



Guidelines for Boraflex Use in Spent-Fuel Storage Racks

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Data from laboratory tests and spent-fuel pool silica measurements have identified Boraflex as a source of silica in these pools. EPRI has developed and applied a kinetic model based on silica to define factors influencing Boraflex service life. The guidelines in this report present a model for estimating the service life of Boraflex and performing appropriate surveillance activities.

INTEREST CATEGORIES

Radioactive waste
management
Light water reactor fuel

KEYWORDS

Spent-fuel storage
Radioactive waste
management
Neutron absorbers
Materials testing

BACKGROUND Utilities use neutron absorber materials such as Boraflex in spent-fuel storage racks to maximize fuel packing density. Fuel storage racks are normally designed for a service life of 30–40 years. EPRI report NP-6159 identified two issues with respect to using Boraflex. The first related to Boraflex shrinkage and the potential to develop tears or gaps after receiving high levels of gamma radiation. EPRI report TR-101986 addressed this issue, concluding that the phenomena is now well understood and manageable. The second issue, which is addressed in this report, concerned long-term Boraflex performance in the spent-fuel pool environment.

OBJECTIVES

- To perform tests to quantify the chemical composition and behavior of Boraflex in the spent-fuel pool environment.
- To collect and evaluate silica data from utility spent-fuel pools.
- To develop a model to predict spent-fuel pool silica levels based on a Boraflex silica source term.

APPROACH The project team developed chemical assay techniques to quantitatively determine the chemical composition of Boraflex. They conducted a test matrix of experiments to measure the rate of silica release from Boraflex over a range of conditions and to determine the sensitivity of the release rate to key variables. The team also collected silica data from 34 LWR spent-fuel pools and used that data to develop and apply a model for assessing factors influencing Boraflex service life.

RESULTS Chemical analyses of Boraflex indicate that the polymer matrix converts to silica (or a silica-dominated material) when exposed to gamma radiation in the spent-fuel pool. In this state, the material consists of about one-half boron carbide by weight and one-half silica by weight. In a typical pool, the silica in Boraflex amounts to several thousand kilograms, representing a significant potential source for pool contamination.

Long-term laboratory testing of irradiated Boraflex identified factors that influence the rate of silica release from Boraflex. This laboratory data also formed the basis for quantifying the source term in the preliminary EPRI model developed to predict pool silica levels. When applied to a specific pool and racks, the model can be used

to estimate the rate of Boraflex thinning and, accordingly, remaining service life. To date, modeling indicates that Boraflex service life is very sensitive to specific design features of the spent-fuel rack. Guidelines contained in this report will help utilities use Boraflex to gain maximum service life from spent-fuel racks.

EPRI PERSPECTIVE In the early 1980s, Boraflex became the material of choice for providing the neutron poison necessary to maximize fuel packing density in spent-fuel racks. As in-pool experience accumulated, some anomalies in Boraflex performance appeared, requiring close monitoring of the material. EPRI successfully developed a model to describe the shrinking and gapping that occurred after high levels of gamma irradiation. Analyses indicated that the phenomenon did not significantly affect the basic safety function of Boraflex. Research, however, identified a second factor that could impact service life—the potential gradual release of silica from Boraflex following gamma irradiation and long-term exposure to the wet pool environment. This EPRI report documents follow-up work performed to understand silica release mechanisms and to formulate a predictive service life model that helps estimate the useful life of spent-fuel storage racks containing Boraflex.

PROJECT

RP2813-04

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Guidelines for Boraflex Use in Spent-Fuel Storage Racks

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ABSTRACT

New data, since the issuance of EPRI Reports NP-6159 in December 1988, and TR-101986 in February 1993, have been acquired and evaluated to further assess the in-pool performance of the neutron absorber material Boraflex. The data are from ongoing EPRI test programs as well as utility measurements of spent fuel pool silica levels.

This new data provides a basis for identifying Boraflex as a source of silica contamination in spent fuel pools. Other data from long-term laboratory tests have identified those factors which have the greatest influence on the rate of silica release from Boraflex. A model has been developed which describes the kinetics of silica transport from the Boraflex into the bulk volume of the spent fuel pool. With further refinements the model may provide a basis for projecting Boraflex service life on a plant-by-plant basis. Guidelines have been developed for utilities with spent fuel racks containing Boraflex for extending the service life of this material and for surveillance.

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INTRODUCTION

The Electric Power Research Institute (EPRI) in 1987 instituted the research project RP2813-4 "An Assessment of Borated Material Performance in Spent Fuel Storage Racks." The need for the project was prompted by unanticipated performance of Boraflex™ surveillance coupons at one plant and the detection of tears or gaps in the full length panels of Boraflex in the racks at another plant. Report NP-6159 "An Assessment of Boraflex Performance in Spent-Nuclear-Fuel Storage Racks¹" was issued in December of 1988 and documented the results of the initial data collection and evaluation conducted under RP2813-4. NP-6159 had identified two issues with respect to the use of Boraflex in fuel storage racks.

- The potential for gap formation and the effect of such gaps on the reactivity state of the fuel/rack system
- The long-term integrity of the polymer matrix to retain the boron carbide neutron absorber material

It had been noted that qualification testing of this material by BISCO, the manufacturer of Boraflex, did not address the combined effects of gamma radiation and long term exposure to the pool aqueous environment. It was therefore recommended that utilities continue their surveillance programs on a plant-by-plant basis.

NP-6159 further noted that factors likely to influence the service life of this material would include:

- Integrated gamma dose
- Pool water chemistry
- Pool water temperature
- Rack design features which would allow for local flow around the Boraflex
- Boraflex thickness
- Boron carbide and other filler composition in Boraflex

With regard to the Boraflex filler material, it was hypothesized that as-produced Boraflex contained 20 to 25 w/o of silica as added filler. While, at the time, this was not confirmed by BISCO, the presence of silica could be inferred from the elemental

composition of this material cited by BISCO. The presence of silica was later confirmed by BISCO and also by chemical analyses conducted as part of this project.

Subsequent to the issuance of NP-6159, the EPRI program continued to collect data and initiated testing and evaluation programs to fully understand both the gap phenomenon as well as the changes Boraflex undergoes during long term exposure to gamma radiation in an aqueous environment. A second report, TR-101986 "Boraflex Test Results and Evaluation,"² was published in February of 1993. This report documented the results as a series of EPRI test programs as well as an industry-wide database of gap measurements via blackness testing. This provided the basis for the development of conclusions with respect to maximum gap sizes, the spatial distribution of gaps in the spent fuel storage racks, and the frequency of gap occurrence. This, along with special calculational methods developed as part of this project, demonstrated that the reactivity effect of gaps is small and can generally be accommodated within the existing design basis of the racks. The data and analyses presented in TR-101986 served, therefore, to close the first issue with respect to the use of Boraflex in spent fuel racks.

It was reported in TR-101986 that EPRI had several ongoing programs in place, the objective of which were to assess changes in material properties of Boraflex during long term exposure to gamma radiation and the aqueous pool environment. The interim results from these programs have been reported to EPRI's members at a series of workshops^{3,4,5,6,7}.

The ongoing EPRI programs include:

- A special test assembly at Beaver Valley 2 which contains 3 full size panels of Boraflex and a number of large coupons. To date three inspections have been performed.
- The special test coupons at Millstone 2 which have been designed to determine the effects of water flow and water accessibility to the Boraflex during irradiation. Two inspections have been completed as of this writing.
- Test irradiations in a Co-60 facility to determine Boraflex property changes as a function of dose in an aqueous environment.
- A series of long term aging experiments conducted in a laboratory in simulated spent fuel pool water.
- The development of a model to predict trends in pool silica levels and project Boraflex service life.

In the mid 1980's some utilities were beginning to measure elevated silica levels in the spent fuel pool water. Because of the work being conducted under RP2813-4 an

immediate connection between the pool silica levels and Boraflex was made. To verify this, a survey of utility pool chemistry data was initiated which now contains pool data from some 34 LWR spent fuel pools.

Elevated pool silica levels are an indication of Boraflex degradation and the potential loss of boron carbide from the matrix. Accordingly, there was a need to understand how Boraflex changes in its service environment. Gravimetric methods were developed to determine the chemical composition of both as-produced and irradiated Boraflex. The use of these methods indicate that, after exposure to gamma radiation in the pool water, the polymer matrix in Boraflex is primarily converted to silica and/or a silica-dominated material.

Silica is somewhat soluble in water. There was, therefore, a need to develop data with respect to the solubility of the Boraflex matrix under various conditions. A laboratory test program was initiated to develop solubility data over a range of conditions simulating the pool environment. The data developed was used as a source term for a kinetic model of silica in spent fuel pools. The model was applied to assess factors which influence pool silica levels and hence Boraflex service life. Guidelines were developed, based on these results, for operating practices which may lead to extended Boraflex service life.

The following sections of this interim report describe the results to date of the ongoing EPRI programs as well as the status of the industry-wide pool silica database.

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CHEMICAL COMPOSITION OF BORAFLEX

Elevated levels of silica in the form of monosilicic acid ($\text{Si}(\text{OH})_4$) have been measured in most LWR pools with spent fuel racks which utilize Boraflex. Boraflex had been suspected as a potential source of pool silica but until recently this had not been confirmed. It was noted in NP-6159 that the elemental composition of Boraflex cited by BISCO could not be valid if Boraflex consisted of only polydimethylsiloxane polymer and boron carbide. It is common to use silica (SiO_2) as a filler material in polydimethylsiloxane (PDMS) as a reinforcing agent to improve the tensile strength⁷. If Boraflex is assumed to initially contain about 25 w/o filler (as silica), the elemental composition cited by BISCO is obtained. Subsequently, BISCO confirmed that the "polymer" as received from Dow Corning contains about 50 w/o silica filler⁸. Thus, for Boraflex containing 50 w/o boron carbide, the remainder is about 25% polymer (PDMS) with a siloxane spine (O-Si-O) and about 25 w/o filler as silica.

Chemical analysis techniques have been developed as part of this project and a project completed for the Duquesne Light Company⁹ to assay the composition of both as-manufactured and irradiated Boraflex. The purpose of this work was as follows:

- To provide a means through chemical analysis to verify the boron-10 areal density of Boraflex
- To determine what chemical changes occur as this material is exposed to gamma radiation and the pool water.
- To determine the mechanism of silica release from Boraflex.

With regard to the second of these, it was thought that an understanding of any changes in the chemistry of the polymer may lend insight into the long term performance of this material in the spent fuel pool environment.

With regard to the third objective, a key question to be answered by this work is whether silica release is primarily a surface phenomenon or whether water permeation into the Boraflex leaches the silica filler from the interior of the material as well. A surface phenomenon would be characterized by the dissolution of the silica on the surface of Boraflex as the combined effects of gamma radiation and water change the polymer matrix. As the matrix changes, the silica filler would be exposed to the water and would go into solution. In this case, the release process can

be visualized as an "onion skin" mechanism and the rate of boron carbide loss (which is not soluble in water) would be proportional to the rate at which the surface dissolves. In this case the Boraflex would eventually show thinning and the rate of boron carbide loss would be proportional to the rate of silica loss.

Another possible mechanism of silica release from Boraflex is the permeation of water into the Boraflex and the dissolution of the silica into the pool water. In this case there may be no significant degradation of the polymer matrix or loss of boron carbide. If this were the case, silica loss may present a problem in terms of maintaining pool water purity but would not necessarily be indicative of any compromise in the integrity of the Boraflex.

Test Methods for Gravimetric Methods for Analysis of Boraflex

Overview

Quantitative methods of chemical analysis were developed to determine the quantities of silica and boron carbide in small specimens of Boraflex. The methods were applied to determine differences in chemical composition between unirradiated and irradiated specimens of Boraflex, and to determine whether the silica (and/or boron carbide) composition of Boraflex varies according to the degree and extent of exposure to the pool water. With respect to the latter, specimens were prepared from both the edge areas of Boraflex where water permeation is believed to occur first due to the open porosity along the cut edge, and interior areas where water permeation is believed to be less. Typically, when Boraflex is exposed to gamma radiation and the pool water, it gradually discolors, turning a greyish color first at the edges and corners where water permeation is the greatest. If the mechanism of silica release were characterized by a "leaching" process then one would expect less silica remaining in the discolored areas and greater amounts away from the edge where the Boraflex had not significantly discolored. If, on the other hand, the release mechanism is characterized by a surface effect, then the silica distribution would be expected to be more or less uniform.

Gravimetric Methods for Boraflex Chemical Assay

Two quantitative methods were developed for chemical assay of Boraflex samples. In both methods a small specimen (~0.25 gms) of Boraflex is removed from a piece of Boraflex using a punch. In the first method, the sample is dried via desiccation and weighed. The sample is then placed in a tared crucible and ashed to constant weight at 500°C. After cooling in a desiccator, the ash residue is weighed. The difference between the initial sample weight and the ash weight are the volatiles (from the polymer) which are driven off during ashing.

The ash residue is then flushed with hydrofluoric acid and ignited. This step dissolves the silica and the Si is driven off via ignition as SiF_4 gas. The final residue consists of HF insolubles (boron carbide) which is dried and reweighed.

A second method was developed which is only applicable to irradiated Boraflex. This method was developed to determine whether the initial ashing step in Method 1 significantly alters the silica or silica-like constituents in Boraflex. In this method, a small sample (~0.25 gms) of irradiated Boraflex is ground to a fine powder. (This step is not possible for unirradiated Boraflex as the material has the properties of an elastomer). After drying, the sample is weighed and subjected to an HF flush and ignition. After drying and weighing the residue, the specimen is ashed at 500°C to constant weight, cooled, and reweighed. The residue is then subjected to a final HF flush and ignited followed by drying and weighing.

Composition of As-Manufactured Boraflex

As a test of the first gravimetric method, a series of twelve small specimens were prepared from archive Boraflex retained from the material which is being tested in the EPRI surveillance assembly at Beaver Valley 2. These samples are designated as the L-series of specimens and the results of the chemical analyses are shown in Table 2-1. The initial sample weights as well as the weight after ashing and HF flushing are also given in this table. The average weight loss for the twelve samples during ashing is 20.9% and represents mostly volatiles from the polymer. The HF soluble component is 30.7 w/o and the average boron carbide content is 48.4 w/o. The HF soluble fraction represents the silica filler material plus some residual silicon (or silica) from the polymer. The computed standard deviations for each weighing step is quite low ($\pm 0.53\%$ after ashing and HF flush and ± 0.25 w/o final residue) indicating the method is reproducible. The average boron carbide content of 48.44 w/o can be compared with the material certifications supplied with this material by BISCO which specifies a value of 49.12 w/o for the actual production of this batch of material.

In addition to providing a means for the chemical assay of Boraflex, the method provides alternative means (alternative to neutron transmission methods) to determine the boron-10 areal density. The thickness of the samples were measured prior to punching and the density of the piece of material from which the samples were cut was measured via immersion weighing. The material certifications indicate a boron-10/total boron fraction of 0.1854 and a boron/boron carbide fraction of 0.785. The last column in Table 2-1 contains the calculated boron-10 areal density based on the measured boron carbide weight fraction, Boraflex thickness, and density. The average of the twelve samples is 0.0235 ± 0.0001 gms B-10/cm². This compares with a minimum specified areal density for this batch of material of 0.020 gms/cm². The minimum specified areal density includes allowance for variations in the material thickness up to 10% of the nominal thickness as well as variations in the boron carbide distribution in the Boraflex. That is to say, at a point of minimum specimen material thickness coincident with a minimum boron carbide loading, the areal density will be no less than 0.020 gms B-10/cm². Generally, the actual areal density is 12 to 15 percent greater than the minimum specified value.

Table 2-1
Chemical Analysis of the L-Series Boraflex Specimens

Sample ID	Weight, milligrams			Weight Percentages			Boron-10 Loading, gms/cm ²
	Initial	After Ashing	After HF Flush & Ignition	Loss During Ashing	HF Solubles	Boron Carbide	
L01	270.4	212.8	132.1	21.30%	29.84%	48.85%	0.0237
L02	272.2	213.4	132.1	21.60%	29.87%	48.53%	0.0235
L03	267.6	211.2	129.9	21.08%	30.38%	48.54%	0.0235
L04	271.1	214.0	130.9	21.06%	30.65%	48.28%	0.0234
L05	271.5	214.9	131.8	20.85%	30.61%	48.55%	0.0235
L06	271.4	213.9	131.4	21.19%	30.40%	48.42%	0.0235
L07	270.9	214.0	131.0	21.00%	30.64%	48.36%	0.0234
L08	270.1	213.9	129.4	20.81%	31.28%	47.91%	0.0232
L09	257.8	207.6	125.9	19.47%	31.69%	48.84%	0.0237
L10	271.9	216.8	131.8	20.26%	31.26%	48.47%	0.0235
L11	270.6	213.3	130.8	21.18%	30.49%	48.34%	0.0234
L12	271.7	214.6	130.8	21.02%	30.84%	48.14%	0.0233
Average:	269.8	213.4	130.7	20.90%	30.66%	48.44%	0.0235
Std. Dev.:	3.8	2.1	1.6	0.53%	0.53%	0.25%	0.0001

In summary, the results presented in Table 2-1 provide confidence that Method 1 is a reliable and accurate method for the chemical assay of Boraflex. In addition, the method provides an alternative means to measure the boron-10 areal density of Boraflex. This can be useful, for example, when applied to testing Boraflex surveillance coupons.

Chemical Composition of Irradiated Boraflex

Method 1 was then applied to the assay of two series of irradiated Boraflex specimens. The first series of specimens was prepared from a surveillance coupon from a PWR spent fuel pool. The coupon had received an integrated gamma dose of 3×10^9 rads and had greyed along the edges and corners. There was also a greyed area in the center of the coupon where an inspection port in the coupon capsule had been located. The specimens prepared from this coupon have been designated as the B-series.

Individual specimens were removed from the coupon using a 3/16 inch diameter punch. Two such disks weigh about 0.25 gms. The punching of irradiated Boraflex tended to crack the coupon and sample preparation was by necessity a destructive process. Prior to punching specimens from the coupon, the coupon thickness was measured at each location. The characterization of the B-series of specimens is shown in Table 2-2.

The second set of irradiated specimens were prepared from pieces of a panel of Boraflex removed from a spent fuel rack. This panel had received an integrated gamma dose of 1×10^{10} rads. Specimens were prepared from the edge of the panel where the material had turned to a whitish-grey color as well as the center of the panel where the Boraflex was a dull black color. The characterization of these specimens, designated as the P-series, is shown in Table 2-3.

The results of the B-series analyses are contained in Table 2-4. Also, shown in this table are the boron-10 areal densities for each specimen. Based on the boron carbide fraction, it is believed that this coupon originally had a composition similar to the unirradiated L-series specimen. However, the weight loss during ashing has decreased relative to the L-series and the HF soluble fraction (the silica and/or silica-like component) has increased significantly. This suggests that the combined effects of gamma radiation and exposure to the pool water transforms a substantial portion of the polymer into a silica or a silica-like material as discussed subsequently.

Table 2-2
B-Series Specimen Characterization

Sample ID	Location	Color	Thickness, Inches	
			T1	T2
B-1	Corners	Grey	.067	.066
B-2	Corners	Grey	.066	.0655
B-3	Edge	Grey	.066	.066
B-4	Center	Grey	.066	.066
B-5	Center	Black	.064	.064
B-6	Center	Black	.0655	.0655

Table 2-3
P-Series Specimen Characterization

Sample ID	Location	Color	Thickness, Inches	
			T1	T2
P-1	Panel Center	Black	0.0825	0.0845
P-2	1/4 into Panel	Black	0.0850	0.0845
P-3	Edge	Greyish white	0.0865	0.0865
P-4	Edge	Greyish white	0.0865	0.0875
P-5	Edge	Greyish white	0.0860	0.0865

Table 2-4
Chemical Analysis of the B-Series Boraflex Specimens

Sample ID	Weight, milligrams				Weight Percentages		B-10 Loading gms/cm ²
	Initial	After Ashing	Flush & Ignition	After HF Loss After Ashing	Silica	Boron Carbide	
B-1	230.3	220.5	112.6	4.26%	46.85%	48.89%	0.0225
B-2	231.7	221.4	112.9	4.45%	46.83%	48.73%	0.0222
B-3	230.9	220.1	112.4	4.68%	46.64%	48.68%	0.0223
B-4	228.0	220.1	113.0	3.46%	46.97%	49.56%	0.0227
B-5	230.9	223.4	113.2	3.25%	47.73%	49.03%	0.0218
B-6	228.4	218.5	111.5	4.33%	46.85%	48.82%	0.0222
Average:	230.0	220.7	112.6	4.07%	46.98%	48.95%	0.0223
Std. Dev.:	1.4	1.5	0.6	0.53%	0.35%	0.30%	0.0003

The result of the P-series specimens are shown in Table 2-5. Based on the boron carbide content of these specimens, it is assumed that the initial composition (prior to irradiation) was about 42 w/o boron carbide and 58 w/o polymer and SiO₂ filler. This composition is characteristic of Boraflex manufactured in the late 1970's and early 1980's. Later, BISCO standardized on a composition similar to that of the L and B series.

Two additional specimens were prepared from each unirradiated coupon and from the Boraflex panel and were subjected to analyses via Test Method 2. The results of these tests are shown in Table 2-6. These results can be compared with the results obtained using Method 1 in Tables 2-4 and 2-5. It is noted that the percent weight loss after the first HF flush and ignition in Method 2 (Table 2-6) are close to the weight losses measured after the HF flush and ignition in Method 1. This suggests that the silica or silica-like component in Boraflex is not altered significantly by the initial ashing step in Method 1.

Discussion

Chemical Composition of Unirradiated Boraflex

The analysis, by Method 1, of twelve specimens of as-manufactured Boraflex provides a quantitative determination of Boraflex composition with very little sample-to-sample variation. This verifies the method and demonstrates its reproducibility. Comparison of the measured average boron carbide loading of the twelve specimens (Table 2-1) of 48.44 percent with the manufacture's material certifications for boron carbide content (49.12 percent) verifies the accuracy of the method. This gravimetric method provides an alternative means to determine the boron-10 areal density of Boraflex.

Chemical Composition of Irradiated Boraflex

When the data presented in Tables 2-4 and 2-5 for the irradiated P- and B-series of samples is compared to the data in Table 2-1 for as-manufactured Boraflex, it is clear that the composition is quite different. The as-produced composition (L-series) of Boraflex is 20.9 w/o volatiles, 30.7 w/o HF solubles and 48.4 w/o B₄C. The results for irradiated Boraflex (B-series) are 4.1 w/o volatiles, 47.0 w/o HF solubles and 48.9 w/o B₄C. Since the B-series initially (prior to irradiation) had a composition similar to the L-series, it is clear that gamma radiation and the aqueous pool environment have changed the composition of Boraflex. After irradiation, Boraflex consists of primarily silica and/or a silica-like material and boron carbide with only a small weight fraction (~4.0 w/o) which is volatilized during the ashing step.

