Standard Practice for Rubber--Standard Temperatures for Testing.
- D 618-61 Standard Method of Conditioning Plastics and Electrical Insulating Materials for Testing.
- D 756-78 Standard Practice for Determination of Weight and Shape Changes of Plastics under Accelerated Service Condition.
- D 3767-84 Standard Practice for Rubber-Measurement of Dimensions.
- D 1042-83 Standard Test Method for Linear Dimensional Changes of Plastics under Accelerated Service

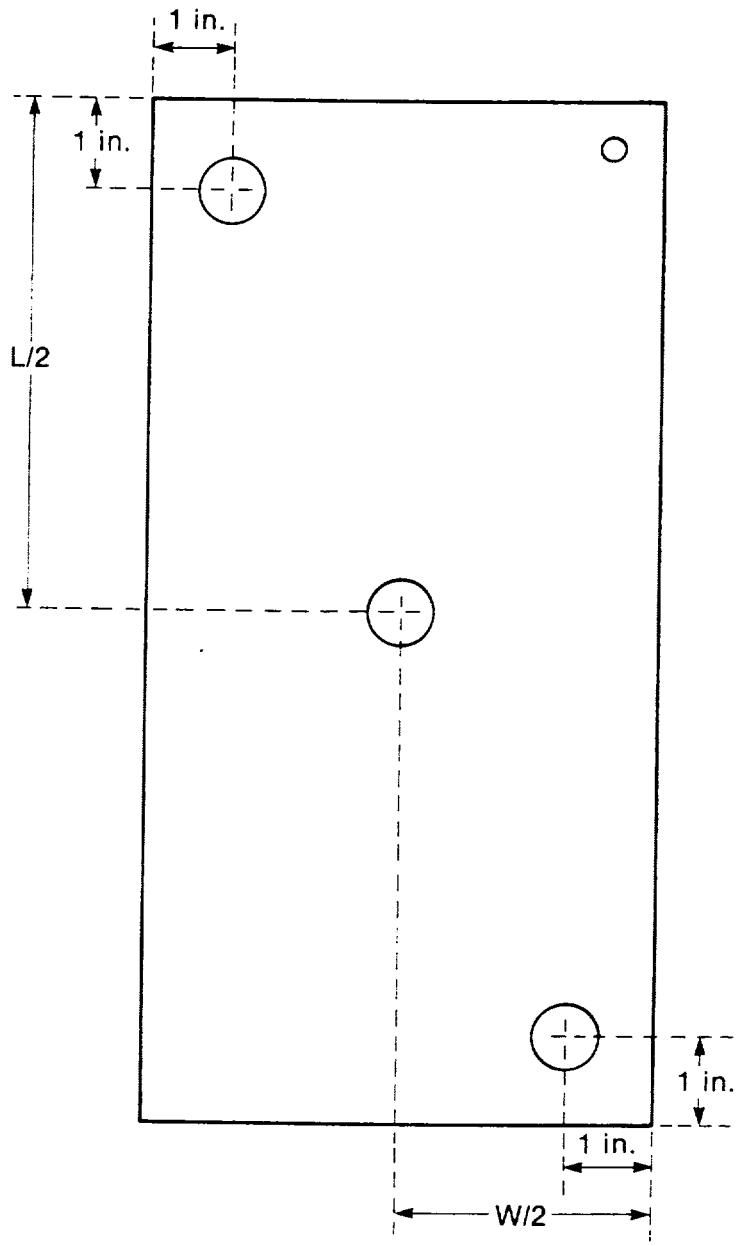

Figure C-4. Locations for Neutron Attenuation Measurements.

Conditions.

- D 792-66 Standard Methods of Test cf Specific Gravity and Density by Displacement.
- D 2240-86 Standard Test Method for Rubber Property--Durometer Hardness.
- D 297-81 Standard Methods for Rubber Products--Chemical Analysis.
- D 8838-66b Standard Definitions of Terms Relating to Plastics.
- C 791-83 Standard Methods for Chemical, Mass Spectrometric, and Spectrochemical Analysis of Nuclear-Grade Boron Carbice.

7.0 ACCEPTANCE CRITERIA

Evaluation of the coupon data described in Section 6.0 should be completed on a plant by plant basis. This is required since the criticality analysis for each fuel rack design is conducted on a plant specific basis. Each analysis contains implicit assumptions as to the nominal Boron-10 loading and the extent of variation in B-10 loading, Boraflex width and thickness. As-produced variations in B-10 loading, Boraflex width and thickness are provided by the manufacturer and their effect on the reactivity of the fuel and rack is determined by a series of differential reactivity calculations. The acceptance criteria are therefore determined by the range in variation of these quantities assumed for the criticality analysis. Coupon measurements should be compared with the following assumptions used in the criticality analysis:

- Minimum Boron-10 loading.
- Minimum sheet width.
- Minimum sheet length.
- Minimum sheet thickness

The results of the coupon measurements are acceptable if the measured coupon data exceed the minimum range implicit in the criticality analysis.

8.0 ENVIRONMENTAL CONDITIONS

8.1 Spent Fuel Pool Water Chemistry

The spent fuel pool water chemistry should be monitored periodically and average values of the following recorded.

- Water ph.
- Temperature, average, maximum and minimum.
- Boric acid concentration (ppm Boron).
- Conductivity (anion and cation).
- Activity levels (isotopics).

8.2 Fuel Placement and Gamma Exposure

The location of the coupon train should be recorded as to position and date of residence at that position. In addition, the fuel assembly identification number of assemblies located in storage cells adjacent to the train should be recorded. Fuel management records should be available to provide at a minimum the following data for those assemblies located adjacent to the train:

- Fuel assembly operating power exposure history prior to discharge.
- Reactor shutdown time and date.
- Time and data of fuel placement in the racks.

The above data should be available for all assemblies located adjacent to the coupon train.

The integrated gamma exposure to the coupons may be calculated by suitable means or measured. Suitable calculational methods include simulation of the fuel operating history and shutdown cooling history to determine the gamma photon source terms as function of cooling

time. A second photon transport calculation is then required to provide the gamma dose rate at the coupon location as a function of fuel cooling time.

Alternatively, the gamma exposure may be calculated from a "point in time" measurement of the gamma dose rate at the coupon location obtained with suitable survey instrumentation. The dose rate versus time may then be estimated using a standard prescription for the decay of fission product gamma activity.

Irrespective of which method is selected, an estimate of the uncertainty in the integrated dose should be determined.

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Printed on recycled paper in the United States of America

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