Table 2-5
Chemical Analysis of the B-Series Boraflex Specimens

Sample ID	Weights, milligrams			Weight Percentages			Calculated B-10 Loading
	Initial	After Ashing	After HF Flush & Ignition	Loss After Ashing	Silica	Boron Carbide	
P-1	271.0	254.7	113.8	6.01%	51.99%	41.99%	0.0245
P-2	278.3	258.9	113.6	6.97%	52.21%	40.82%	0.0246
P-3	283.4	266.3	118.5	6.03%	52.15%	41.81%	0.0258
P-4	268.3	251.2	112.5	6.37%	51.70%	41.93%	0.0260
P-5	276.4	259.5	115.3	6.11%	52.17%	41.71%	0.0257
Average:	275.5	258.1	114.7	6.30%	52.04%	41.65%	0.0253
Std. Dev.:	5.4	5.1	2.1	0.36%	0.19%	0.43%	0.0006

Table 2-6
Chemical Analysis of B and P Series Specimens: Method 2

Sample ID	Initial Weight (gms)	% Loss HF Flush & Ignition	% Loss on Ashing @ 500°C	% After 2nd HF Flush & Ignition	% Final Residue
B-7	0.1956	45.30%	0.87%	2.76%	51.07%
B-8	0.1805	44.93%	2.21%	2.60%	50.24%
P-6	0.2359	52.81%	3.01%	1.61%	42.56%
P-7	0.2858	52.83%	3.46%	1.15%	42.54%

A postulated mechanism for this chemical transformation of the polymer component in Boraflex is as follows. As Boraflex is exposed to gamma radiation it shrinks, hardens, and undergoes a density increase. All of these physical changes are attributable to abstraction, by gamma radiation, of CH_3 or H radicals and the subsequent formation of cross-link bonds between adjacent chains in the polymer. It is believed that once a vacancy is created on a chain, it diffuses along the chain until it lines up with a vacancy in an adjacent chain and a cross-link bond is formed. At higher doses the material becomes more highly cross-linked and the mobility of these vacancies is impeded due to the cross-link bonds. At this stage, when a vacancy is formed it may pick up free radicals in the pool water instead of forming a cross-link bond. Free radicals such as O or OH are likely to be available so that the polymer is converted to a composition consisting of Si, O, and perhaps OH, or silica or a silica-like material. Accordingly, after exposure to gamma radiation and water, Boraflex consists of boron carbide in a matrix of primarily silica or a silica-like material.

The results of the chemical analyses via Method 2 suggest that the initial ashing step (Method 1) does not result in a significant change in the HF soluble constituent of Boraflex. Comparing the B-series and P-series weight loss after the initial HF flush and ignition (Method 2) in Table 2-6 with the results in Tables 2-4 and 2-5 suggest a similar, though not exactly the same, HF soluble fraction.

The spatial distribution of silica in the P- and B-series samples is rather uniform. In fact, the standard deviation of the silica constituent for the B-series samples is $\pm 0.35\%$ and 0.19% for the P-series. This suggests that loss of silica is via a surface mechanism and not a leaching of the silica filler from inside the material. As silica on the surface of the Boraflex slowly dissolves in water, the altered matrix of Boraflex is no longer available to retain the boron carbide. Boron carbide loss would then be proportional to silica loss. The mechanism of silica dissolution in water is discussed subsequently.

3

SPENT FUEL POOL SILICA LEVELS

Until the last several years many utilities had not routinely monitored spent fuel pool silica levels. However, elevated reactor coolant system (RCS) silica levels, particularly after refueling outages, prompted the utilities to identify the source of silica. During refueling activities the spent fuel pool and RCS water volumes can mix as fuel assemblies are moved through the fuel transfer canal. Nuclear fuel manufacturer's warranties normally limit RCS silica to low levels because of the potential for silica deposition on the fuel cladding and the potential for degraded heat transfer and fuel performance.

As utilities began to sample spent fuel pool water for silica, elevated levels of reactive silica were measured, particularly in PWR pools. It should be noted that, unless stated otherwise, all silica data presented in this section are for reactive silica as determined by either the heteropoly blue (for low levels) or silicomolybdate (for high levels) colorimetric methods. Total silica (reactive plus colloidal) is not typically measured as routine and reliable measurement techniques are generally not available.

As a result of the possible connection between elevated pool silica levels and Boraflex, EPRI initiated a survey of utilities for spent fuel pool water silica data. The current status of that survey, which is ongoing, is described below.

Scope/Status of the Spent Fuel Pool Water Silica Database

Data collection for the silica database was initiated approximately four years ago and now contains data from 23 PWR spent fuel pools and 11 BWR pools. The scope of the PWR database is shown in the Table 3-1. The extent of the data varies from plant to plant and in some cases includes silica data for the RCS and refueling water storage tank (RWST) as well as for the spent fuel pool. Some of the utilities provided point-in-time data while others sent chronological data over extended periods of time. Table 3-1 provides a description of the data and the average silica and/or maximum silica levels measured in each pool. For comparative purposes, the PWR database contains pool silica data for plants which do not have Boraflex in the racks.

For those plants where chronological data have been supplied, a linear regression of the data was used to compute a best-fit slope. This provides the rate of increase in pool silica levels with time and is also shown in Table 3-1.

Table 3-1
Utility Silica Data: PWRs

Plant	Sample Location			Type of Data		SFP Silica,		Slope* (ppb/day)	SFP Data for Dates	Comments:
	RCS	RWST	SFP	Pt. in	Chron.	Ave.	Max			
PWRA			✓		✓	1.09	4.19	0.06	4-Jan-88 to 27-Jul-92	
PWRB1	✓	✓	✓	✓			4.00			
PWRB2	✓	✓	✓	✓			0.30			No Boraflex in racks
PWRC1			✓		✓	1.41	1.68	0.62	12-Apr-91 to 5-Jun-92	
PWRC1	✓	✓	✓	✓		1.36			Jan-93, Jul-93	
PWRC2			✓		✓	2.30	3.00	2.95	12-Apr-91 to 5-Jun-92	
PWRC2	✓	✓	✓	✓		2.89			Jun-92, Jun-93	
PWRI			✓		✓	5.42	7.95	0.64	2-Oct-85 to 5-Oct-90	
PWRJ1	✓		✓	✓		6.80				
PWRJ2	✓		✓	✓		0.06				
PWRL	✓	✓	✓		✓	4.50	9.80	3.62	4-Aug-89 to 8-Jun-93	Just installed Boraflex
PWRM			✓		✓	1.30	2.50	4.92	15-Feb-90 to 28-Dec-90	
PWRN			✓		✓	0.71	2.30	6.21	8-Jan-88 to 1-Jan-91	
PWRP			✓		✓	17.10	87.52	36.21	27-Feb-84 to 11-Jul-93	
PWRQ1			✓		✓	3.27	5.97	3.70	1-Feb-91 to 4-Jun-93	
PWRQ2			✓		✓	2.86	4.37	2.54	1-Feb-91 to 4-Jun-93	
PWRR1	✓		✓	✓		17.50			13-Jun-92, 18-Jul-93	
PWRR2	✓		✓	✓		19.75			13-Jun-92, 18-Jul-93	
PWRS		✓	✓		✓	0.88	1.47	1.80	30-May-91 to 13-May 93	
PWRS	✓	✓	✓	✓					Sep-91, May-93	

Table 3-1 (continued)

Plant	Sample Location			Type of Data		SFP Silica,		Slope* (ppb/day)	SFP Data for Dates	Comments:
	RCS	RWST	SFP	Pt. in	Chron.	Ave.	Max			
PWRT	✓	✓	✓		✓	2.03	2.65	2.19	13-Mar-91 to 5-Jul-93	
PWRU			✓		✓	4.65	6.10	1.25	11-Nov-91 to 19-Jul-93	
PWRV		✓		✓						No Boraflex in racks
PWRW1	✓	✓	✓	✓		1.80			Jun-92, Jul-93	
PWRW2	✓	✓	✓	✓		1.80			Jun-92, July-93	
PWRX			✓		✓	5.49	8.00	11.59	Apr-91 to May-92	

NOTES: * The slope is only as precise and accurate as the available data. It is a time-weighted average of the rate of change of silica concentration per day. For PWRs, the averages are taken over periods that do not contain refueling outages or discrete cleanup efforts (eg, reverse osmosis). For BWRs, the slope is calculated using all data and without correcting for demineralizer backwashing or resin changes.

NSD: not sufficient data

Table 3-2
Utility Silica Data: BWRs

Plant	Sample Location			Type of Data		SFP Silica, ppm		Slope* (ppb/day)	SFP Data for Dates	Comment:
	RCS	RWST	SFP	Pt. in Time	Chron. Trend	Average	Maximum			
BWRA1			✓		✓	0.55	0.98	-0.07	1-Jan-89 to 30-Oct-90	
BWRA2			✓		✓	0.50	0.97	-0.06	1-Jan-89 to 30-Oct-90	
BWRD1	✓	✓	✓	✓		0.18			Jun-92, Jul-92	Boral
BWRD2	✓	✓	✓	✓		0.16			Jun-93, Jul-92	Boral
BWRE2			✓	✓			0.70			Connected to Unit 1 Pool (Unit 1 has non-Boraflex racks)
BWRF1		✓	✓		✓	0.08	1.14	0.05	3-Feb-87 to 28-Jun-92	No Boraflex in racks
BWRF2		✓	✓		✓	0.05	0.15	0.06	9-May-89 to 23-Jul-92	No Boraflex in racks
BWRG	✓		✓		✓	0.25	0.33	0.01	5-Jan-91 to 17-Jul-92	
BWRH1		✓	✓		✓	0.70	3.20	0.18	19-Nov-85 to 22-Jul-92	
BWRH2		✓	✓		✓	0.32	1.48	0.15	10-Nov-85 to 22-Jul-92	
BWRJ	✓		✓		✓	NSD	0.15	NSD	1-Jul-91 to 1-Jul-92	

NOTES: * The slope is only as precise and accurate as the available data. It is a time-weighted average of the rate of change of silica concentration per day. For PWRs, the averages are taken over periods that do not contain refueling outages or discrete cleanup efforts (eg, reverse osmosis). For BWRs, the slope is calculated using all data and without correcting for demineralizer backwashing or resin changes.

NSD: not sufficient data

Table 3-2 contains the scope of the pool silica database for BWRs. As there are fewer BWRs which have spent fuel racks with Boraflex the database is somewhat less extensive than for PWRs. The data contained in Table 3-2 is similar to that contained in 3-1. The database contains silica levels for pools which do not have Boraflex in the racks or which use alternative neutron absorber materials for comparative purposes.

Pool Silica Levels in PWRs

Because of the volume of data contained in the database, only select data are presented here. The data presented have been selected to illustrate typical trends, as well as bounding levels of pool silica levels experienced by various utilities.

Figure 3-1 contains a plot of SFP reactive silica versus time for PWRs. This set of data is particularly useful as it illustrates the effect of exposing the Boraflex to gamma radiation for the first time in the pool. Prior to mid 1991, the spent fuel racks at this plant had never been used to store spent fuel assemblies. Up to the first refueling outage, the pool silica was fairly constant at 0.25 to 0.30 ppm. During the first refueling outage, the entire core was moved into the spent fuel pool for a few weeks. Subsequently, approximately two-thirds of the core was returned to the reactor vessel and one-third of the fuel assemblies remained in the racks as discharged fuel. Figure 3-1 shows that coincident with the first refueling outage the pool silica level increased from about 0.25 ppm to about 0.40 ppm and continued to increase at a rate of 1.7 ppb/day. During the second refueling outage, the spent fuel pool silica levels decreased due to mixing and dilution with low silica water from the RCS. After the refueling outage, when the SFP and RCS were again isolated, the pool silica levels continued to increase at a rate of about 2.0 ppb/day. This increased rate is due to the exposure of additional storage cells to gamma radiation and to the increased accumulation of dose to cells exposed to spent fuel assemblies during the first refueling outage.

The effect of mixing between the SFP and RCS during refueling outages has been noted at several PWRs. Figure 3-2 shows the RCS pool silica levels versus time for a fuel cycle at PWRQ1. At the beginning of the fuel cycle, the elevated silica levels are noted. With the soluble boron concentration in the RCS typically about 1000 ppm at the beginning of cycle, the demineralizers are ineffective in removing silica. This is also true of the mixed bed demineralizers normally provided for the spent fuel pool cleanup system. Typical soluble boron levels in PWR spent fuel pools are about 2000 ppm. Referring again to Figure 3-2, as the fuel cycle progresses and the soluble boron levels are reduced to compensate for fuel depletion, the demineralizers become more effective in removing silica and the RCS silica levels diminish.

Figure 3-3 contains a plot of pool silica versus time at PWRP which is the plant in the database with the highest pool silica levels. The spent fuel racks at this plant were installed in the early 1980s so that they have been in service for a period of more than 10 years. There are several other factors which have contributed to the high silica levels at PWRP. This PWR is a two unit plant with both units sharing a

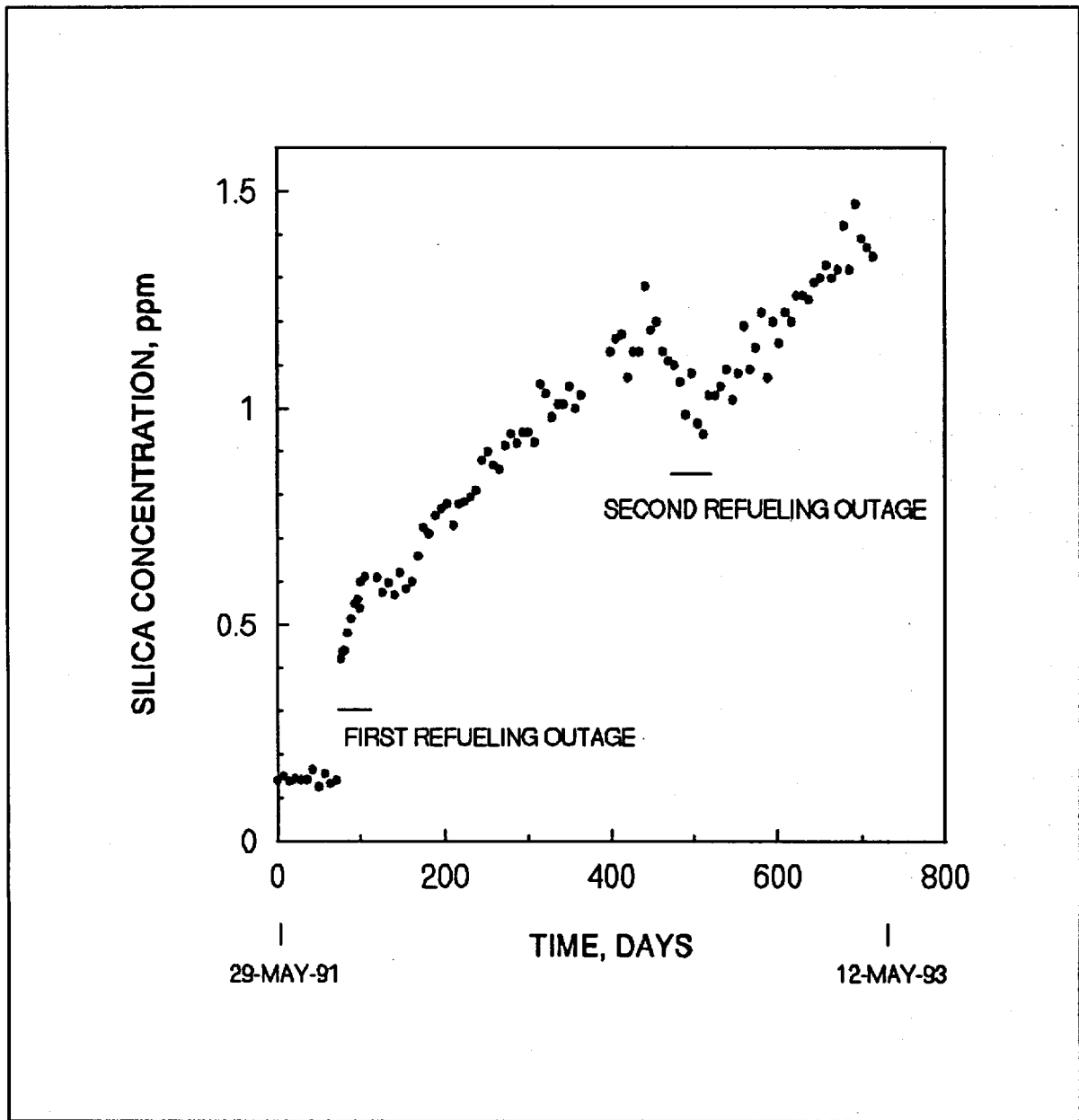


Figure 3-1
Pool Silica Levels as a Function of Time for PWRS

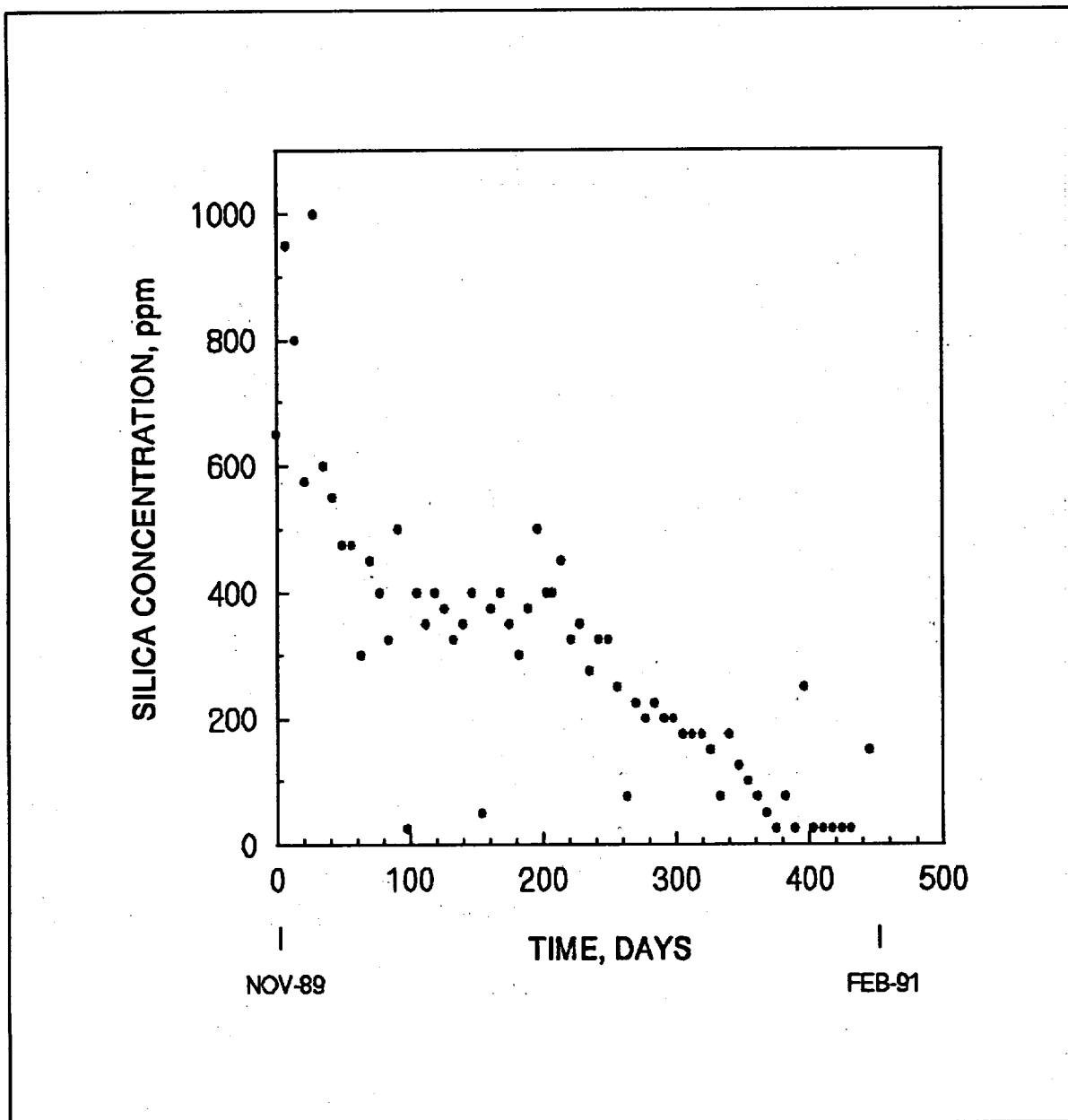


Figure 3-2
RCS Silica Concentration as a Function of Time at PWRQ1

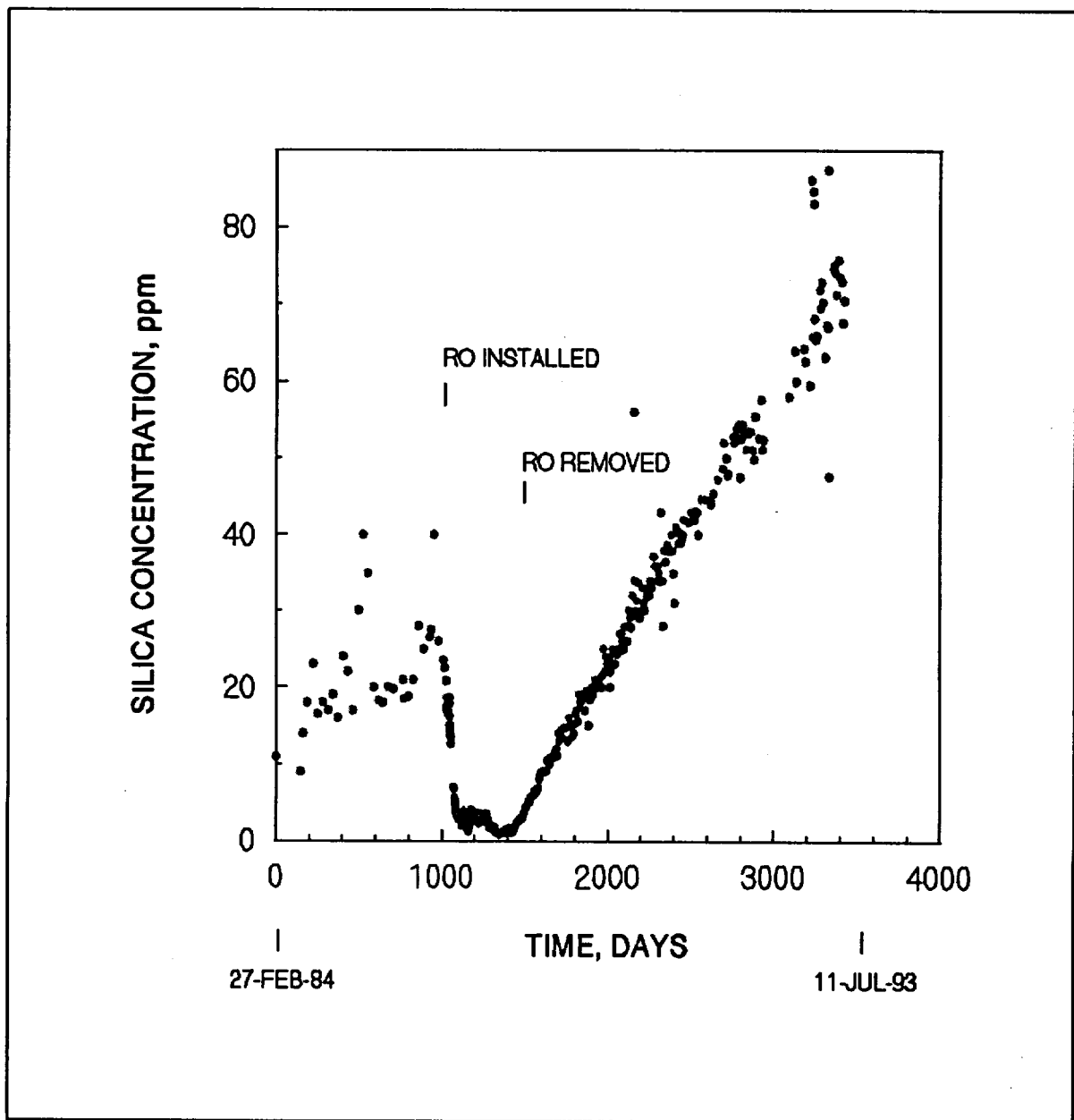


Figure 3-3
Pool Silica Levels as a Function of Time at PWRP

common spent fuel pool. The spent fuel storage racks are almost filled to capacity and every storage cell in the racks has been exposed to spent fuel. Many of the storage cells have been exposed to freshly discharged fuel assemblies several times so that the integrated gamma exposure to the Boraflex is high (probably in excess of 1×10^{10} rads).

Pool silica levels had showed an increase from the time the racks were installed and, in an attempt to reduce contamination of the RCS with SFP water, reverse osmosis (RO) equipment was installed to process the pool water. Figure 3-3 shows that the RO equipment was effective in reducing the pool silica, but after the equipment was removed the pool silica increased at a rate of about 36 ppb/day. Recently pool silica levels in excess of 80 ppm have been measured.

In order to confirm some laboratory testing described subsequently, a pool sample for PWRP was taken and sent to NETCO's laboratory facilities for analysis for total silica and reactive silica. Utilizing the technique for total silica based on inductively coupled plasma spectroscopy (ICPS) the total silica concentration in this pool was determined to be 147 ppm. The analysis of reactive silica using the silicomolybdate method provided a value of 84 ppm which seems to compare favorably with the data in Figure 3-3. The difference between the total silica and reactive silica is colloidal silica. Colloidal silica is a polymer form of reactive silica in which several monosilicic acid molecules agglomerate. The relationship between colloidal silica and reactive silica is governed by a complex equilibrium as discussed subsequently.

The data in Table 3-1 contains SFP chemistry data from a few plants with fuel racks which do not utilize Boraflex. PWRB Unit 1 has Boraflex in the pool and the pool silica has increased to a level of 4 ppm. Unit 2 at this site has a separate pool and racks which do not use Boraflex. The maximum pool silica measured at PWRB Unit 2 was 0.3 ppm. PWRJ Units 1 and 2 both have racks with Boraflex. At Unit 1 the racks were installed several years ago and the pool silica levels have increased to an average value of about 7 ppm. At Unit 2, the Boraflex racks had just been installed when the chemistry sample was received and the pool silica levels were about one hundredth of that for Unit 1. These data as well as the chemical analyses described in Section 2 serve to identify Boraflex as a primary source of silica in spent fuel pools.

Silica Levels in BWR Spent Fuel Pools

The situation at BWRs is somewhat different as can be seen in Table 3-2. The maximum pool silica levels are substantially lower than for the PWR plants, by as much as an order of magnitude. Laboratory test data described subsequently suggests that the silica source term from Boraflex in BWR racks does not substantially differ from the source term in PWR racks. The major difference between BWR and PWR pools is the presence of soluble boron in the latter. Without soluble boron in the BWR pools, the demineralizers are effective at removing silica and so the pool silica levels are generally low (1 ppm or less). However, there are differences between pools with and without Boraflex in the spent fuel racks.

Figure 3-4 contains some seven years of pool silica data for BWRH2. The spent fuel racks with Boraflex as a neutron absorber were installed in the early 1980's. The spikes in pool silica at 2000 days and near 2500 days are probably a result of degraded demineralizer performance and the need for service as described subsequently. While the silica concentration is low relative to some PWR pools, levels approaching 1.5 ppm have been measured and the average silica concentration is increasing at a rate of 0.15 ppb/day.

The data in Figure 3-4 can be contrasted with the silica history in Figure 3-5 at BWRF1 which has spent fuel racks without Boraflex. With the exception of one spurious data point, the pool silica level at this plant has typically been less than 0.2 ppm. Both BWRH2 and BWRF1 are operated by the same utility and, accordingly, the water treatment procedures and practices may be similar. The major difference in the two plants is the presence of Boraflex at BWRH2. Referring again to demineralizer performance at BWRs, Figure 3-6 contains the spent fuel pool silica history at BWRA2 which has Boraflex in the spent fuel racks. In this case, the maximum pool silica has been maintained at 1 ppm or less but there is a clear indication of a "saw tooth" trend in the data. It is believed that this "saw tooth" behavior of the data can be traced to demineralizer service. That is, immediately following backflushing or resin changeout, the demineralizers are most efficient in removing silica and the pool levels are low. With continued service, the resins become saturated with silica and the pool levels rise. Silica "breakthrough" in the effluent of the demineralizer has traditionally been used as an indication that the demineralizers require service.

Boraflex as a Potential Source of Silica in Spent Fuel Pools

Given the composition of irradiated Boraflex determined previously, it is possible to estimate spent fuel pool silica concentrations assuming small amounts of the Boraflex silica undergo dissolution. For illustrative purposes, consider a typical PWR spent fuel pool containing Boraflex fuel racks for 2000 spent fuel assemblies. If it is assumed that 200 of the cells are Region 1 racks with four panels of Boraflex in each cell* there will be 800 panels of Boraflex. The balance of the cells (1800) are the Region 2 type with each cell having effectively 2 panels of Boraflex*. The total number of panels of Boraflex in the pool will then be 4400.

For the purpose of this example assume that each panel of Boraflex is 144 inches long by 7 inches wide and 0.070 inches thick (not strictly true as the Region 1 Boraflex is generally thicker and the Region 2 Boraflex thinner.) Based on an initial Boraflex density of 1.76 gm/cm³ there will be a total of approximately 9000 kg of Boraflex in this panel. If it is assumed that after irradiation the Boraflex consists of 45 w/o silica or a silica-like material, there will be about 4000 kg of silica in the Boraflex.

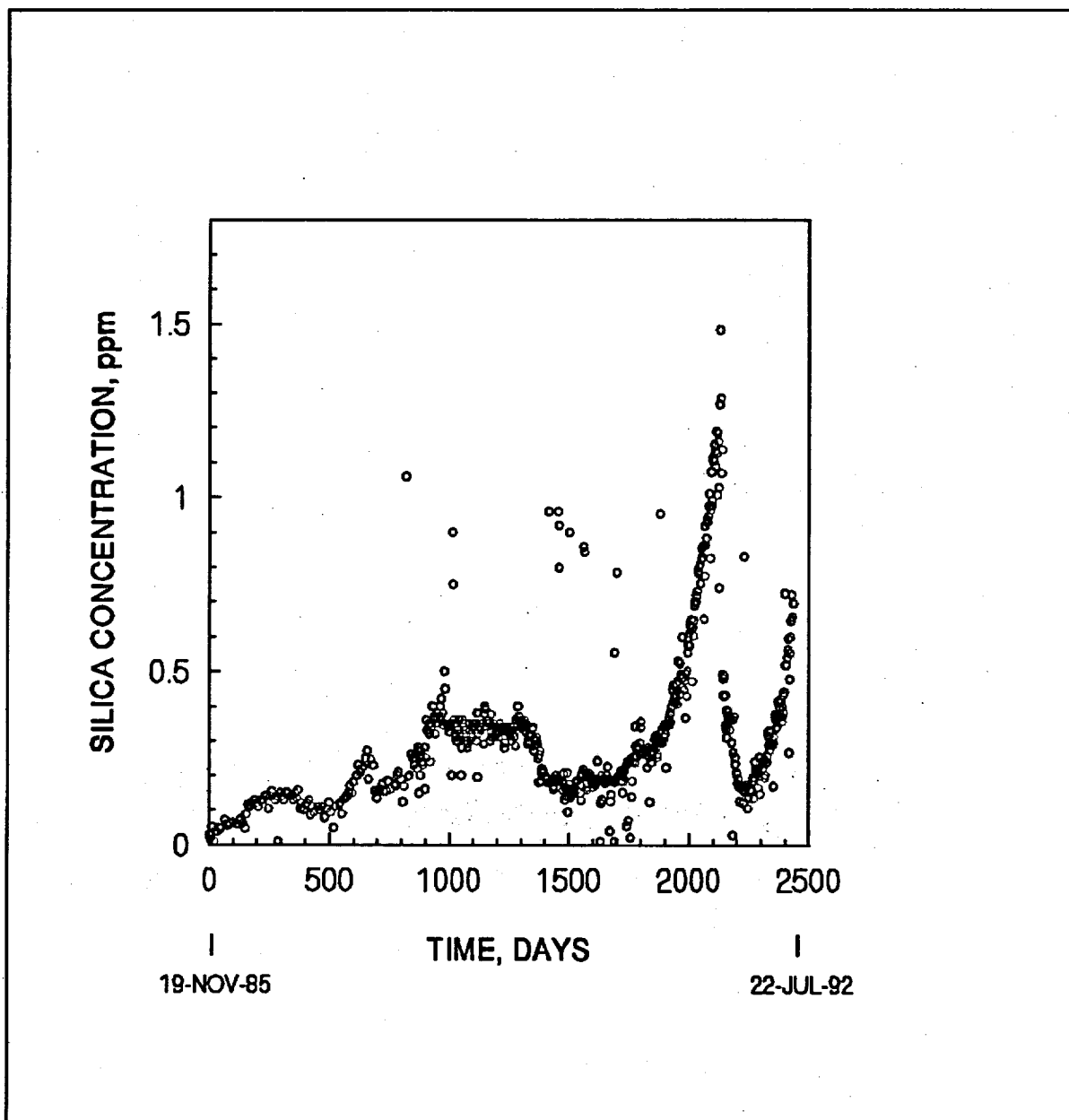


Figure 3-4
Silica Concentration as a Function of Time for BWRH2

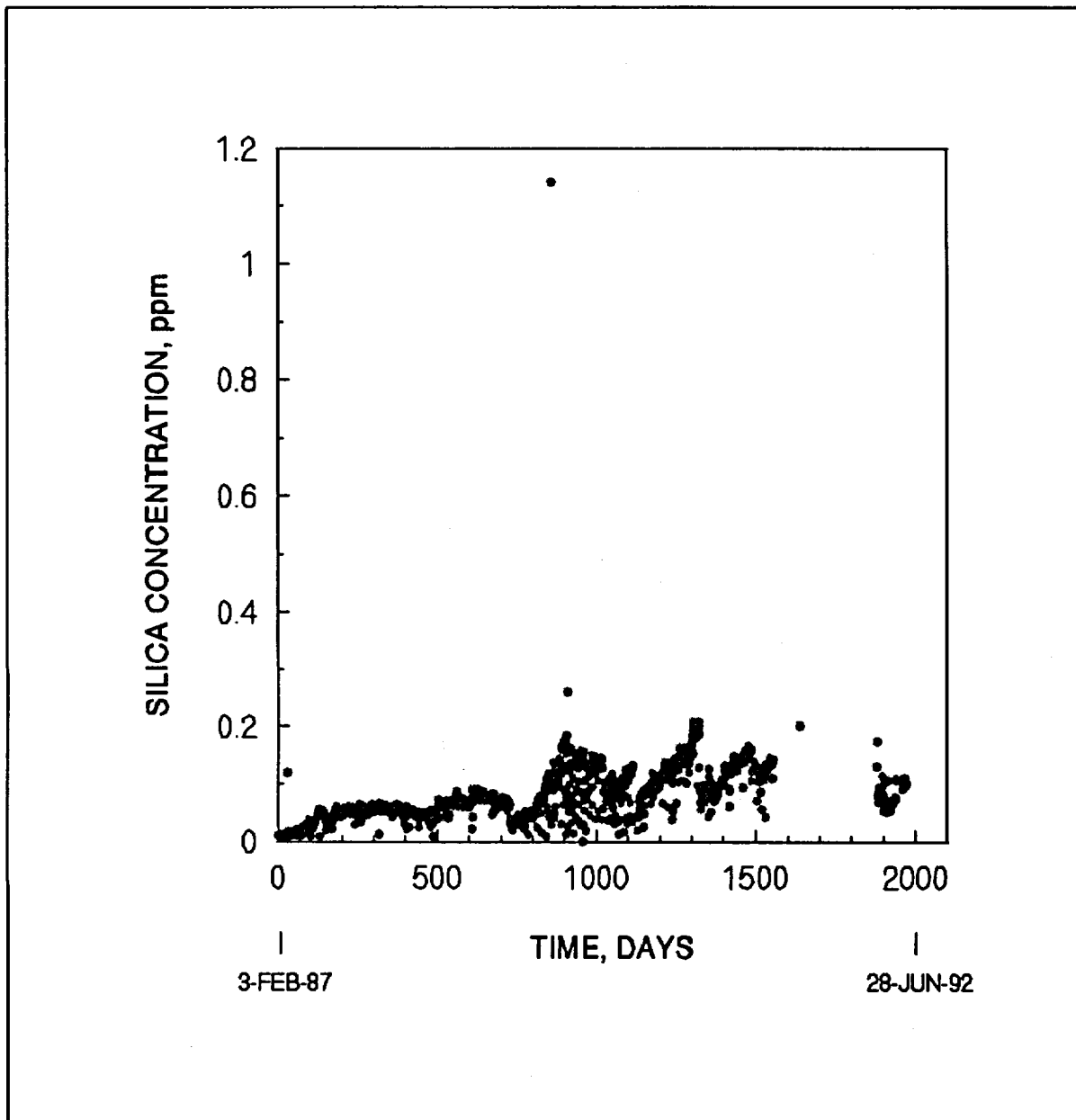


Figure 3-5
Pool Silica Concentration as a Function of Time at BWR1

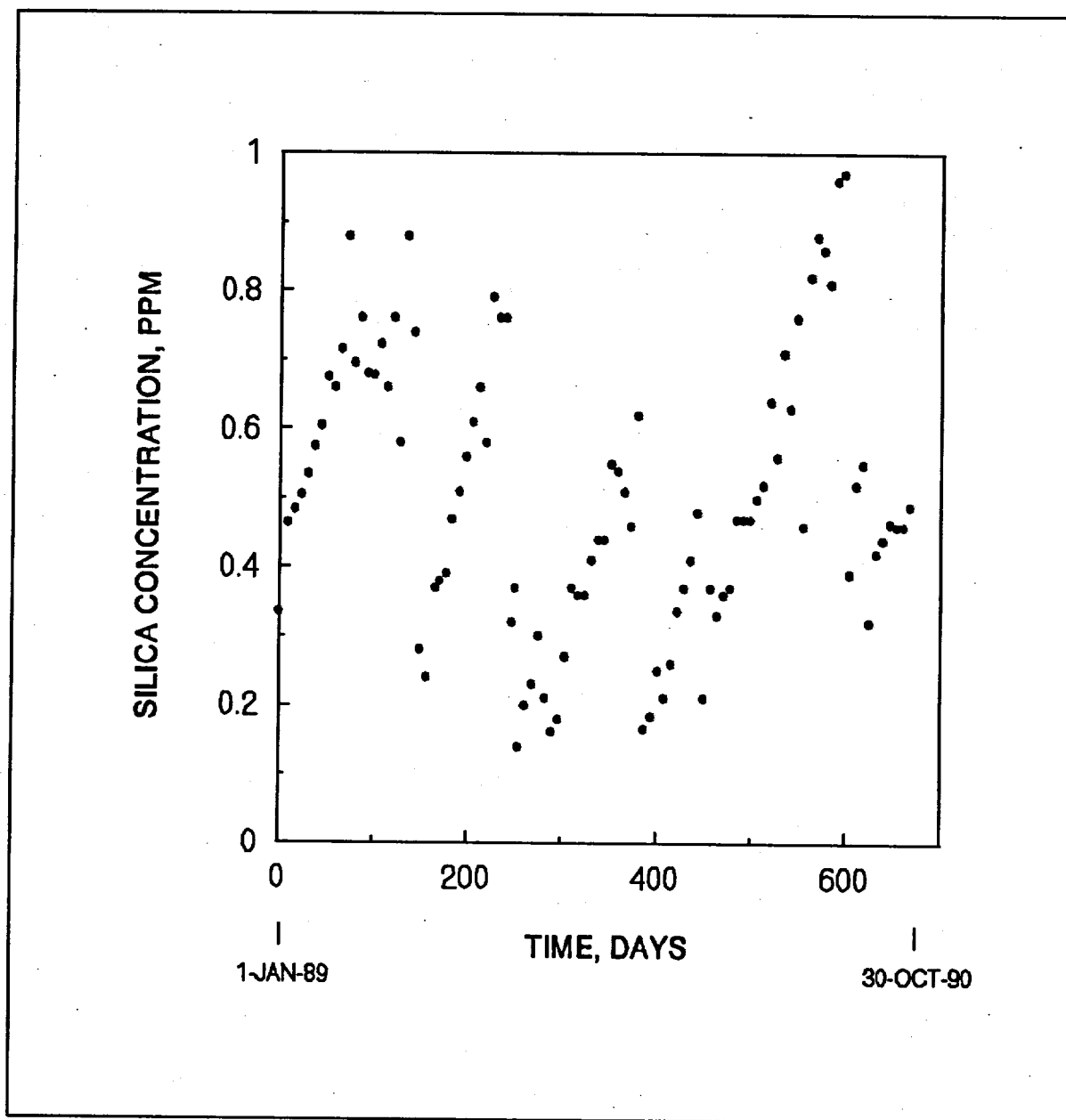


Figure 3-6
Pool Silica Concentration as a Function of Time at BWRA2

For a spent fuel pool which is 40 feet long, 20 feet wide, and 40 feet deep, the approximate water volume is $3.2 \times 10^4 \text{ ft}^3$ or $9.1 \times 10^5 \text{ l}$. If it is assumed that a tenth of a mil (0.0001 inches) of each surface of the Boraflex panels goes into solution, the corresponding pool silica concentration would be about 12 ppm.

The above example, while not rigorous, does serve to illustrate the following points. First, the silica tied up in Boraflex represents a very large potential source of silica (4000 kgs). Second, if only small amounts of the silica in Boraflex dissolve in the pool water, pool silica concentrations can be raised significantly to the levels experienced in LWR pools.

4

SILICA RELEASE FROM BORAFLEX: LONG-TERM LABORATORY TESTING

Test Objectives and Scope

Initially, two specimens of irradiated Boraflex were immersed in simulated PWR pool water (with 2000 ppm of soluble boron), one at 85°F and one at 150°F. Periodically the immersion fluids were tested for reactive silica. The purpose of this exercise was to test the hypothesis that Boraflex was indeed a source of silica in spent fuel pools. Both immersion fluids tested positively for silica and the test matrix was expanded to include some 21 individual tests.

The objectives of this expanded test program were as follows:

- To track long term changes in irradiated Boraflex in simulated pool environments (PWR and BWR)
- To determine those factors which influence silica release
- To develop rate data for silica release
- To provide source term data for modeling pool silica trends
- To provide data for developing projections of Boraflex service life

The test matrix developed to achieve these objectives is shown in Table 4-1. In addition to specimens of irradiated Boraflex, there are two control samples of unirradiated Boraflex and two blank immersion fluids (containing no Boraflex.) The purpose of the blank fluids was to determine whether the addition of low silica makeup water and associated concentrating effects would have a significant impact on measured silica.

The test variables which were investigated include:

- Clad versus unclad specimens to determine the effect of the rack enclosure
- Demineralized water versus water containing 2000 ppm (as boron) boric acid
- Grey versus black Boraflex
- Immersion fluid temperature (85°F and 150°F)
- Gamma radiation exposure (1×10^8 rads, 1×10^9 rads and 1×10^{10} rads)

Table 4-1
Test Matrix: Boraflex Long Term Aging Experiments

Sample ID	Source of Sample	Dose, Rads	Temp. °F	Immersion Fluid	Sample Color*	Test Type*
P8	Rack panel	1×10^{10}	85	Boric acid	G/B	UC
P1	Rack panel	1×10^{10}	150	Boric acid	G/B	UC
N1	Archive control	0	85	Demin. H ₂ O	B	UC
N2	Archive control	0	150	Demin. H ₂ O	B	UC
N3	Surveillance coupon	1×10^8	85	Demin. H ₂ O	B	UC
N4	Surveillance coupon	1×10^8	150	Demin. H ₂ O	B	UC
N5	Surveillance coupon	1×10^9	85	Demin. H ₂ O	B	UC
N6	Surveillance coupon	1×10^9	150	Demin. H ₂ O	B	UC
N7	Blank	-	85	Demin. H ₂ O	-	-
N8	Blank	-	150	Demin. H ₂ O	-	-
P21	Rack panel	1×10^{10}	85	Demin. H ₂ O	G/B	UC
P22	Rack panel	1×10^{10}	150	Demin. H ₂ O	G/B	UC
P23	Rack panel	1×10^{10}	85	Demin. H ₂ O	B	CA
P24	Rack panel	1×10^{10}	150	Demin. H ₂ O	B	CA
P25	Rack panel	1×10^{10}	85	Demin. H ₂ O	G	UC
P26	Rack panel	1×10^{10}	150	Demin. H ₂ O	G	UC
P27	Rack panel	1×10^{10}	85	Demin. H ₂ O	B	UC
P28	Rack panel	1×10^{10}	150	Demin. H ₂ O	B	UC
P29	Rack panel	1×10^{10}	85	Demin. H ₂ O	B	FL
P25	Rack panel	1×10^{10}	85	Demin. H ₂ O	G	T & R
P26	Rack panel	1×10^{10}	150	Demin. H ₂ O	G	T & R

*Key: G/B - Specimen has some grey and some black areas
 B - Specimen is primarily black
 G - Specimen is primarily grey

UC - Unclad
 CA - Capsule
 FL - Flow test
 T&R - Total and

reactive silica

- Fluid flow across the Boraflex surface
- Reactive versus total silica

With regard to dose effects, all irradiated samples had, prior to these tests, been exposed to the reported dose levels. The specimens received no further exposure during the long-term tests described here. This, of course, is not necessarily the case in spent fuel racks where the Boraflex can continue to accumulate dose.

Most of the test data reported in this section are for reactive silica only. In the latter stages of the testing a reliable method was identified for measuring total silica release and some additional testing is still in progress. As of this writing many of the tests have been terminated as further testing would not provide additional useful data.

Test Methods

The irradiated Boraflex used for these tests was obtained from a number of sources including pieces of panel removed from a PWR spent fuel rack and surveillance coupons from both BWR and PWR spent fuel pools. Prior to testing, the specimens were characterized with respect to visual inspection, dimensions, Shore A hardness, dry weights, and specific gravity. During the tests all of the specimens were immersed in stainless steel laboratory pans with covers. With the exception of the flow test, all specimens were immersed in a volume of either 1 liter or 0.5 liters. As the number of tests increased, the smaller volume was adopted owing to space limitations in the constant temperature ovens. As the covers of the test pans were not vapor tight, an aluminum foil wrapper was used over the covers to minimize water loss. Periodically, low silica makeup water was added to the baths to maintain a consistent volume.

The immersion fluid was prepared from low silica water which had been demineralized and distilled. Typically, the initial silica concentration in the immersion fluid was <50 ppb. The simulated PWR pool water was prepared from this water using reagent grade boric acid added in a quantity to provide a solution containing 2000 ppm as boron. For all tests the volume of immersion fluid was determined gravimetrically.

During testing the vessels were housed in one of two constant temperature ovens, one maintained at 85°F and one at 150°F. The ovens were thermostatically controlled and their temperature was constantly measured using thermocouples. The temperatures inside the ovens was maintained to within $\pm 2^\circ\text{F}$ of the nominal values. The atmosphere in the ovens during the testing was air.

Periodically, the immersion baths were removed from the ovens, cooled, and weighed to determine the water volume. The pH of the immersion fluid was measured and a small specimen of the immersion fluid removed (between 2 ml and 5 ml depending on the silica concentration). The frequency of testing varied from about once every two weeks to once every two months depending on the rate of silica release.

Colorimetric methods were used to determine the reactive silica level in the immersion fluids. The samples were diluted to a volume of 25 ml and placed in an optical cell. For fluids with low silica concentrations (0 ppm to 2.0 ppm) the heteropoly blue reagent was used. For high levels (0 ppm to 40 ppm) the silicomolybdate reagent was used. The optical transmission of the sample was determined using a Hach DR3 colorimeter. Standard solutions were prepared and measured to verify the accuracy of the method. The estimated reproducibility of the high range method was ± 1 ppm, and ± 0.2 ppm for the low range reagent.

For the total silica determinations described subsequently, inductively coupled plasma spectroscopy (ICPS) was used. Small samples (2 ml) were withdrawn from the immersion fluid and were evaporated to a dryness in a platinum crucible. The residue was fused with 1.0 gms of LiBO_2 and the melt dissolved in dilute metric acid. The silica was determined by ICPS using a Leeman Labs PS 3000UV spectrometer.

After silica testing the baths were covered and returned to the ovens. At the end of each series of tests the Boraflex specimens were dried in a desiccator and weighted to determine weight loss. All specimens have been retained should further testing be required in the future.

Test Results: Reactive Silica

The measured silica concentration using the colorimetric methods described are determined in units of ppm ($\text{mg SiO}_2/\text{l}$) silica in each of the immersion baths. Since the Boraflex specimens varied in size and weight and two bath volumes were used, (0.5 liter and 1 liter), the data have been normalized and are reported in the units $\text{mg SiO}_2/\text{gms of Boraflex}$.

PWR versus BWR Pool Water Environment

The initial tests were conducted in demineralized water containing 2000 ppm soluble boron. The Boraflex specimens were unclad and rested in the bottom of the immersion bath in direct contact with the fluid. Both Boraflex specimens were prepared from material which had received an estimated dose of 1×10^{10} rads. The silica release for these tests at 85°F and 150°F is shown in Figure 4-1 as the curves with the spline fits. Initially, the silica release is rapid, particularly at 150°F, but then appears to reach an equilibrium value. At 150°F, in the boric acid solution, an equilibrium is reached at 165 ppm and at 85°F the equilibrium is 85-90 ppm. This equilibrium represents a saturation condition for reactive silica. At this point, the rate at which silica can be dissolved into the solution is limited by the rate at which the reactive silica is being polymerized into colloidal silica. Data presented subsequently shows the relationship between reactive, colloidal, and total silica.

After the 150°F specimen had reached equilibrium, the immersion fluid was diluted to 3 liters from its initial volume of one liter with demineralized water containing 2000 ppm soluble boron. With the reactive silica below its saturated condition, silica

release (as indicated by reactive silica) commenced reaching a second equilibrium, again at a bath concentration of ~165 ppm. The oscillations in reactive silica concentration around this value probably represents some type of quasi-equilibrium between reactive and colloidal silica. At approximately 400 days into the test the bath water was replaced with low silica makeup water (with 2000 ppm soluble boron). The silica release was seen to again increase rapidly, although at a rate diminished somewhat from that at the beginning of the experiment. When the experiment was terminated, the reactive silica was approaching the 165 ppm equilibrium value.

The initial immersion fluid was retained as there appeared to be fine black particles in the bottom of the bath. The fluid was then passed through a millipore filter to recover the particles. The filtrate was then subjected to qualitative chemical analyses and the particles were identified as boron carbide.

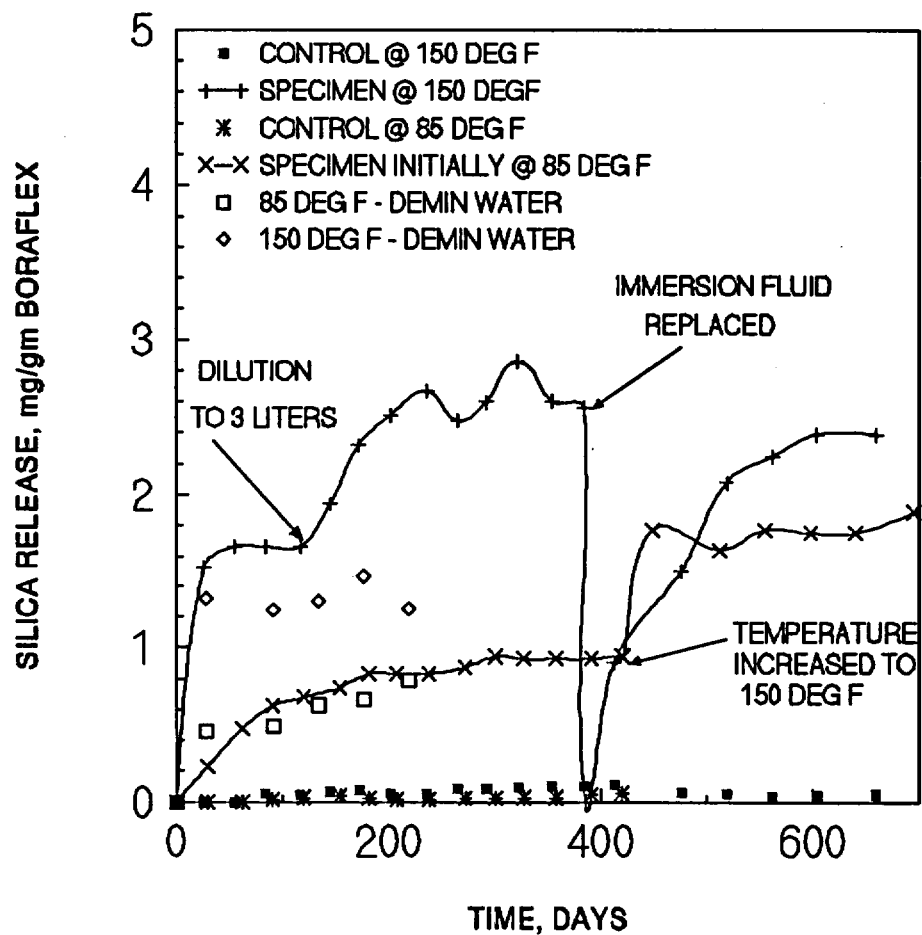
The release in the 85°F bath was somewhat slower as one might suspect with the silica concentration reaching an equilibrium value of ~85 ppm. Once this equilibrium had been achieved, the temperature of this bath was raised to 150°F. This was followed by a rapid increase in reactive silica with the immersion fluid reaching an equilibrium of ~165 ppm after a short period of time.

In order to determine whether there was any significant difference in the rate of silica release in the BWR pool water, (demineralized water without boric acid), a second set of two specimens was prepared from the same Boraflex used in the PWR pool water tests. The results of these tests are also plotted in Figure 4-1. It can be seen that there is no significant difference in the initial rate of silica release at either 85°F or 150°F. The only observable difference is a slightly higher equilibrium value for reactive silica at (~100 ppm). At 150°F the equilibrium concentration was 165 ppm.

Control specimens were also run using unirradiated Boraflex at both temperatures. It can be seen that the silica release from these controls is low, thus demonstrating that radiation is a necessary condition for elevated rates of silica release from Boraflex. Typically, the measured reactive silica in the control fluids was 5 ppm or less. It is believed that some silica from the silica filler initially in the Boraflex is going into solution. It is likely that exposed silica particles along the edges of the samples where the samples were cut to size are dissolved.

Integrated Gamma Radiation Dose Effects

Boraflex specimens irradiated to three gamma exposures were immersed in baths at 85°F and 150°F. In addition, unirradiated control samples were immersed at each temperature. Figures 4-2 and 4-3 contain plots of the measured immersion fluid silica concentration versus time at 85°F and 150°F, respectively. At 85°F, the effect of gamma exposure is the predominant factor influencing the rate of silica release. The rate of release from the specimens irradiated to 1×10^{10} rads is several times greater than either the specimen irradiated to 1×10^8 rads or 1×10^9 rads. The difference in



NOTE: SPECIMENS IN 2000 PPM BORIC ACID UNLESS NOTED OTHERWISE
ALL IRRADIATED COUPONS HAVE RECEIVED 1×10^{18} RADS

Figure 4-1
Silica Release at 85°F and 150°F - PWR versus BWR Pool Environment

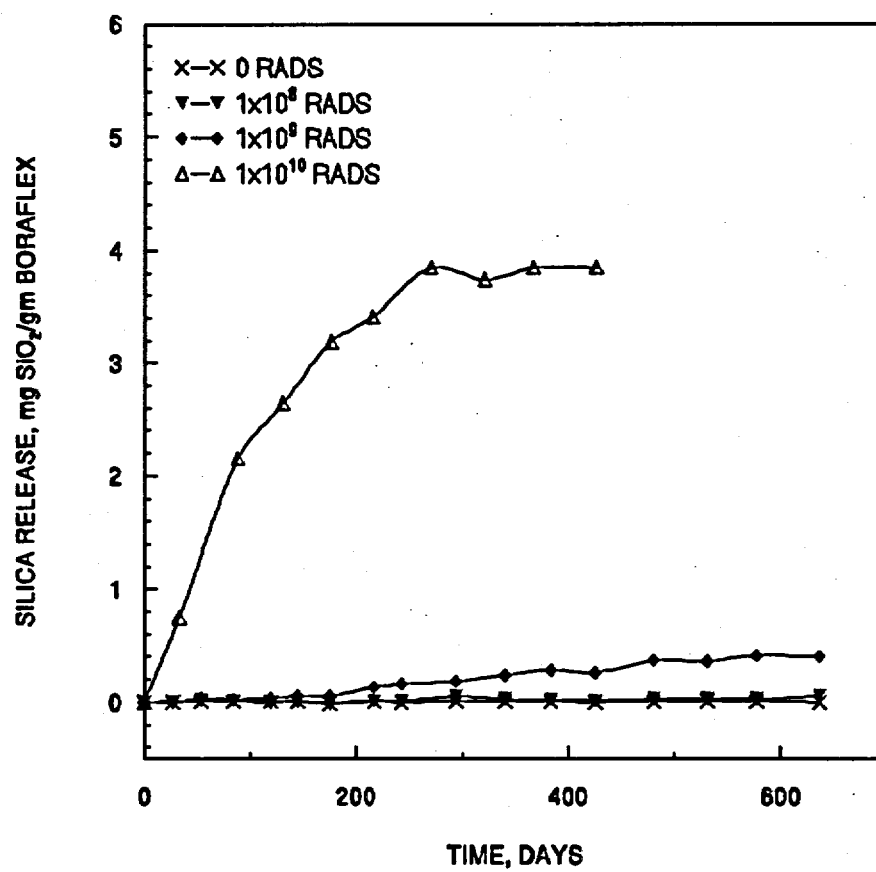


Figure 4-2
The Effect of Gamma Exposure on Silica Release at 85°F

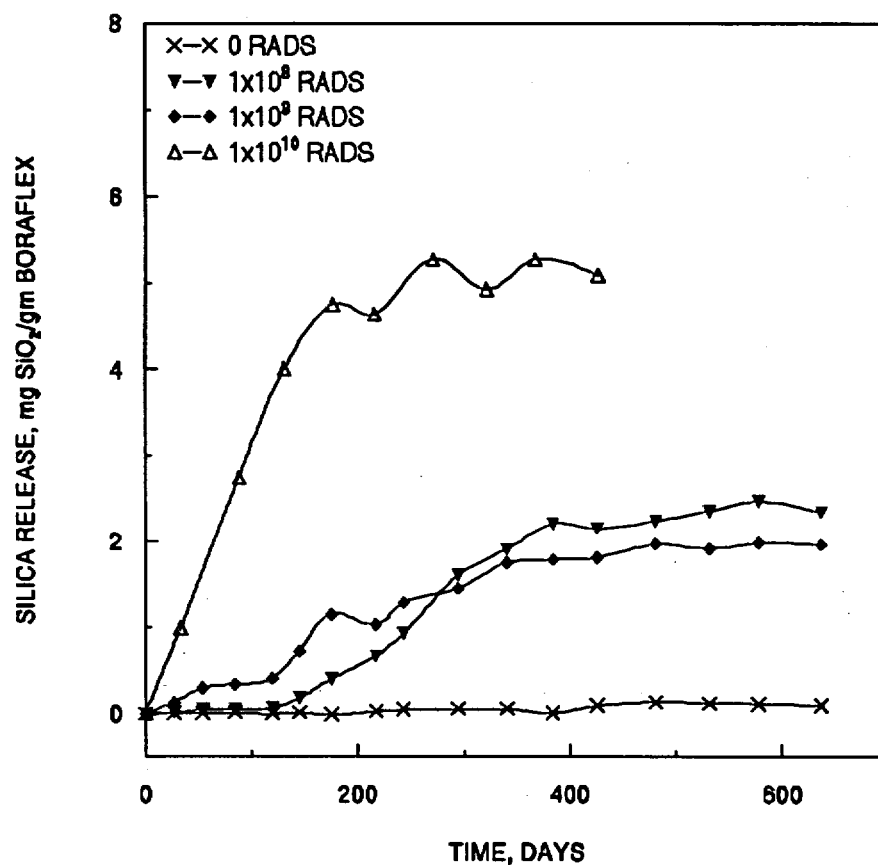


Figure 4-3
Effect of Gamma Exposure on Silica Release at 150°F

release between 1×10^8 rads and 1×10^9 rads is small.

At 150°F a similar trend is observed although the release rate of all specimens is accelerated. At this temperature, there appears to be little difference in the release characteristics of the two lower dose specimens. The erratic nature of the data for the 1×10^8 rads and 1×10^9 rads specimens is probably due to experimental uncertainties associated with these measurements. These specimens were relatively small (~10 gms) and the low silica range (heteropoly blue) reagent was used for the reactive silica determinations.

Grey versus Black Boraflex

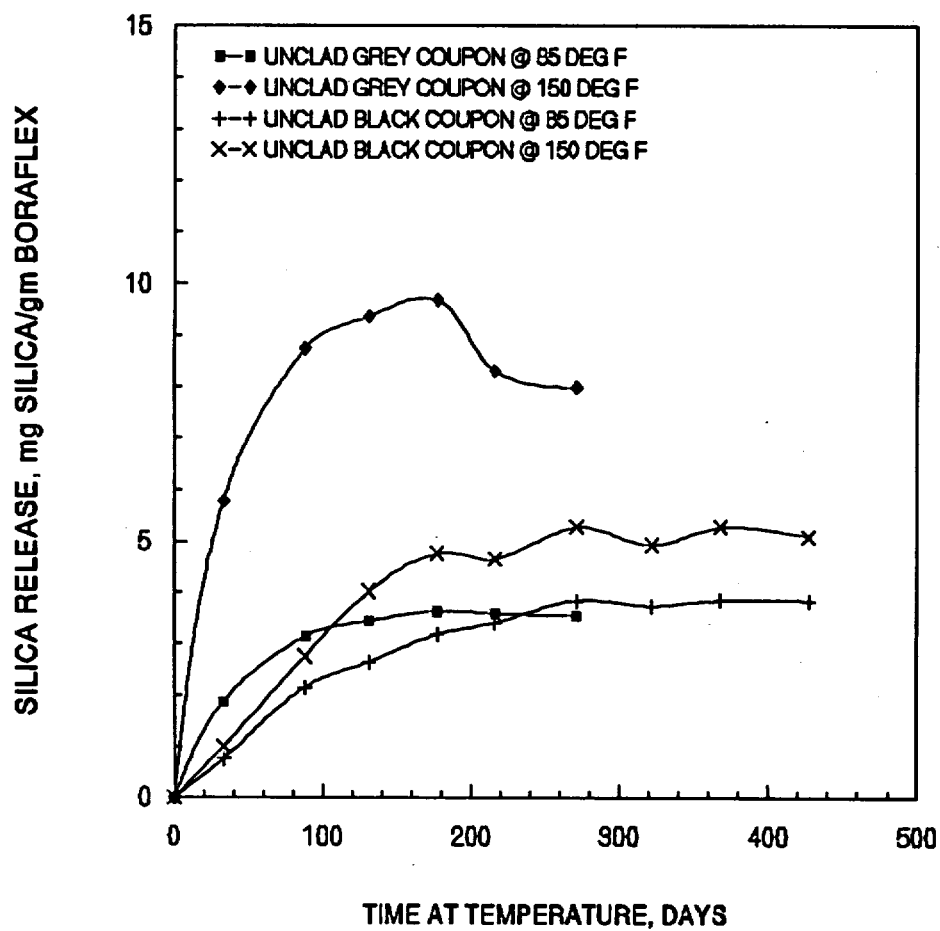
This test was performed to determine whether the silica release characteristics of Boraflex depend on whether the material has discolored after exposure to gamma radiation in the pool water. Two specimens ~2 inches by 4 inches were cut from grey scalloped regions of a rack panel section. Two identical specimens were prepared from the central portion of the panel which was of a dull black color. All specimens had received an integrated gamma exposure estimated to be 1×10^{10} rads.

Figure 4-4 contains plots of silica releases versus time for these tests. Considering the grey and black specimens at 150°F, it is clear that the release rate from the grey specimen is several times greater than from the black specimen. A similar behavior is also observed at 85°F although the difference in release rate is not as pronounced. It is noted that the measured reactive silica in the immersion fluid of the grey sample at 150°F decreases after about 160 days. This may be attributable to some change in the equilibrium condition between reactive and colloidal silica in the immersion solution. The immersion solution of the black specimen appears to reach an equilibrium condition after about 200 days although the reactive silica has not saturated. The silica concentration in the fluid at this equilibrium condition was ~115 ppm which compares with 160 ppm for the grey sample. One possible explanation for this may be that, as a result of previous long-term testing of this sample, it has become depleted in available silica for dissolution. Additional irradiation of this sample in an aqueous environment would be expected to produce additional silica which would then be available for dissolution. It is noted that the immersion fluid for grey and black samples at 85°F reach saturation conditions at 91 ppm and 87 ppm, respectively.

Effect of Encapsulation

When Boraflex is used in spent fuel racks, it is contained in a stainless steel enclosure. All test results described to this point have been for unclad Boraflex specimens in a stagnant bath. A test was initiated to investigate the effect of Boraflex encapsulation on silica release.

Two stainless steel capsules were designed and fabricated to test the effect of encapsulation. The capsules consisted of a base plate of stainless steel with a "picture



NOTE: ALL COUPONS HAVE RECEIVED 1×10^{19} RADS

Figure 4-4
Silica Release versus Time - Grey and Black Boraflex Specimens

frame" enclosure tack welded to it. The picture frame construction provided a cavity to house a 2 inch wide by 4 inch long piece of Boraflex. A thin gauge cover plate with deformable tabs was used to cover the capsule. When the Boraflex is in the cavity the cover plate is placed over it and the capture tabs are deformed around the base plate. When assembled the capsule is not sealed to water as a small gap is present between the cover plate and the "picture frame".

The Boraflex specimens used for these tests were cut from a rack panel exposed to $\sim 1 \times 10^{10}$ rads. Because of a limited supply of greyed material on this panel the specimens were cut from the central panel region which was a dull black color.

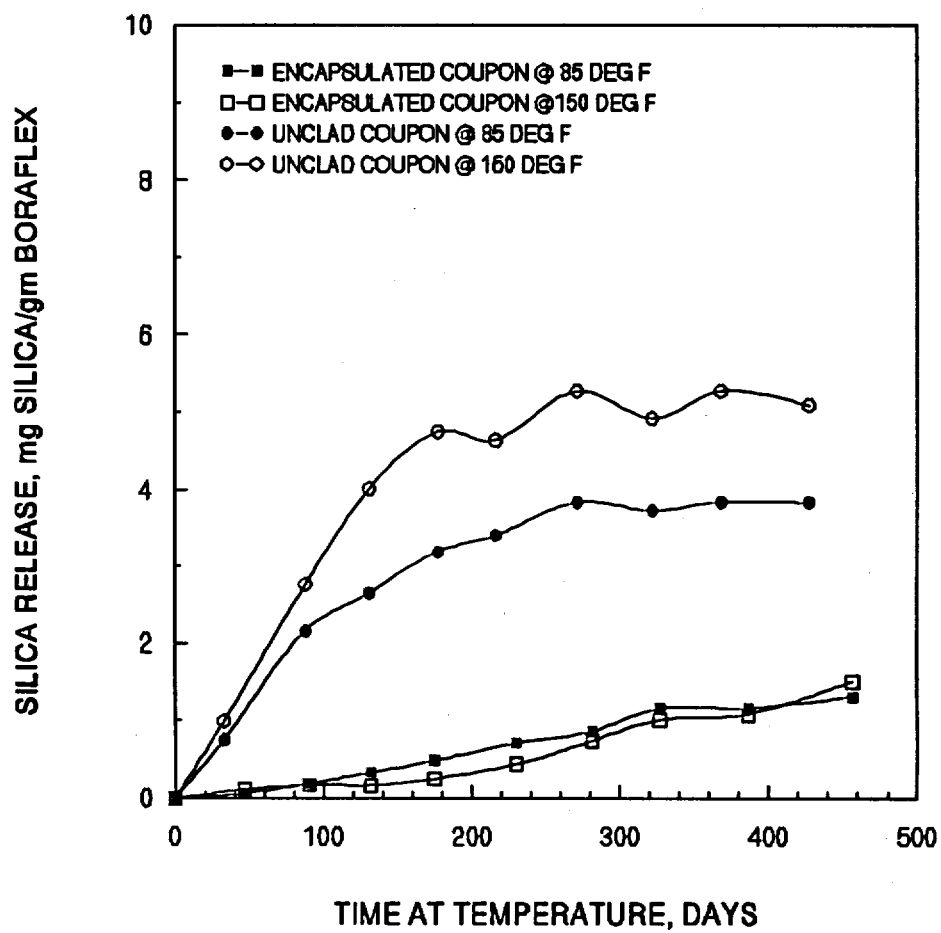
Figure 4-5 compares the silica release characteristics of the encapsulated samples to the release for unclad samples at 85°F and 150°F. The results plotted in Figure 4-5 are for the bulk immersion fluid and not the fluid inside the capsules. No attempt was made to open the capsules once the tests were initiated. The effect of encapsulation is seen to be about a ten fold reduction in the release rate.

As described in more detail subsequently, it is believed that the following mechanisms are at play. Once the capsule is filled with fluid, the reactive silica comes to equilibrium at about 90 ppm (at 85°F) and 165 ppm (at 150°F). At this point, the rate of dissolution of reactive silica is equal to the rate at which silica is redeposited on the sample and little further silica is lost from the specimen. Coincidental with this dissolution–redeposition equilibrium, reactive silica in the capsule can also be polymerizing to colloidal silica or be diffusing through the small gap in the capsule to the bulk fluid of the bath. The rate of silica dissolution from the Boraflex is therefore a complex process in encapsulated samples and depends on the relative rates of deposition, resolution, and polymerization in the capsules as well as diffusion into the bath.

The data from this test suggest that silica release from Boraflex housed in spent fuel racks will also be a complex process. As described above, the rate of release may be governed by the establishment of equilibrium conditions for reactive silica in the enclosure cavity and the complex processes of polymerization and diffusion of the silica into the pool.

Effect of Flow

Natural circulation cooling of the residual decay energy in spent fuel presents the potential for flow, not only in the fuel storage cells but also the cavities provided to house the Boraflex panels. To determine the effect of flow, a special flow cell was designed and constructed. The cell was fabricated from lucite and was similar in configuration to the stainless steel capsules described previously. The cell contained a cavity for a 2 inch by 4 inch specimen of Boraflex. A tight fitting cover plate secured by stainless steel machine screws held the Boraflex in place. At the ends of the cell a series of holes formed an inlet manifold at one end and an outlet manifold on the other end. The cell was connected to a small positive displacement pump and



NOTE: ALL COUPONS HAVE RECEIVED $\sim 1 \times 10^{10}$ RADS

Figure 4-5
Silica Release versus Time - Effect of Encapsulation

placed in a stainless steel constant temperature bath at 85°F. The volume of the bath was eight liters and during the test the bath water was continuously pumped through the cell.

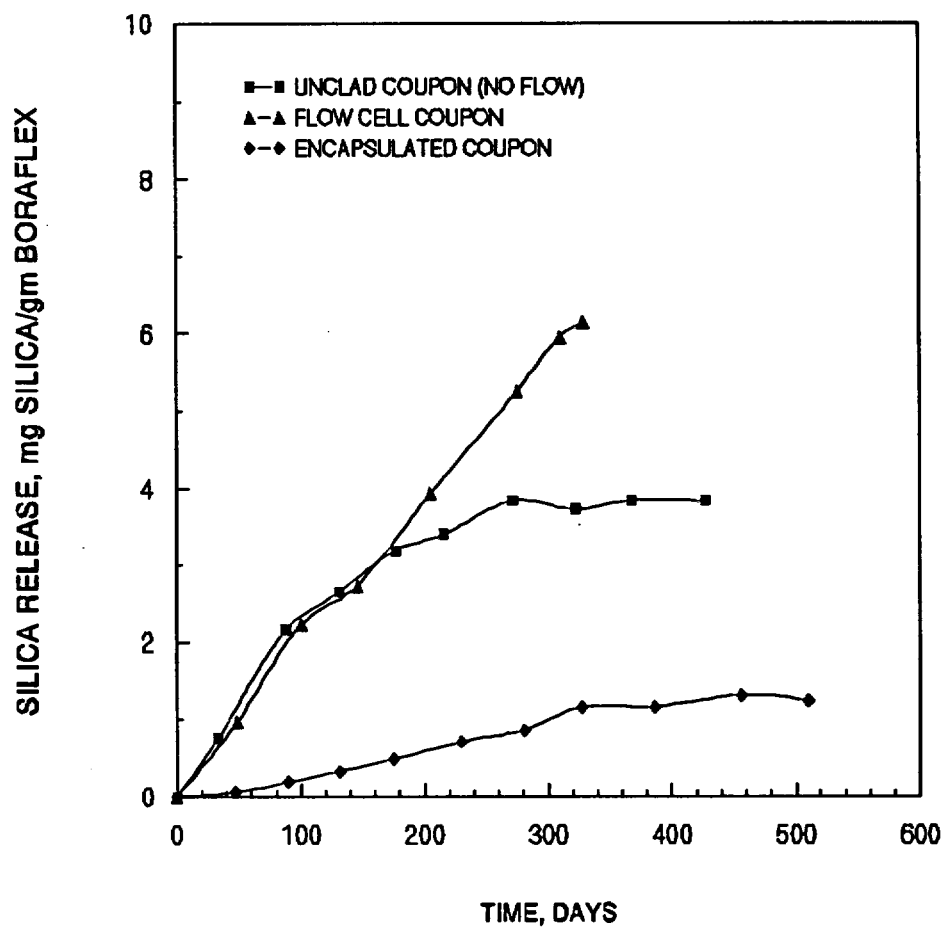
The Boraflex sample used for the test was cut from the central portion of the rack panel which had been exposed to $\sim 1 \times 10^{10}$ rads. The color of this specimen was a dull black.

The flow rate in the cell was selected to be similar to the rate expected in spent fuel storage racks during natural circulation cooling. It is noted in Reference [10] that flow velocities in spent fuel racks have been calculated to be in the range of 0.01 to 0.09 ft/sec. The flow velocity in this test was maintained at 0.015 ft/sec. Figure 4-6 compares the silica release from the specimen in the flow cell with the corresponding release for the unclad and clad specimens without flow. Initially, there is no difference in the rate of silica release between the unclad black specimen and the black specimen in the flow cell at 85°F. After about 180 days, the unclad stagnant specimen appears to be reaching an equilibrium condition for reactive silica (87 ppm) whereas the release in the flow cell continues to increase. This is attributable to the larger volume of the flow cell immersion fluid (8 liters) relative to the bath volume for the unclad specimens (0.5 liters).

As one might expect the silica release from the flow cell specimen is significantly greater than from the clad specimen. In the former test the flow is continuously being replenished with water of relatively low silica concentration, thereby promoting dissolution of the Boraflex. In the latter, the reactive silica concentration in the capsule comes to a saturation condition, thereby retarding silica release.

The effect of flow around Boraflex can have one of two possible effects. The first is the constant replenishment of the water around the Boraflex with water relatively low in reactive silica. In this case dissolution is promoted on the surface of the material as SiO_2 forms monosilicic acid at the boundary layer between the Boraflex and the flowing stream. The rate of dissolution being governed by the concentration of reactive silica in the flowing stream. In this case, one might expect the unclad and flow specimens to exhibit similar release as was observed in this test.

The other possible effect is erosion, defined as the physical wearing away of the material due to impingement of water on its surface. If erosion were a significant effect, one might expect the flow cell specimen to have stream accelerated release relative to the unclad specimen. This was not the case in these tests, at least under the flow and temperature conditions which prevailed.



NOTE: ALL COUPONS HAVE RECEIVED 1×10^{10} RADS

Figure 4-6
Silica Release versus Time - Effect of Flow

Tests Results - Total Versus Reactive Silica

The previous discussion has illustrated the importance of the kinetics of the formation of reactive silica from the dissolution of SiO_2 in Boraflex and its subsequent polymerization to colloidal silica. If data from spent fuel pool measurements of reactive silica are to be used as an indicator of Boraflex performance, then the relationship between reactive and total (reactive plus colloidal) silica needs to be established.

As an initial step, the grey specimen which was tested at 150°F was removed from the bath, dried in a desiccator, and weighed. Using the chemical composition cited in Section 2 for this material and the weight loss measurements, the total silica lost to the bath water was computed. This is plotted in Figure 4-7 along with the reactive silica versus time.

A sample of the immersion fluid was then taken and subjected to analysis for total silica via the ICP spectroscopy technique described previously. The results of this analysis is also plotted in Figure 4-7 where it can be seen that the ICP spectroscopy and weight loss determination of total silica are in close agreement.

For the purpose of discussion, the total silica data points have arbitrarily been fitted with a parabolic equation to illustrate how the total silica may vary with time. The difference between the dotted curve and the solid curve (reactive silica) is the colloidal component of the total silica in solution.

To accurately determine the relationship between reactive silica and total silica, the tests with the grey specimens were rerun. During these several tests both the reactive and total silica were determined periodically. Figure 4-8 contains the results of the total reactive silica test at 150°F to date. The total silica from the second test as well as the total silica at the end of the first test are compared with the reactive silica from both tests to provide the colloidal component of silica. Several features of the data in Figure 4-8 are worthy of mention. First, it can be seen that reactive silica from both tests compare very closely. The reactive silica is approaching an equilibrium in the range of 85-90 ppm, the same as was observed in the first test. Second, the total silica from the second test is trending toward the total silica determined at the end of the first test. Finally, at relatively low values of reactive silica (<50 ppm) the reactive and total silica are essentially the same. This would suggest that significant polymerization of reactive silica to form colloidal silica does not occur until the reactive component is above 50 ppm at this temperature.

The results of the total/reactive silica test at 85°F are contained in Figure 4-9. The scale for the ordinate and abscissa in Figures 4-8 and 4-9 are the same so the reader can easily distinguish temperature effects. In the second test, the rate of silica (reactive) release is considerably slower than in the first test. This may be

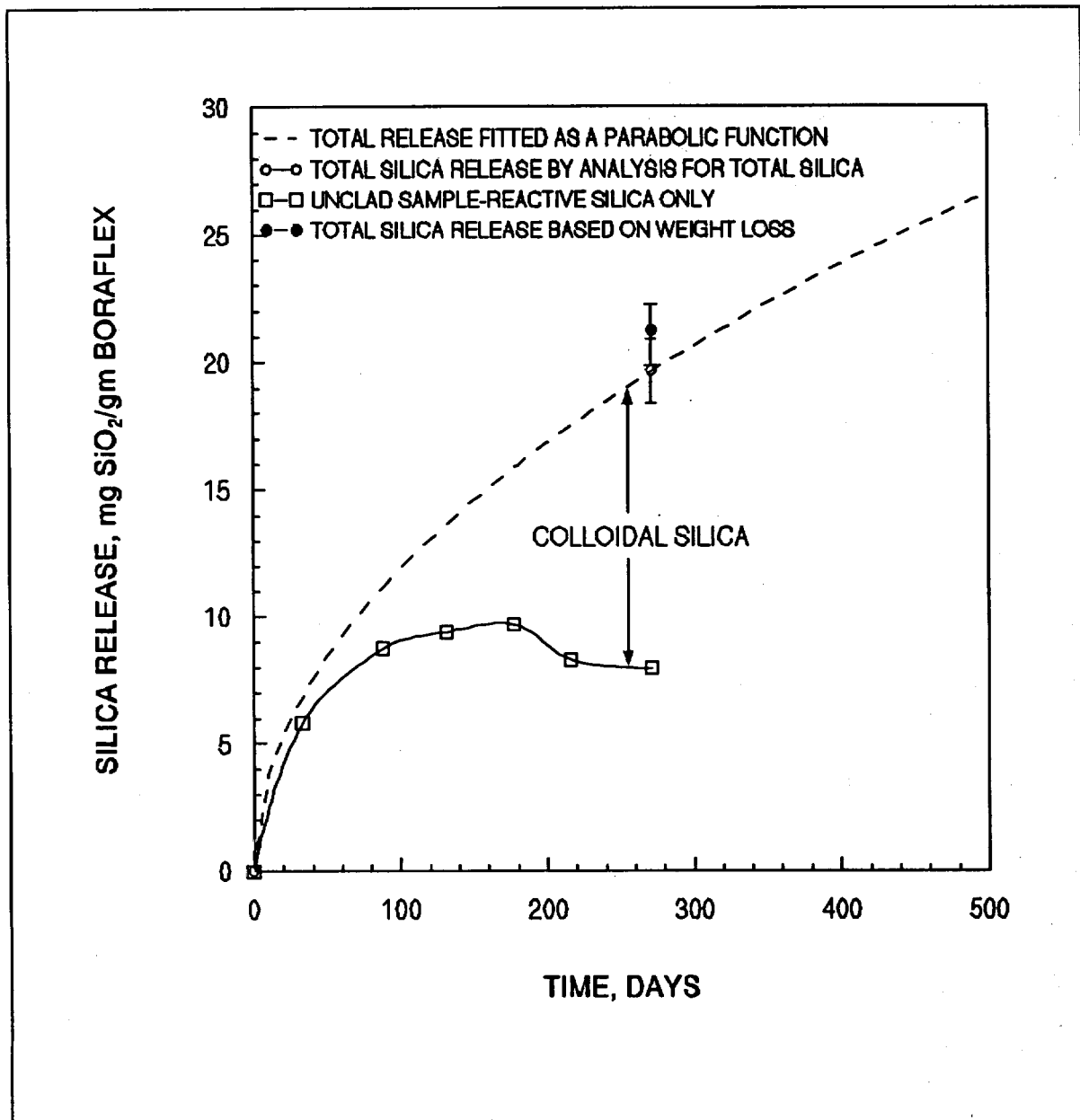


Figure 4-7
Total versus Reactive Silica for the Grey Specimen at 150°F

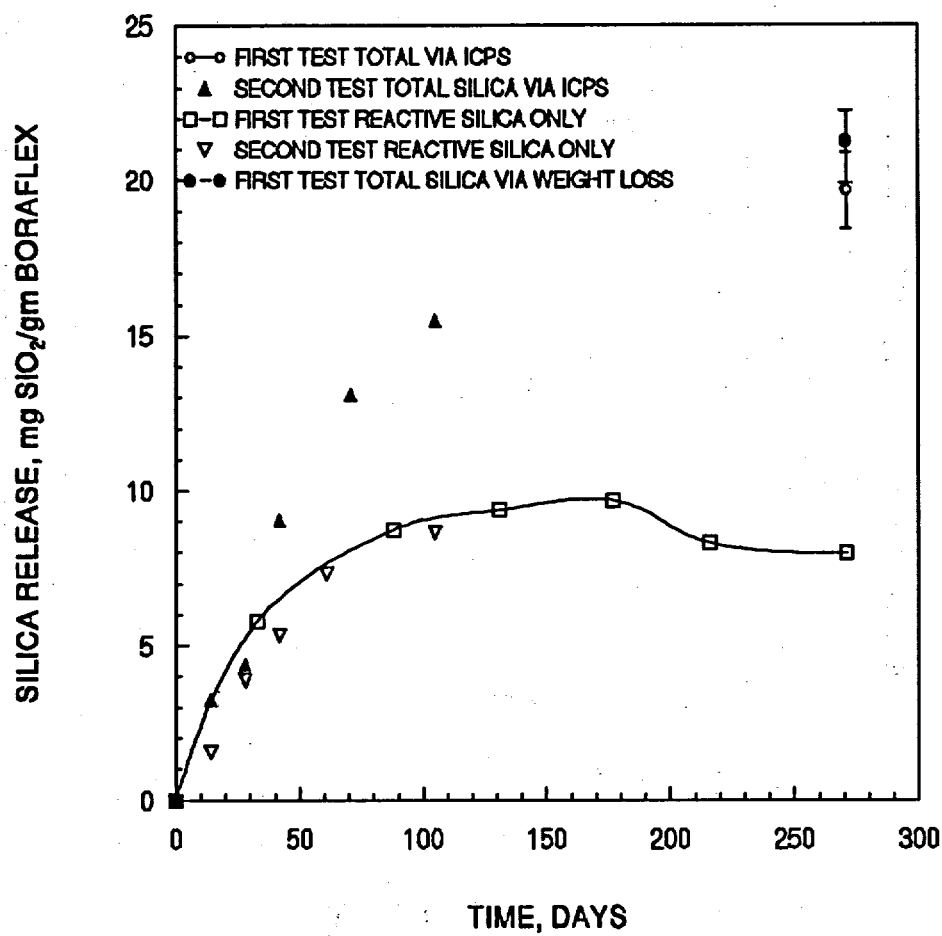


Figure 4-8
Total and Reactive Silica - First and Second Tests at 150°F

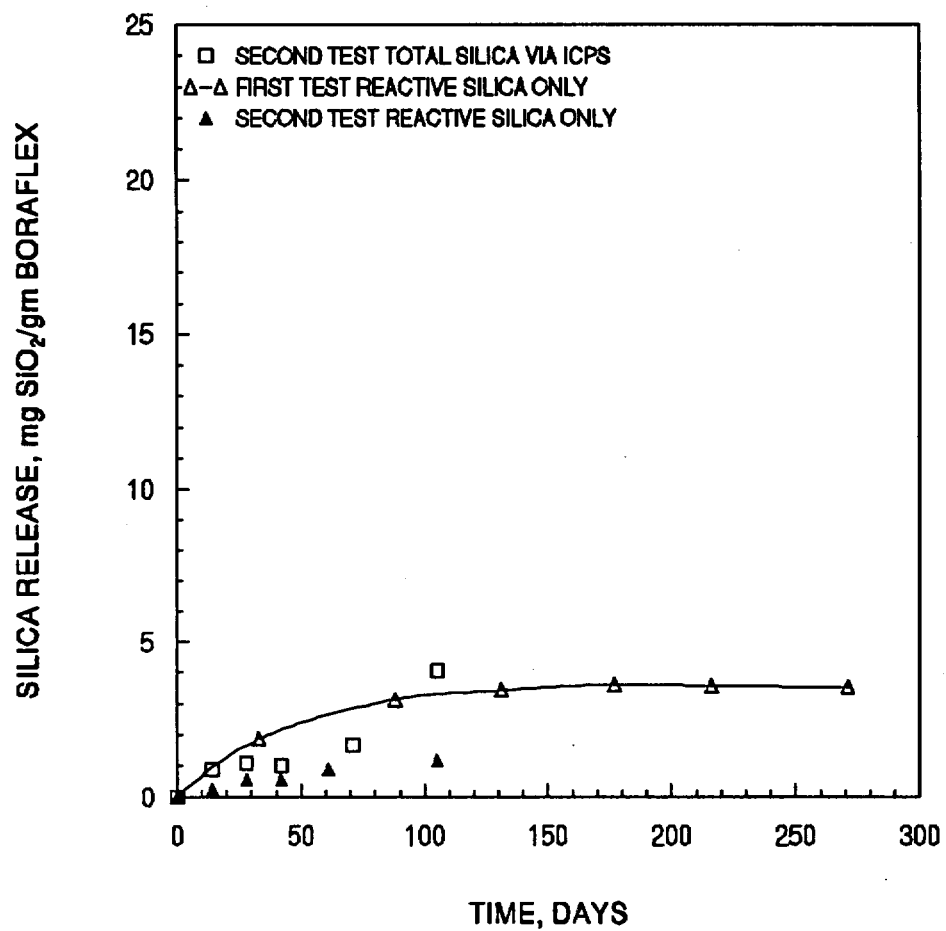


Figure 4-9
Total and Reactive Silica - First and Second Tests at 85°F

attributable to silica depletion during the first test and thus a reduction in the available silica for solubilization. The reactive and total silica are very nearly the same except for the last data point. This is consistent with the data from the 150°F test. At the last data point the total silica measured in the fluid was 51 ppm and the reactive 15 ppm.

During the second series of tests the specimens were removed from the immersion fluid and dried in a desiccator at each sampling point. After drying, the specimens were weighted to determine weight loss from the beginning of the test. Using the composition of this material described in Section 2.0, the silica release was computed independent of the ICPS determination. Table 4-2 compares the weight loss and ICPS

determined silica release. At 150°F the weight loss determination would indicate twice the release as the ICPS determination. This is likely due to the condition of the specimen, which appears to be crumbling. In addition to fine black particles in the bottom of the immersion vessel, there are some greyish-tan deposits. These may be silica particles which have not gone into solution. At 85°F the ICPS and weight loss determination for the 85°F experiment are in relatively close agreement.

Table 4-2
Comparison of Total Silica Release via ICPS and weight loss at 63 days

<u>Temp., °F</u>	<u>Silica Release, mg SiO₂/gm Boraflex</u>	
	ICPS	Weight Loss
85	1.20	1.34
150	13.70	30.60

Discussion

Reactive Silica Test Results

The data presented in the previous sections lead to some significant conclusions with respect to the release of silica from Boraflex in an aqueous environment. These conclusions include:

- The initial rate of reactive silica release from Boraflex appears to be independent of whether soluble boron is present in the immersion fluid. Testing in demineralized water and demineralized water with 2000 ppm soluble boron at 85°F and 150°F confirms this conclusion.

- The equilibrium concentration of reactive silica is relatively insensitive to the solute (water with and without soluble boron) but is sensitive to the temperature. If, as suggested, the release of silica into the immersion fluid is primarily governed by solubilization of silica, a strong temperature dependence is expected.
- At low integrated gamma exposures ($\leq 1 \times 10^9$ rads) the release rate is a weak function of dose, but is greater than for unirradiated Boraflex. At higher doses (1×10^{10} rads) the rate of release increases significantly relative to low doses.
- The degree of aging (grey versus black Boraflex) is perhaps the single most significant factor influencing silica release. The degree of aging is a function of dose and the length of time the Boraflex has been exposed to the pool water. The rate of release is five times greater once the material has greyed.
- Encapsulation of Boraflex in non-sealed capsules greatly retards the rate of silica transport to the bulk fluid volume. This has significant implications on the performance of Boraflex in spent fuel racks. In cases where the water exchange rate between the rack enclosure and the pool is low, silica release is likely to be low. This will vary among fuel rack designs and manufacturers.
- At the temperature and flow velocity investigated, flowing fluid around the Boraflex does not appear to result in physical erosion. It does, however, provide a continuous source of water with relatively low reactive silica levels which increases dissolution of the silica in Boraflex.

Total versus Reactive Silica

The testing completed to date for reactive and total silica lead to the following conclusions:

- Measurement data from either laboratory tests or pool water samples based on reactive silica alone would suggest that silica release from Boraflex saturates at a concentration which depends on temperature.
- Test data for total silica demonstrate that release continues in spite of unchanged reactive silica concentration.
- The test data relative to total and reactive silica is providing the relationship between total and reactive silica as a function of temperature. This data is used in the pool silica kinetic model described in the following section of this report.

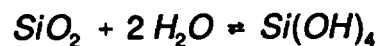
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SPENT FUEL POOL SILICA MODEL AND BORAFLEX SERVICE LIFE PROJECTIONS

The data and discussion presented in the previous sections of this report demonstrate that elevated spent fuel pool silica levels can be traced to Boraflex in spent fuel racks. As the presence of silica in the spent fuel pool water is direct evidence of the degradation of the matrix in Boraflex, it was thought that historical or trend data on pool silica may provide a means to assess the in-service performance of this material. That is, the rate at which the silica concentration in a specific pool is increasing should be related to the rate at which boron carbide is being lost from the Boraflex. Accordingly, a kinetic model describing the dissolution and subsequent transport of silica into the pool water has been developed and applied. The basis for this model and its application are presented subsequently after some background discussion relative to the mechanism of silica dissolution in water.

Mechanisms of Silica Dissolution in Water

Silica is by far the most abundant constituent of the earth's crust. In spite of its abundance, the chemistry of silica and, in particular, its solubility in water is not fully understood¹⁰. The dissolution of silica is via the following chemical reaction:



This process is believed to occur as a series of steps as shown in Figure 5-1. An ambient hydroxyl radical near the surface of silica (a) is adsorbed and coordinated to two silica atoms at the surface of the silica (b). This weakens the Si-O bonds and a silica atom goes into solution as a silicate ion (c). The silicate ion then hydrolyzes to form soluble silica and a free hydroxyl ion. The soluble form of silica is Si(OH)_4 or monosilicic acid, which is also referred to as reactive silica. This form of silica is traditionally monitored in spent fuel pools. In water, silica only undergoes dissolution to monosilicic acid. The other form of aqueous silica, referred to as polymerized or colloidal silica, may form subsequently in the solution but not as a direct product of the dissolution of SiO_2 .

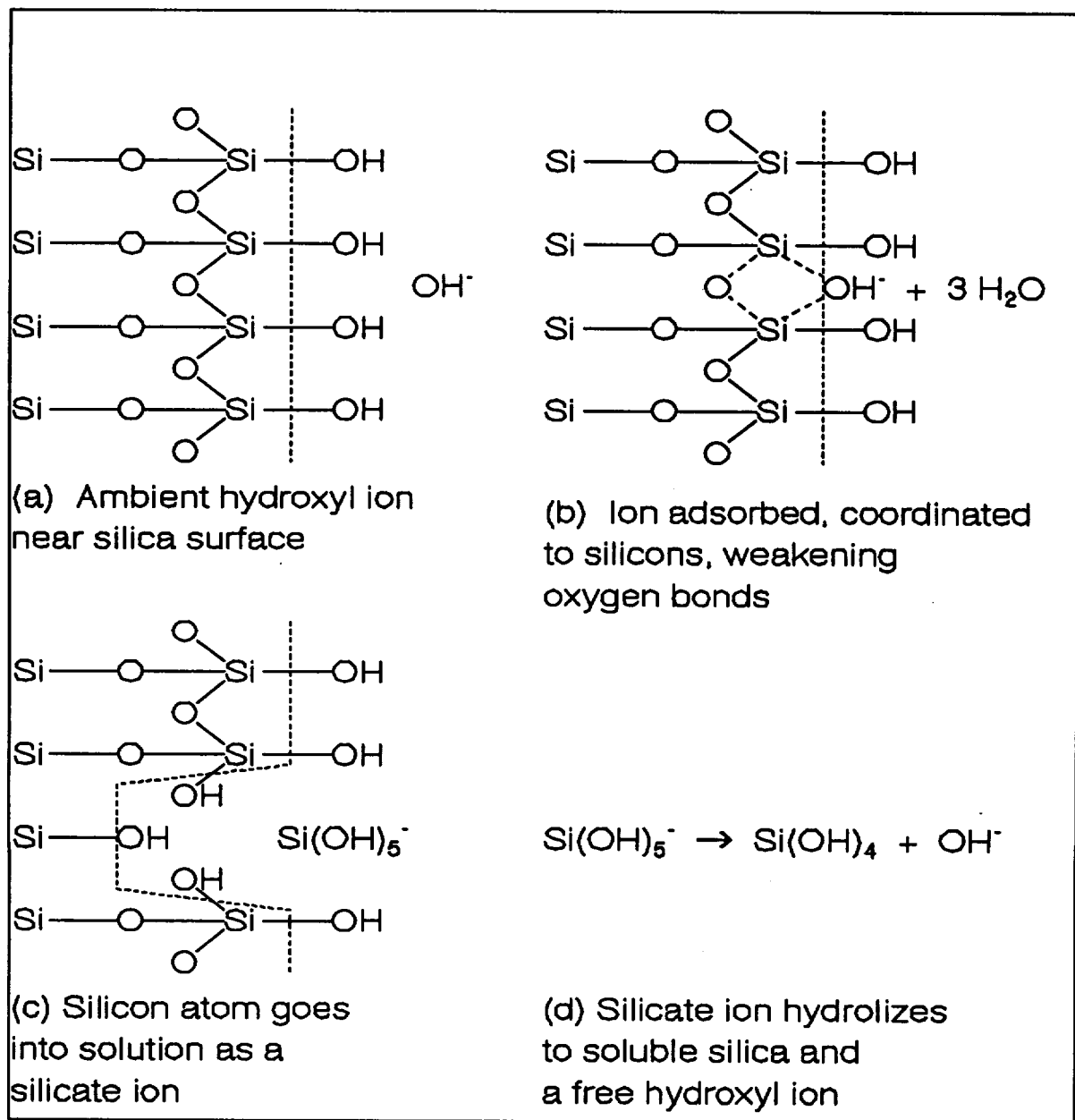
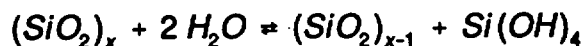


Figure 5-1
Mechanism of Dissolution of Silica in Water

The dissolution reaction is reversible and redeposition of SiO_2 back on the surface of the silica may occur. This involves hydration and dehydration reactions which are catalyzed by OH^- ions:



The rate of hydration (dissolution) is a relatively strong function of temperature. The rate of dehydration (deposition) depends primarily on the concentration of monosilicic acid in solution. As discussed in Section 4, at sufficiently high concentrations the reactive silica in solution reaches an equilibrium saturation condition which depends on temperature. At this condition the rates of dissolution and deposition are equal and, in the absence of polymerization, there is no further net loss of silica from the surface. If, on the other hand, reactive silica is undergoing polymerization, the above reaction will favor hydration. At 85°F the saturation condition was reached at a reactive concentration of 85-90 ppm (as SiO_2). At 150°F the saturation occurred at 160-165 ppm.

Colloidal silica is formed when the reactive silica concentration in solution becomes large. Colloidal silica results from the polymerization of monosilicic acid molecules, first forming dimers, then trimers, and eventually cyclic polymers:



In the above reaction silicic acid monomers condense (shed) H_2O molecules to form polysilicic acid as shown in Figure 5-2. Further polymerization can result in very large molecules with a cyclic structure as shown in Figure 5-3. In this process the number of siloxane bonds (Si-O-Si) is maximized in a ring forming a three dimensional structure. As polymerization continues and larger and larger molecules are formed the colloidal silica can then appear as a particle. Further aggregation of this three dimensional network will eventually form a gel.

In a solution containing silica both forms of silica may be present at the same time. Data presented in Section 4 would indicate that at concentrations of reactive silica of less than 50 ppm the amount of colloidal silica is very low. Above 50 ppm the colloidal component increases and has been determined to represent as much as one half of the total silica in some tests.

The kinetics of silica dissolution and subsequent polymerization have a strong influence on the rate at which the silica matrix of irradiated Boraflex dissolves. In a spent fuel storage rack the Boraflex is housed between two sheets of stainless steel. The cavity between these two sheets of stainless steel containing the Boraflex is vented to the pool to allow off gas to escape. When the racks are first installed the

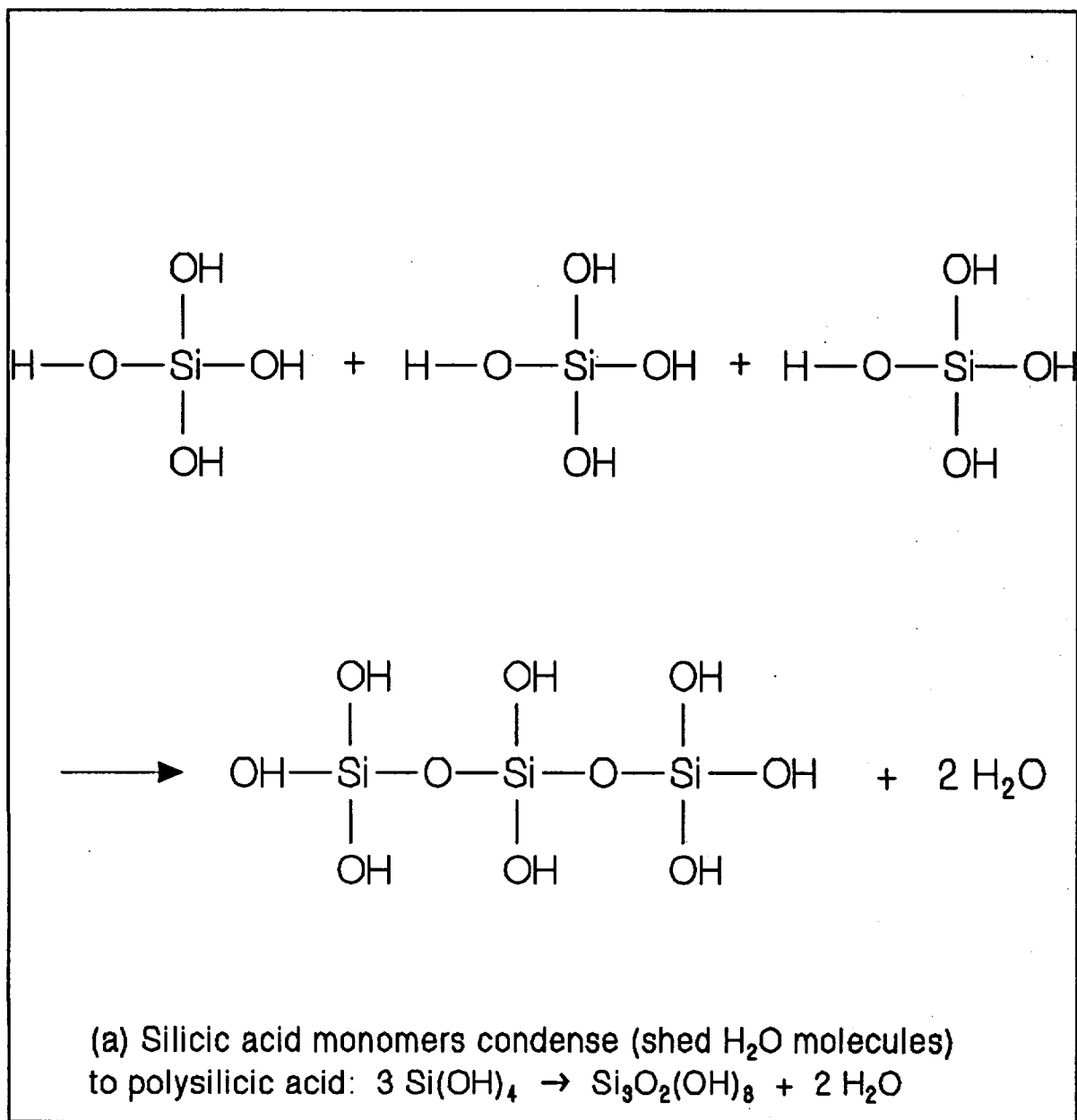
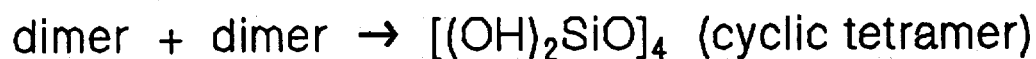
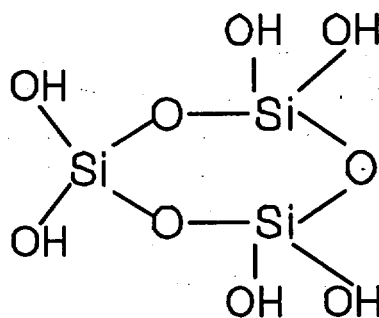
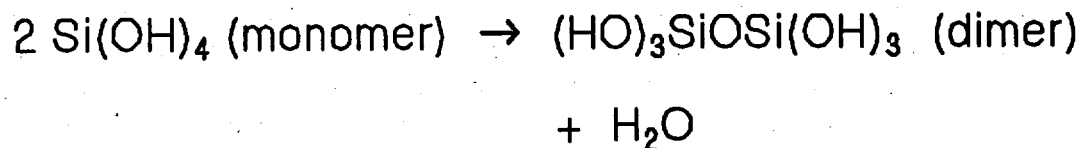


Figure 5-2
Polymerization of Silicic Acid



(b) Polymers form by maximizing siloxane (Si - O - Si) bonds in ring and 3D structures inside, and by minimizing uncondensed SiOH groups which generally are only found on the outer surface

Figure 5-3
Polymerization of Silicic Acid (continued)

cavities will fill with pool water such that the water surrounds the Boraflex. After the Boraflex has been exposed to large amounts of gamma radiation, the silica matrix of the Boraflex will begin to undergo dissolution. If the water exchange rate between the Boraflex cavity and the pool is low, the volume of water in the cavity will come to saturation equilibrium with respect to reactive silica. At this stage, the silica dissolution rate from the Boraflex and the deposition rate back onto the Boraflex will be in equilibrium and there will be little further loss of silica from the surface. As reactive silica in the cavity diffuses from the cavity into the pool or as the reactive silica polymerizes, the concentration of reactive silica in the cavity will theoretically be reduced. This will promote further dissolution from the surface of the Boraflex in an attempt to bring the cavity water back to its equilibrium saturation. Accordingly, the dissolution rate of silica from the Boraflex matrix will be limited by either its polymerization to colloidal silica or the diffusion of reactive silica (and for that matter colloidal as well) out of the cavity.

If, on the other hand, the volume exchange rate between the Boraflex cavity and pool is large, the equilibrium condition for reactive silica will never be established. In this case the dissolution of silica from the Boraflex can be fairly rapid, approaching the initial rates of silica release from unclad specimens as presented in Section 4. If the rack design is such that flow, due to natural circulation cooling, is present in the Boraflex cavity, the rate of dissolution will be accelerated. The flow will continuously bring the bulk pool water with relatively low reactive silica concentration in contact with the Boraflex.

The rate of silica dissolution from Boraflex in spent fuel racks is likely to vary from rack to rack and among racks from various manufacturers. For some rack designs, relatively low pool silica levels would indicate a low rate of water exchange between the Boraflex cavities and the bulk pool water volume, even after the racks had been in service for some time. In other rack designs, high pool silica levels may indicate a large rate of volume exchange between rack cavities and the bulk pool volume.

Kinetics Model of Silica in Spent Fuel Pools

A model has been developed which describes the formation of reactive silica within the rack cavity due to the dissolution of silica in Boraflex and its subsequent transport to the bulk pool volume. The overall model is depicted graphically in Figure 5-4. As reactive silica is produced in the rack cavities and its concentration within the cavity increases, some of the silicic acid will polymerize, some will be deposited on the Boraflex and other surfaces, and some will leave the cavity and enter the bulk pool volume. The rate at which the reactive and polymerized silica leaves the rack cavities is characterized by a volume exchange rate. The volume exchange rate is the number of times the cavity volume is replaced with pool water per unit time.

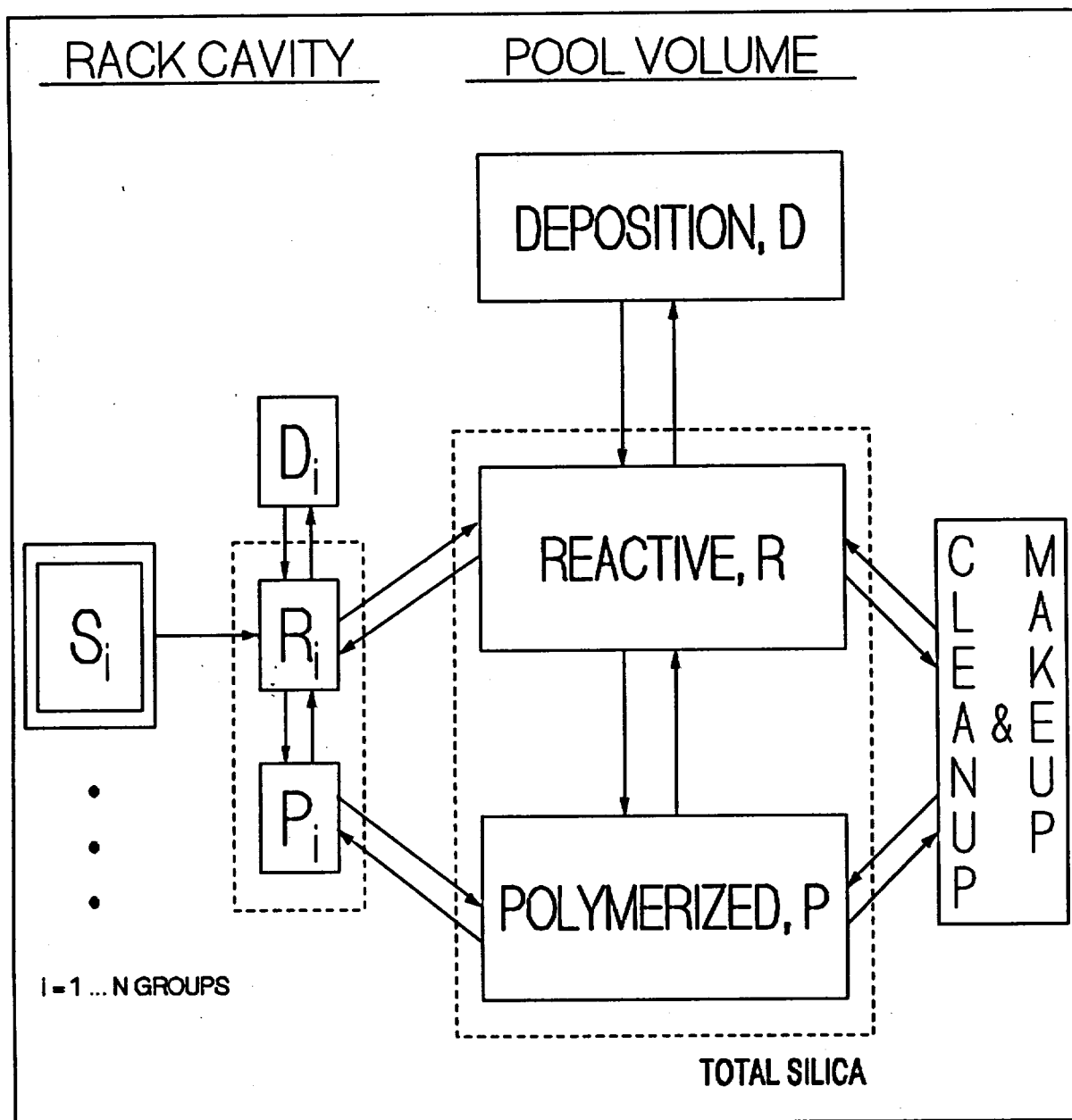


Figure 5-4
Kinetics Model of Silica in Spent Fuel Pools

In the pool volume a similar situation prevails. The silica source term for the pool volume is the reactive and polymerized silica which is exiting the rack cavities. Once in the pool volume the reactive silica can polymerize, deposit on surfaces in the pool, and be removed by the spent fuel pool cleanup system. The makeup system is modeled to account for water makeup due to leakage and evaporative losses. The makeup system model can also be used to account for dilution effects during refueling outages. Once polymerized silica is present in the pool it may be subject to depolymerization or complete or partial removal by the cleanup system.

Groups of rack cavities containing Boraflex can be treated as a single volume, where each volume consists of a number of cavities which have been exposed to a similar integrated gamma exposure. Within a particular cavity in group i out of N groups the source term for reactive silica is

$$S_i = \lambda_i(1 - R_i/R_{eq}) \quad (5-1)$$

where

$$\lambda_i = f(T(t), E(t), A(t)) = \text{dissolution rate into 0 ppm silica water} \quad (5-2a)$$

t = time

T = temperature

E = integrated gamma dose

A = extent of aging (greyness)

and

$$R_{eq} = f(T(t)) = \text{equilibrium concentration for reactive silica} \quad (5-2b)$$

R_i = concentration of reactive silica in the i^{th} group of rack cavities

Again for a particular rack cavity in group i , the time rate of change of the reactive silica concentration is given by

$$\frac{dR_i}{dt} = \lambda_i(1 - R_i/R_{eq}) \quad \text{source term} \quad (5-3)$$

$$- [k_{RR} R_i - k_{RR_i} R]$$

net leakage of reactive
silica out of the cavity

$$-k_{RP_i} R_i + k_{PR_i} P_i$$

net polymerization

$$-k_{RiDi} R_i + k_{PiRi} D_i$$

net deposition/resolution

where the k coefficients are the rate constants for each process.

The time rate of change in pool reactive silica due to the reactive silica from all of the groups of cavities can be written:

$$\frac{dR}{dt} = \sum_{i=1}^N [k_{RiR} R_i - k_{RR_i} R]$$

(5-4)

net leakage into
pool from all N
groups of cavities

$$-k_{RP} R + k_{PR} P$$

net polymerization
in the pool

$$-k_{RD} R + k_{PR} D$$

net deposition/resolution

$$-k_{RC} R$$

removal via pool
cleanup system

$$-k_{RM} (R-M)$$

makeup system

$$+k_{ER} M$$

concentration due
to evaporation

Two similar equations describe the time rate of change of the polymerized (colloidal)

silica in the rack cavities and spent fuel pool. The resulting model was implemented on an electronic spreadsheet and the equations solved numerically using Euler's Method.

The solution of these equations provides $R_i(t)$, $R(t)$, $P_i(t)$, and $P(t)$ which all vary with time.

To determine the total silica loss from a particular panel, the source term is integrated over time:

$$\int_0^T S_i(t) dt = \int_0^T \lambda_i(t) (1 - R_i(t)/R_{eq}(t)) dt \quad (5-5)$$

If there are N_i panels of Boraflex in group i , then the total silica lost by this group of panels after pool exposure for T days is given by

$$N_i \int_0^T S_i(t) dt \quad (5-6)$$

It was shown in Section 2 that after irradiation Boraflex consists of approximately equal parts (by weight) of boron carbide and silica. Accordingly, it can be assumed that the loss of silica is accompanied by an equal loss of boron carbide. If the panel has a surface area of A cm², the total thinning of the panel will be

$$\frac{N_i}{A\rho_{B,C}} \int_0^T S_i(t) dt \quad (5-7)$$

The total silica lost from all groups of panels, each panel within a group having a similar service history, will be

$$\sum_{i=1}^N N_i \int_0^T S_i(t) dt \quad (5-8)$$

where N is the number of panel groups.

All coefficients in Equations 5-3 and 5-4 have been developed based on the long-term laboratory tests described in Section 4 except the k_{RIR} and k_{RRI} . These parameters are the rate coefficients for silica transfer in and out of the Boraflex panel cavities. These will depend on specific design and manufacturing features of each rack design and are generally not known. In applying the model, these coefficients are adjusted until the calculated rate of pool reactive silica increase matches the rate from plant pool silica measurements.

Model Application

The model was first tested by applying it in a single volume mode to the first series of long-term tests with the grey panel specimens described in Section 4. Figure 5-5 compares the model prediction versus measured data at 150°F.

The EPRI pool silica database contains data from a PWR plant called PWRS. This pool was selected for modeling as data were available from the time at which the spent fuel racks were first subjected to gamma radiation. Figure 5-6 compares the calculated pool reactive silica and the model predictions. Also shown is the predicted pool total silica concentration. Prior to the first refueling outage pool reactive silica levels were quite low (0.10 to 0.20 ppm). Coincident with the first refueling outage, which occurred at about 80 days in Figure 5-6, the pool reactive silica concentration began to increase at a rate of 1.7 ppb/day. At 440 days, the reactive silica decreased slightly during the second refueling outage due to dilution and mixing with the RCS water. This mixing and dilution of the pool water is also simulated in the model. After the second refueling outage the reactive silica again began to increase, this time at a rate of about 2.0 ppb/day. The increase in rate is attributable to the additional Boraflex panels irradiated during and after the second refueling outage, which resulted in a larger source term for reactive silica.

For modeling purposes, the Boraflex panels were divided into four groups as shown in Figure 5-7 depending on service history. For each of the four groups of panels, the thickness of Boraflex lost is also shown in Figure 5-7 during the first 600 days of rack use. It can be seen from this figure that total thinning after this time period is calculated to be less than 0.1 mils.

The model has been applied to computing Boraflex thinning over a forty-year service life for this plant. For these purposes it has been assumed that the racks are irradiated on a schedule dictated by annual refueling. Figure 5-8 shows the model prediction of Boraflex panel thinning for PWRS over a 40-year service period. At the end of this period the model predicts a reduction in the thickness of the Boraflex of 7 to 8 mils.

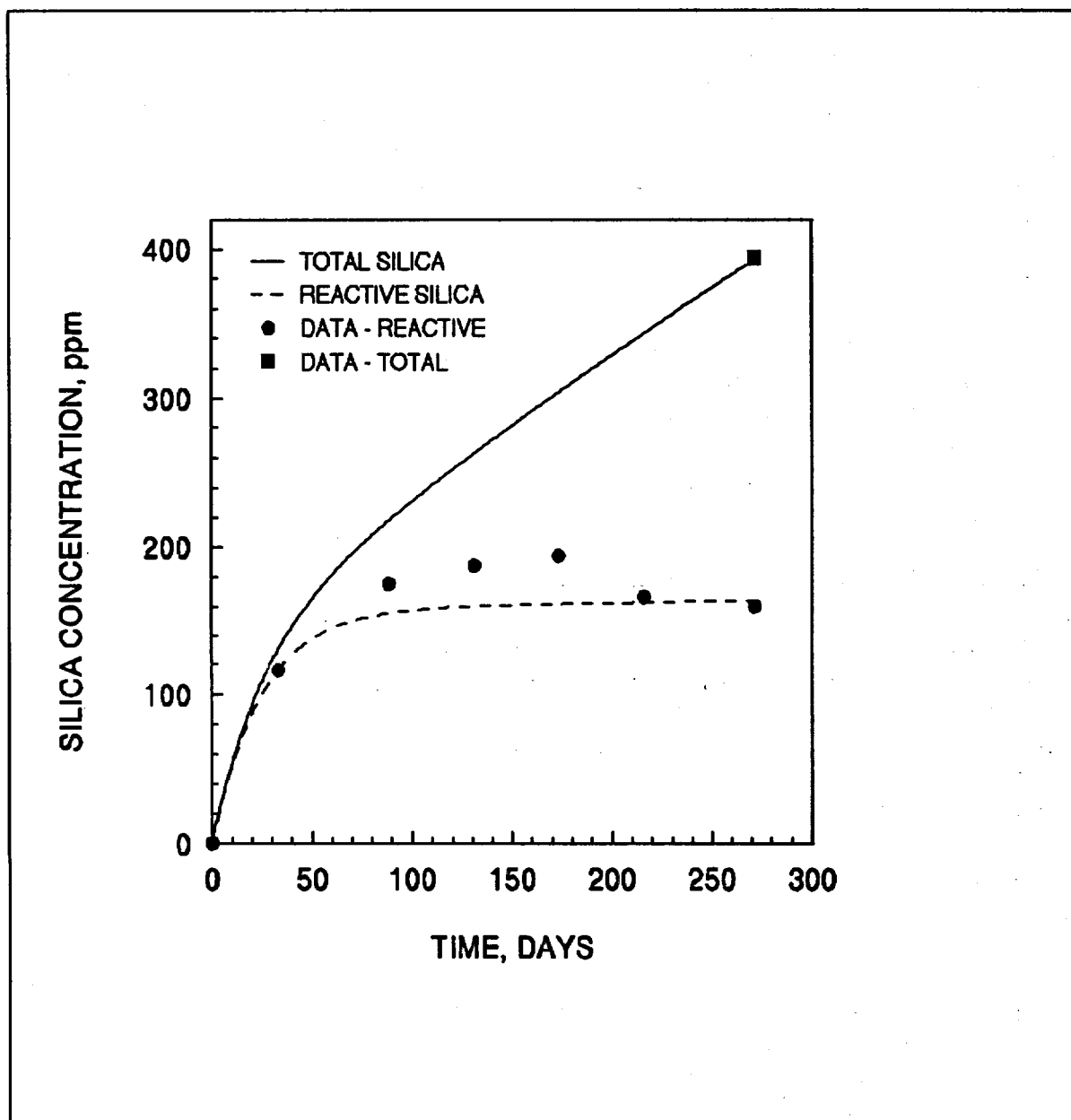


Figure 5-5
Model Prediction versus Long-term Aging Test at 150°F

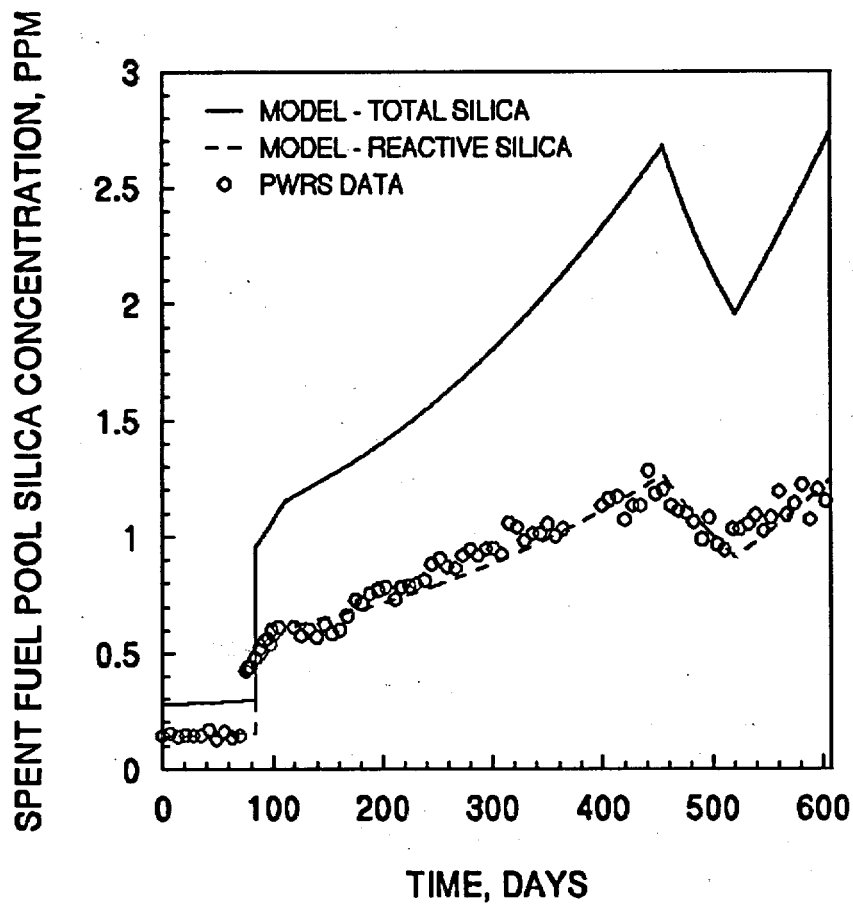
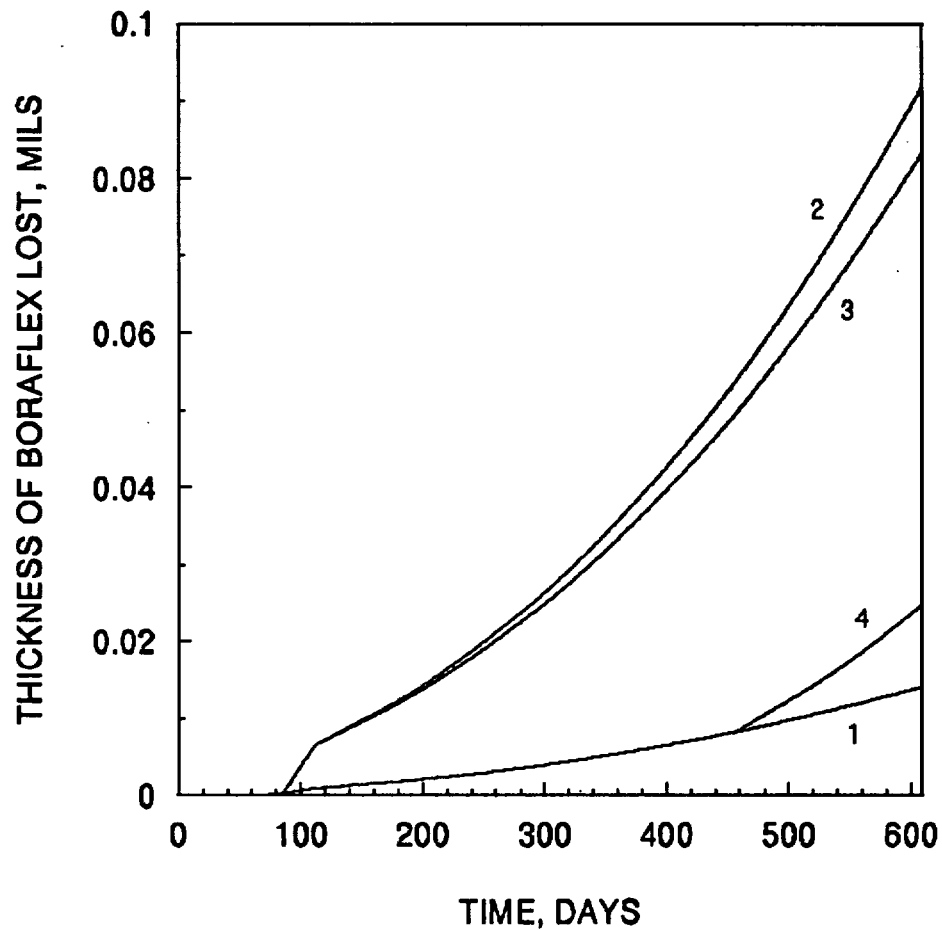


Figure 5-6
Predicted versus Measured Pool Silica for PWRs



- 1: 1532 UNIRRADIATED PANELS
- 2: 240 PANELS IRRADIATED FROM CYCLE 1 DISCHARGE TO PRESENT
- 3: 532 PANELS IRRADIATED FROM CYCLE 1 DISCHARGE TO CYCLE 2 RELOAD
- 4: 264 PANELS IRRADIATED FROM CYCLE 2 DISCHARGE TO PRESENT

Figure 5-7
Boraflex Panel Thinning versus Time - PWRS

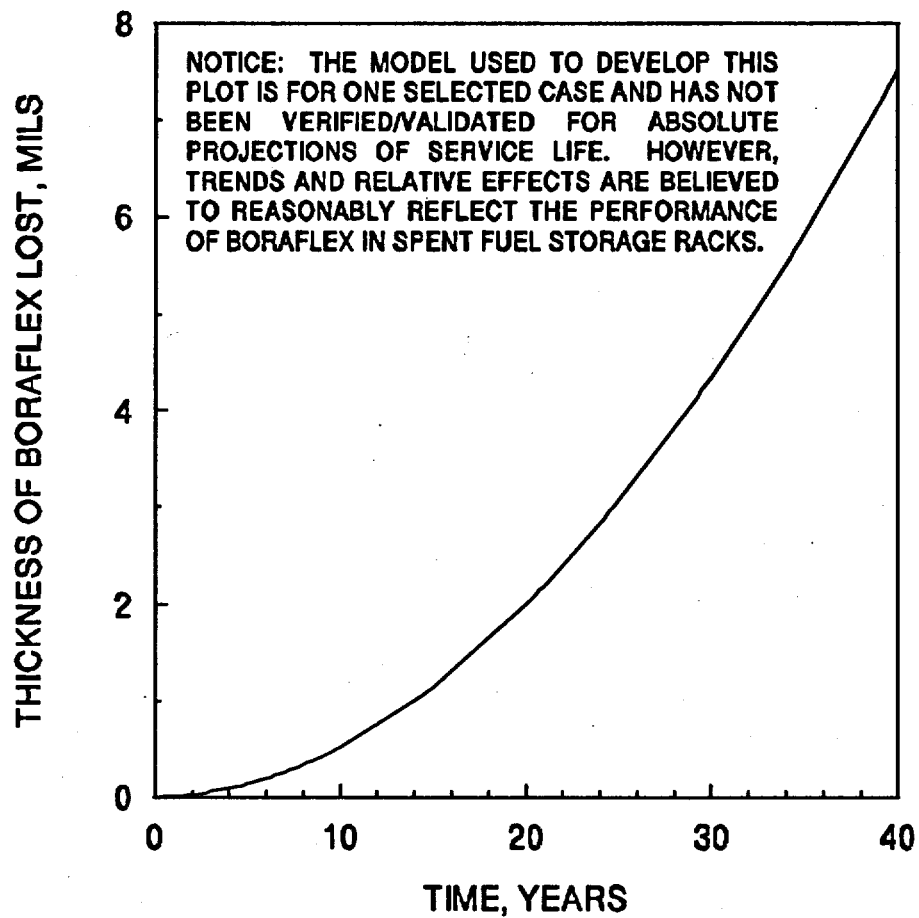


Figure 5-8
Boraflex Panel Thinning Over a 40 year Service Life - PWRS (Low Leakage Racks)

The rate coefficient used to match the slope of the measured reactive silica data for PWRS (Figure 5-6) was 0.4 volumes/day. That is, about 40% of the free fluid volume in the rack cavities is transferred in and out per day. On a relative scale this appears to be a fairly low value and hence the spent fuel racks at PWRS have been termed "low leakage" racks.

If the PWRS model is applied to the reactive silica data measured at another PWR plant called PWRP, an example of a "high leakage" rack is seen. PWRP had experienced relatively high pool silica levels and instituted a cleanup campaign using reverse osmosis (RO) equipment (see Figure 3-3). After the cleanup campaign the reactive silica concentration increased at a rate of 36 ppb/day. When the model is applied to PWRP, a volume exchange rate of 7.2 volumes/day is required to match the rate of reactive silica increase after the RO cleanup campaign. This is approximately 20 times the exchange rate for PWRS and hence the racks at PWRP are considered "high leakage".

The effect of volume exchange rate on Boraflex thinning is significant as shown in Figure 5-9. For the nominal case, which assumes no further RO cleanup operations, about 60 mils is lost from the surface of the panels after 40 years of service. To assess the effect of RO cleanup, a scenario in which RO cleanup was initiated once every five years was also considered. As seen in Figure 5-9, the periodic reduction in pool silica levels via cleanup accelerates the rate of Boraflex thinning so that after 40 years of service ~100 mils is lost from the thickness of the panels. This would suggest that RO cleanup is not a recommended practice in spent fuel pools with Boraflex.

To date the model has not been applied to a BWR pool. In its current form, as implemented on an electronic spreadsheet, the model is at its limit of utility. Further application will require a FORTRAN version, particularly for the application to BWR pools. In the BWR pools, without soluble boron in the pool water, the demineralizers in the pool cleanup system are quite effective in removing reactive silica. While the model includes a demineralizer submodel, the additional computer storage and time required to use it would be restrictive.

Use of the Model for Boraflex Service Life Projections

Panel thinning and the loss of boron carbide results in a net increase in the reactivity status of the fuel-rack system. If the panel thinning is assumed to be uniform, the calculations of the panel thinning versus time presented in the previous section provide a means for estimating the useful service life of this material. If panel thinning is not uniform, but occurs most rapidly at the edges of the panels, similar methods as those described here could be applied to assess reactivity effects.

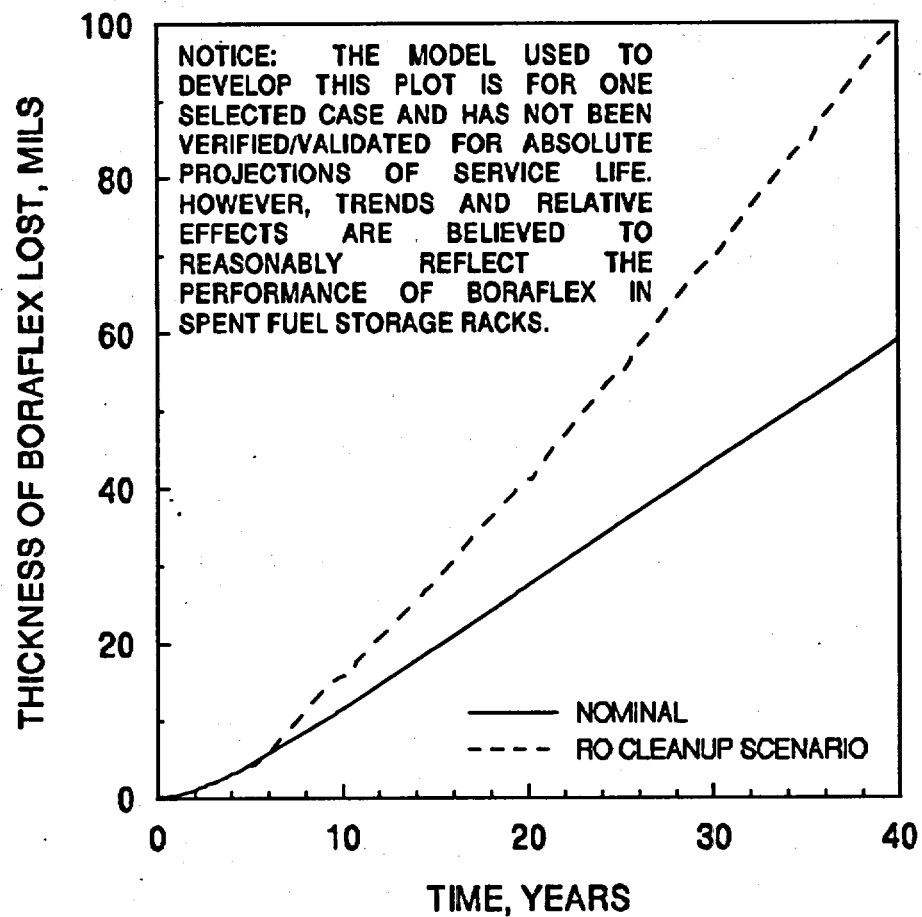


Figure 5-9
Boraflex Panel Thinning versus Time - High Leakage Racks

The amount of boron carbide loss which can be accommodated within the design basis of a fuel rack varies from plant to plant and depends on the inherent margin to the design limit. As the neutron absorber material in a spent fuel rack is the single most expensive material, designers have sharpened their analytical pencils in order to minimize absorber requirements. This has normally resulted in very small margins relative to design limits.

Table 5-1 illustrates the typical margin inherent in a spent fuel rack design calculation. The best estimate eigenvalue (k_{∞}) of the fuel rack system is 0.935. To this must be added any calculational bias as well as the root mean square (RMS) sum of the effect of manufacturing tolerances which yields a design basis k_{∞} of 0.945. The margin between this value and the design limit is $0.005 \Delta k$ which would be available to accommodate boron carbide loss.

Many rack designers, though not all, have designed spent fuel racks based on the minimum B-10 areal density as certified by BISCO. As discussed in Section 2, the actual supplied B-10 areal density is typically 12 to 15% higher. If the actual B-10 areal density is used in the design and variations in panel thickness and B_4C uniformity treated as RMS contributions, some additional margin can be obtained. In the example in Table 5-1, this additional margin is $0.007 \Delta k$, making the total available margin $0.012 \Delta k$.

Figure 5-10 contains a plot of Δk_{∞} versus loss of Boraflex panel thickness for a flux trap PWR spent fuel rack. The analyses have been completed with KENO for unirradiated fuel with an enrichment of 4.3 w/o. For this example, with a total available margin of $0.012 \Delta k_{\infty}$, the maximum thinning which can be accommodated within the design basis is 34%. This can be compared with the results of calculated thinning versus time (see e.g. Figure 5-8 or 5-9), or in-pool measurement of B-10 areal density as discussed subsequently to estimate the useful service life of Boraflex on a plant by plant basis.

Table 5-1
Margin to Accommodate B₄C Loss from Boraflex

Example

Best estimate k_{∞} of fuel and rack 0.935

Calculational Bias +0.002

Root Mean Square of Tolerances +0.008

Design Basis k_{∞} 0.945

Margin: $0.95 - 0.945 = 0.005$

Credit for Actual B-10 Loading:

15% in B-10 Loading +0.007

Total Margin 0.012

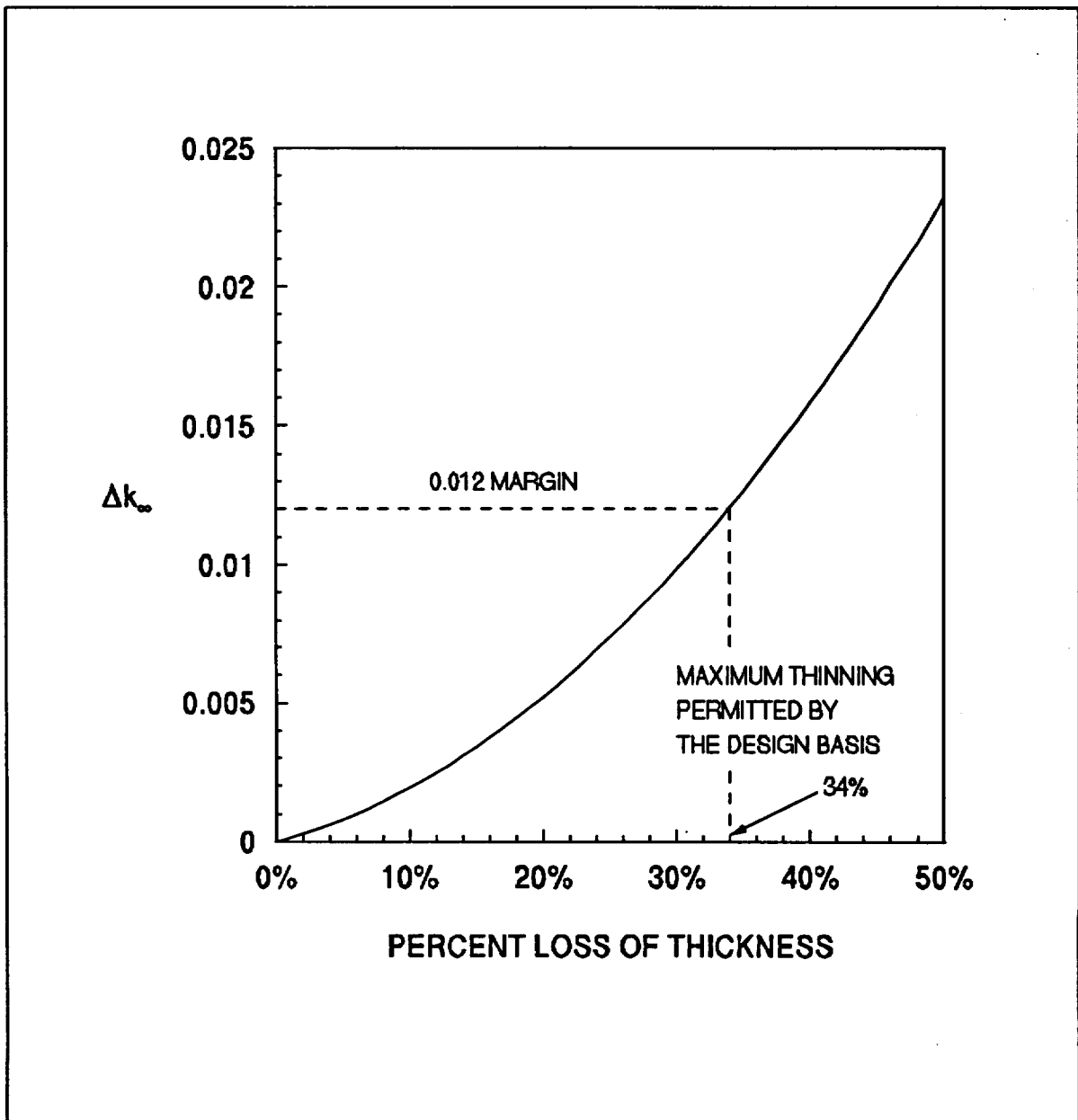


Figure 5-10
Increase in k_{∞} With Thinning Boraflex

6

CONCLUSIONS AND RECOMMENDATIONS

Guidelines for Boraflex Use in LWR Spent Fuel Pools

The test and survey data presented in the previous sections of this report support the following conclusions. When Boraflex is subjected to gamma radiation in the pool aqueous environment, the polymer matrix is transformed into silica and/or a silica-dominated material. At this stage Boraflex consists of about equal parts (by weight) of boron carbide and silica and the silica now serves as the primary matrix to retain the boron carbide. In a typical spent fuel pool the irradiated Boraflex represents a significant source of silica (several thousand kilograms). As such the silica in Boraflex is the most likely source of pool silica contamination in some LWR spent fuel pools.

Silica is slightly soluble in water. The rate of dissolution of the silica in Boraflex depends on:

- reactive silica concentration in the solute
- temperature
- gamma radiation exposure of the Boraflex
- water access to the Boraflex

The rate of boron carbide loss from Boraflex is characterized by the slow dissolution of the silica from the surface of the Boraflex and a gradual thinning of the material. To date, no mechanism has been identified to suggest a change in Boraflex which would result in a rapid loss of boron carbide in spent fuel racks.

With respect to the first of these factors influencing silica dissolution, any remediation activities initiated to reduce pool silica levels will likely accelerate the rate of silica loss, and therefore boron carbide loss, from Boraflex. Increased silica loss has been observed at several plants where reverse osmosis filtration has been implemented. After RO cleanup, pool silica levels have been observed to rise at an accelerated rate. Modeling work described in Section 5 confirms the effect of cleanup operations on Boraflex service life.

Accordingly, it is recommended that, from the standpoint of Boraflex service life, no special measures be initiated to reduce pool silica levels. In order to limit the ingress of silica to the RCS several steps should be taken. During refueling operations the spent fuel pool should be isolated, to the extent possible, from the RCS and the

refueling water storage tank. Consideration should be given to the use of a transfer lock between the fuel transfer canal and spent fuel pool. Such a transfer lock would allow mixing only when a fuel assembly passes through it and not at other times.

The effect of pool ambient silica levels on the rate of silica dissolution in Boraflex suggests that the rate of Boraflex thinning may be more rapid in BWR pools. Survey data described in Section 3 indicate that without soluble boron in the pool water, the demineralizer maintains silica levels at 1 ppm or less in BWR pools. Therefore, in BWR pools low silica levels do not imply satisfactory Boraflex performance, and, in fact, the situation may be just the opposite.

Data from laboratory tests show that the rate of dissolution of silica in Boraflex is a strong function of temperature, as one might expect. This suggests that silica loss from Boraflex can be reduced by maintaining the spent fuel pool at the lowest temperature practical. The practicality of instituting this will vary from plant to plant depending on the heat removal capability of the spent fuel pool heat exchangers and whether both trains of the spent fuel pool cooling system can be operated simultaneously.

The data from laboratory tests show that the rate of dissolution of silica from Boraflex increases at higher gamma exposure. This would suggest that a rack management policy in which the integrated gamma dose is distributed, more or less equally, over all storage cells is prudent. Such a policy would preclude placing the freshly discharged fuel assemblies in the same storage cells at each refueling outage. If, on the other hand, a few rack modules were replaced with an alternative neutron absorber material, these replacement modules could be used for interim storage of the core offload during refuelings. In this manner it may be possible to extend the service life of the remaining Boraflex rack modules.

With regard to the last of these rate dependent factors, the access of water to and around the Boraflex panels is perhaps the most significant factor which will influence the rate of silica dissolution from Boraflex. Unfortunately, there is little that can be done to change this. The water transfer rate in and out of the rack cavities is fixed by the design and construction features of a particular fuel rack. This will vary from rack design to rack design depending on the number and spacing of welds to attach the cover plates, as-built tolerances/clearances, and the size and number of inspection ports provided in the stainless steel to verify the presence of the absorber material.

In PWR pools, the rate at which pool reactive silica is increasing is a good indicator of whether a particular rack is a "low leakage" or a "high leakage" rack. In low leakage racks, modeling work described in Section 5 suggests that pool reactive silica levels will be relatively low (<20 ppm) at the end of 40 years of service. In "high leakage" racks, the reactive silica levels will approach saturation after about 15 years of service. The saturation level depends on temperature but is typically 85-90 ppm at 85°F.

Mitigation Measures

There are several potential means of recovering margin to design limits should boron carbide loss from Boraflex compromise design limits. Some of these are specific to either BWRs or PWRs and some apply to both. There is activity underway in the industry to support credit for soluble boron in PWR pools in the design analyses of the fuel-rack geometry. While initially prompted by a trend to fuel with higher charge enrichment, soluble boron credit could also more than offset any potential loss of boron carbide from Boraflex. In fact, full credit (typically 2000 ppm) would more than accommodate the complete loss of all Boraflex. It is therefore recommended that all efforts in seeking soluble boron credit include allowance for potential Boraflex degradation as well as increases in fuel enrichment.

For BWRs, fuel racks are generally designed based on an infinite multiplication factor (k_{∞}) of unirradiated fuel with a maximum anticipated enrichment. As most spent fuel in storage has accumulated significant burnup, the design condition is very conservative relative to the actual reactivity state of the fuel. Figure 6-1 illustrates this inherent conservatism and the margin available when fuel burnup effects are considered. Typically, the k_{∞} of BWR fuel initially increases as burnable poisons are depleted, passes through a peak in the range of 6,000 to 10,000 MWD/MTU, and then monotonically decreases.

Concurrent with burnup credit, the application of mixed region storage in either BWR or PWR racks is another means to accommodate boron carbide loss from Boraflex. This concept relies on administrative procedures to selectively load fuel in the racks. Mixed region storage was first approved by the USNRC in the mid eighties and has been used at several plants to accommodate fuel enrichment increases.

In mixed region storage, fuel assemblies are loaded in the racks selectively according to the burnup they have achieved. Figure 6-2 shows a mixed region storage plan utilizing a checkerboard loading pattern. In this loading scheme, one out of every two assemblies must have accumulated a specified burnup, the value of which will depend on the initial enrichment of the assembly (see Figure 6-3). The alternative storage locations are reserved for new fuel or fuel assemblies which do not meet the enrichment/burnup criterion for Region 2. In this manner, the irradiated fuel is used to partially control the reactivity of new fuel assemblies, thereby reducing the required quantity of neutron absorber material.

Another potential mitigation measure is the use of poison inserts either within the fuel assemblies (e.g. in guide tubes) or between the fuel and the rack structure. This technique has been used at least once to date for the purpose of extending the fuel enrichment.

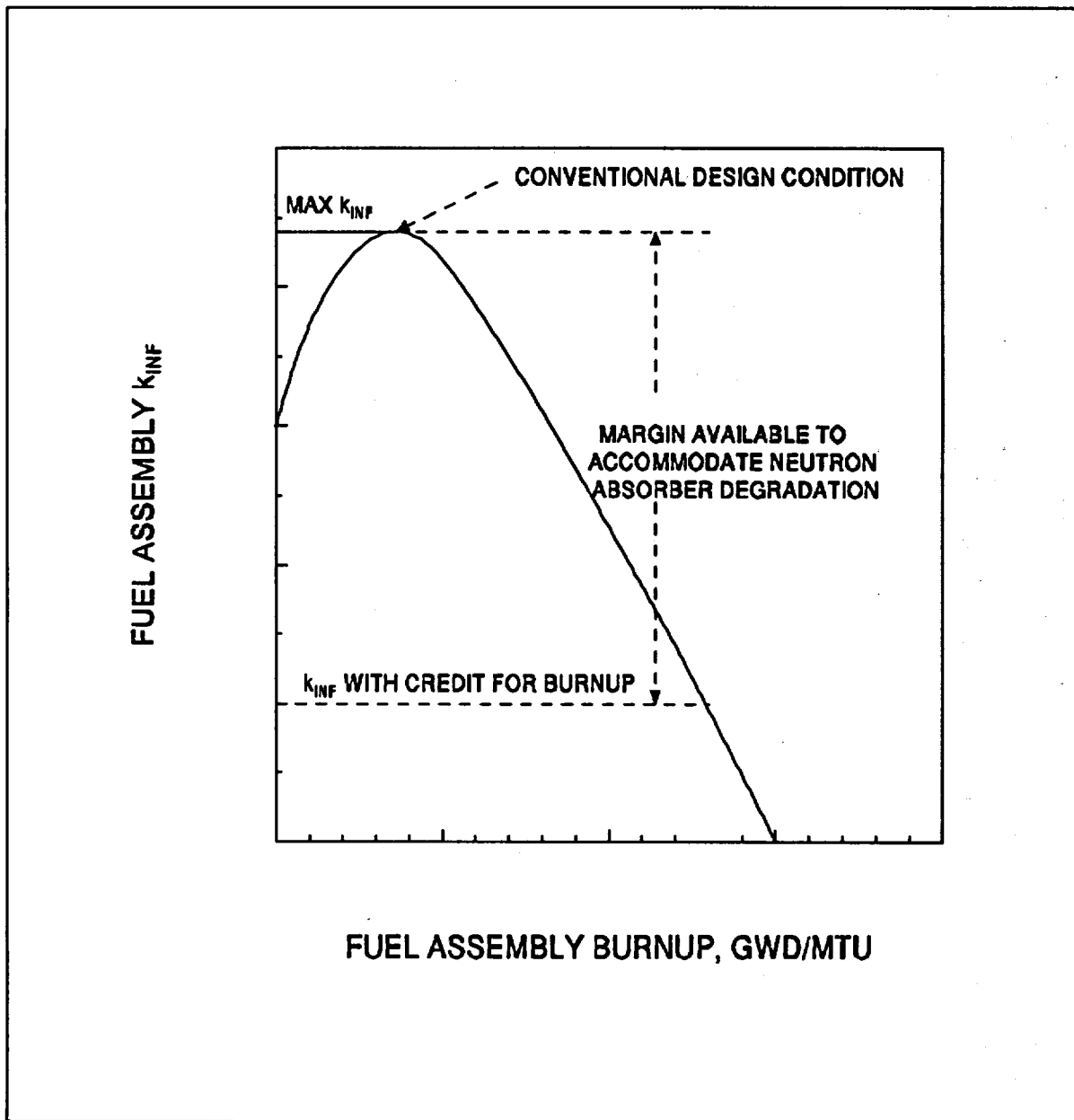


Figure 6-1
Burnup Credit in BWR Racks

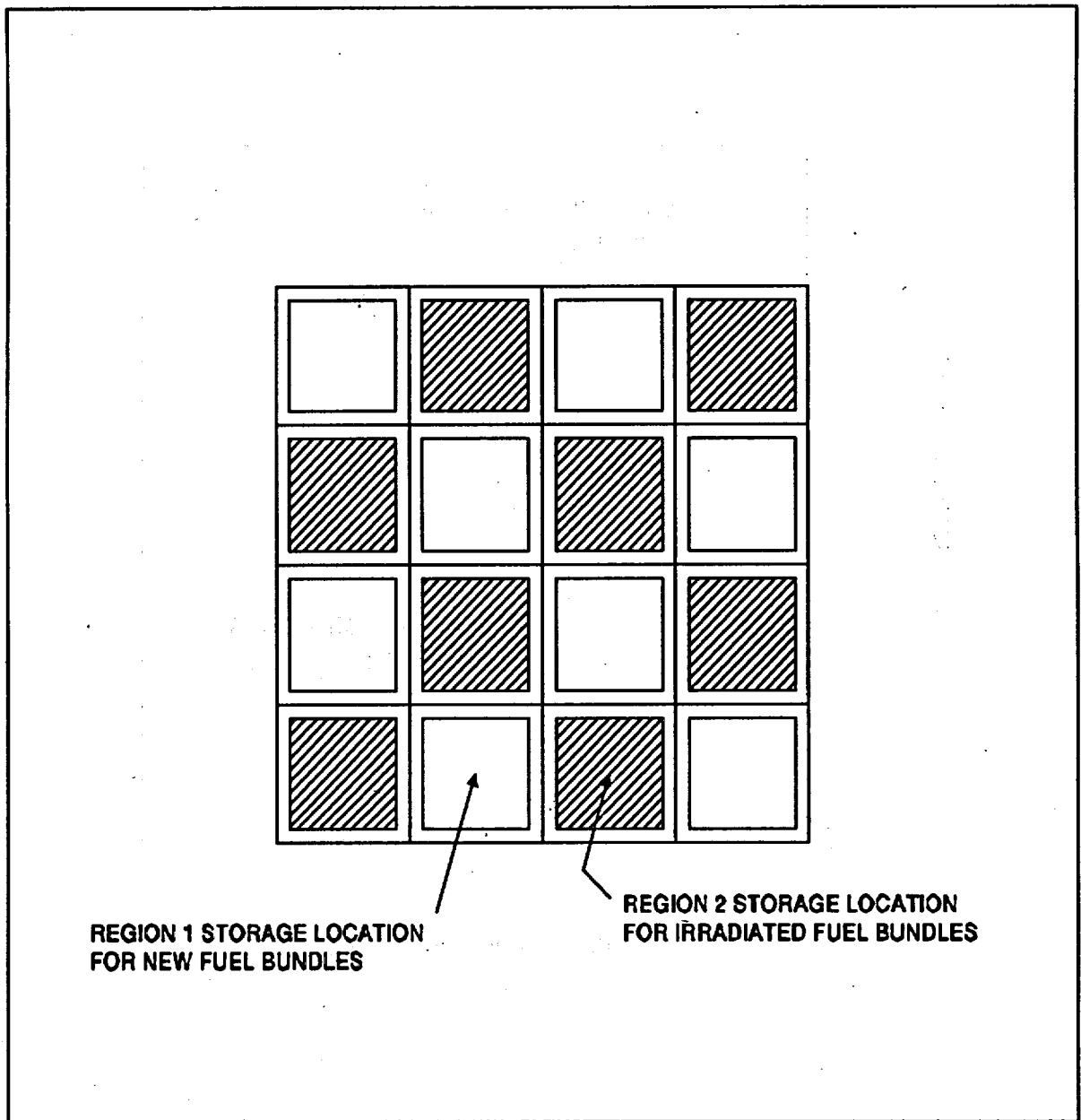


Figure 6-2
Mixed Region Storage Rack

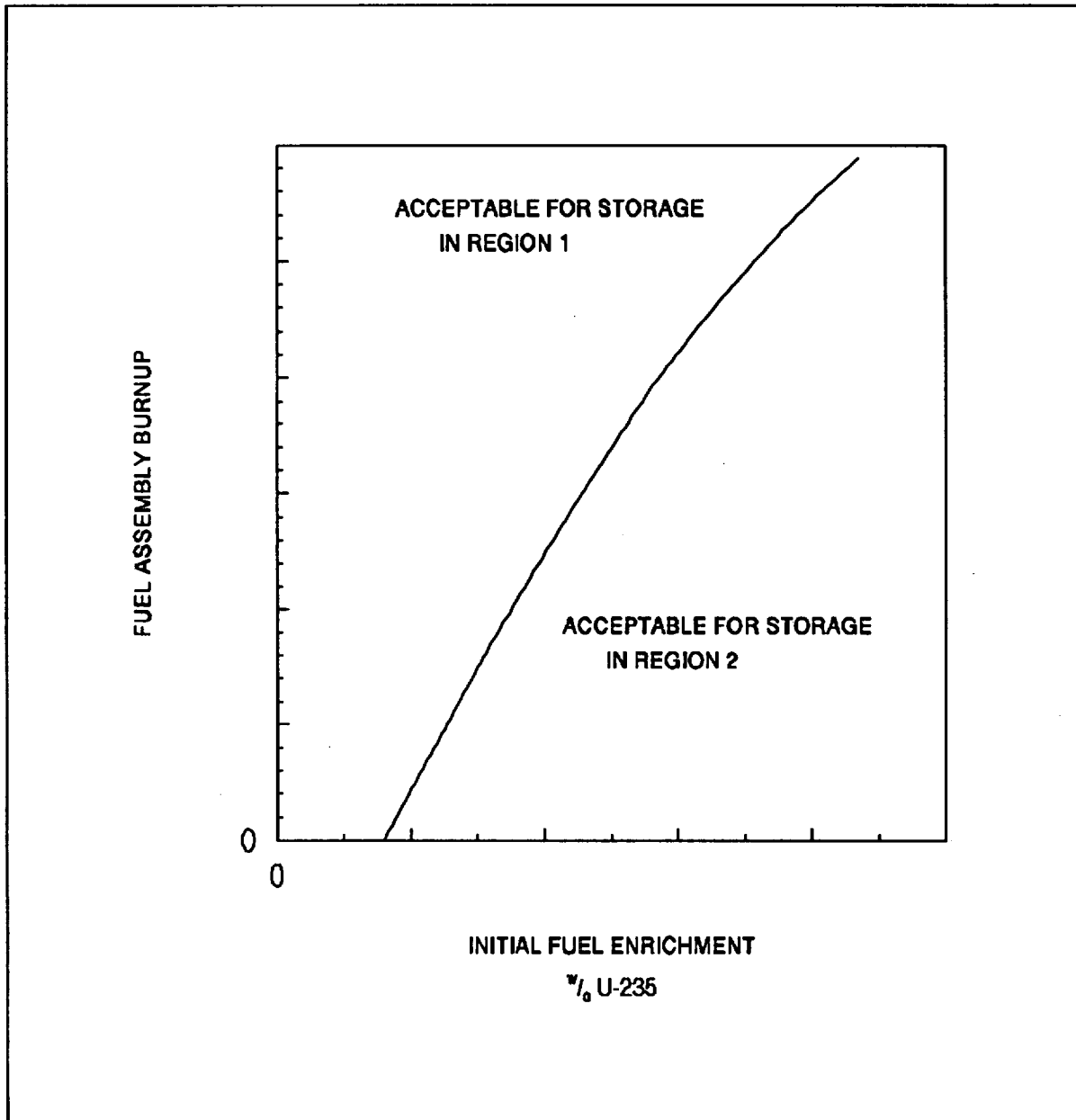


Figure 6-3
Region 1 and Region 2 Criteria for Mixed Region Storage

Surveillance

Most utilities with spent fuel racks which utilize Boraflex have a series of small encapsulated surveillance coupons. Periodically, one or more of these coupons is removed and subjected to inspection and testing. Guidelines for such surveillance procedures have been previously published¹.

The method of coupon encapsulation may or may not accurately simulate the conditions in the racks. Accordingly, water access to the Boraflex and the water transfer rate in and out of the capsules may or may not be representative of conditions in the racks. In spite of this potential shortcoming of coupon surveillance programs, it is recommended that each utility continue the program which is in place. The results from coupon programs may still provide the first indication of a problem with the Boraflex in the racks.

In addition to coupon surveillance programs, pool reactive silica levels should be monitored and recorded frequently. The modeling work described in Section 5 illustrates the usefulness of such data in inferring the actual in-service performance of Boraflex. In addition, it is recommended that less frequent pool samples be subjected to analysis for total silica.

Blackness testing is not recommended for detecting gradual thinning of Boraflex and loss of boron carbide in spent fuel racks. The method does not have sufficient sensitivity for such measurements. Blackness testing will, however, provide an indication of gross deterioration and has been used for gap measurements.

The manner in which Boraflex is housed in spent fuel racks makes it impossible to inspect or test this material while in service by conventional quantitative methods. As part of this project, proof-of-principle tests were completed for an in-situ assay technique to measure the boron-10 areal density in Boraflex installed in spent fuel racks¹². These tests were conducted in a laboratory on sections of simulated rack wall structures containing Boraflex with varying boron-10 areal densities. For fuel racks which have single sheets of Boraflex between storage cells, the tests indicate a measured boron areal density with a one sigma uncertainty of $\pm 5\%$ or less. For fuel racks with two sheets of Boraflex between cells (flux trap design) the measurement uncertainty is somewhat greater. The presence of high gamma radiation fields also adds to the difficulty of obtaining in-situ measurements. A field demonstration is needed to determine to what degree this technology will work.

Recommendations for Future Research

Data has been developed as part of this EPRI program which provides an understanding of the behavior of Boraflex in its service environment. The synergistic effects of gamma radiation and the aqueous pool environment transforms the polymer matrix in Boraflex to silica or a silica-dominated material. The resulting

matrix, which serves to retain the boron carbide, is somewhat soluble in water. As the silica matrix is exposed to water it is subject to slow dissolution and may therefore undergo an associated loss of boron carbide. Dissolution of Boraflex is characterized by a thinning of the material which, over long periods, can compromise the safety function of this neutron absorber.

Evidence of this Boraflex degradation mechanism has shown up at many LWRs as elevated spent fuel pool silica levels. Spent fuel pool chemistry data from some 34 LWR spent fuel pools collected and evaluated as part of this study show a clear relationship between Boraflex and spent fuel pool silica. Calculations presented indicate that the silica contained in irradiated Boraflex represents a very large potential source of spent fuel pool silica, even if only a relatively small fraction of it goes into solution.

In spent-nuclear-fuel racks Boraflex is housed within the stainless steel structure of the individual storage cells. The housing serves to protect the material from mechanical impacts and has the potential to isolate the Boraflex from the pool water depending on the specific design features of the rack. The housing or cavity in which the Boraflex panels reside is, in all cases, vented to the pool water to allow radiation-induced off gas to escape. A major factor influencing the rate of Boraflex thinning has been shown to be dependent on the racks' design and fabrication features which dictate the rate at which pool water enters and exits the panel cavity. This conclusion is supported by test data and modeling work completed as part of this project.

The rate of water exchange will likely vary from rack to rack and among the various rack manufacturers. This introduces a certain element of uncertainty with respect to Boraflex performance in a specific spent fuel storage rack design. In some designs, termed "low leakage" racks, the model described in Section 5 indicates thinning of Boraflex is expected to be fairly modest over a projected 40 years service life. In other designs, termed "high leakage" racks, the thinning may be more severe. Trends in pool silica levels may provide a reliable indication of Boraflex performance in spent fuel racks.

These conclusions lead to the following recommendations with respect to follow-on work to more fully define and project the useful service life of Boraflex. First, the results of proof-of-principle testing, conducted as part of this project, suggests that it may be possible to perform in-situ measurements of the Boraflex boron-10 areal density in spent fuel racks. The test results indicate an overall accuracy of $\pm 5\%$ or better may be possible in some spent fuel racks. The availability of equipment to perform such measurements would provide an indication that the Boraflex is still performing its intended function. Accordingly, it is recommended that the detail design, fabrication, and demonstration of test equipment for in-situ boron-10 areal density assay in spent fuel racks be pursued.

Second, the results of modeling work presented in this report clearly illustrates the usefulness of such models in understanding those factors which influence the in-service performance of Boraflex. The use of models may provide a means to indicate

the useful service life based on historical data of pool silica levels. It is therefore recommended that the existing model be implemented in a user friendly PC-based package and tested at selected utilities. If successful the application to a wide variety of BWR and PWR pool silica histories would then be warranted.

Finally, the industry ppb/silica data presented in this report illustrates the usefulness of such data and collection and evaluation activities in interpreting the behavior of Boraflex in spent fuel racks. It is therefore recommended to continue to support such data collection and evaluation activities so that a current and unified industry-wide database is available. The data collection/evaluation should include pool silica histories, blackness test data, and results from utility coupon surveillance programs.

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