Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

Electrochemical Testing of Boral® Panels from the Decommissioned Zion Nuclear Power Plant Spent Fuel Pool

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ABSTRACT

Neutron absorber materials (NAMs) are used for criticality control in spent fuel pools (SFPs). Boral®, a common NAM material, is an aluminum-clad, aluminum/boron carbide cermet core NAM. The corrosion performance of the Boral® clad and core components over both long-term-service at nominal pool chemistry/temperature conditions, and over short-term, off-normal transients have been evaluated. Boral® materials obtained from the Zion Nuclear Power Plant following 22 years of service in the SFP were physically characterized and were prepared as specimens for electrochemical testing at nominal and off-normal water chemistry conditions. The surface conditions of the cladding were also tested: i) as a freshly ground (initial oxide-free) surface; and ii) a condition following up to several weeks of water immersion during which an attendant oxide film formed. The exposed cermet core was also tested to evaluate corrosion behavior in the postulated case of de-clad material. The testing, testing results, and evaluation of material response to expected long-term and hypothetical transient water chemistry and temperature conditions are presented.

Key words: neutron absorber material, Boral®, spent fuel pool, Zion Nuclear Power Plant

INTRODUCTION

NAMs have been attached to spent nuclear fuel (SNF) storage racks to create “high density” racks that allow SNF to be stored in close proximity in the SFP. One type of NAM that has been used extensively for this purpose, and the focus of this work, is Boral®. Boral® is a composite sheet containing a cermet core of boron carbide particles from 50 to 65 wt.% in aluminum (Al 1100) powder sandwiched between aluminum (Al 1100) sheets, as shown in Figure 1. Boron carbide contains ^{10}B, which is a strong neutron absorber present in natural boron. The cermet core is sintered during hot rolling.

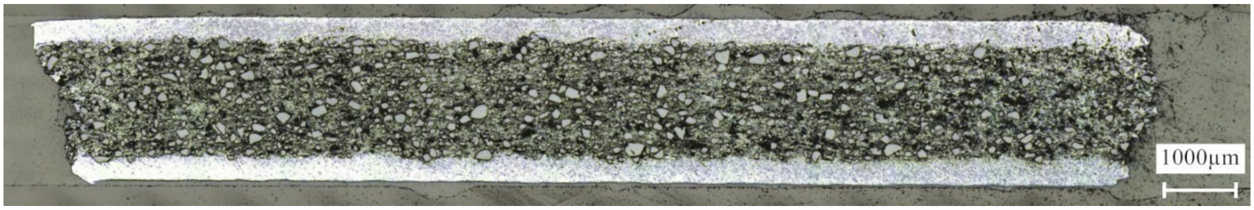


Figure 1: Laser confocal microscope montage image of Boral® panel

When immersed in water, aluminum develops a hydrated oxide film. The film passivates the aluminum to reduce its general corrosion rate. Two fundamental water chemistries are used in SFPs: one for Pressurized Water Reactor (PWR) and one for Boiling Water Reactor (BWR) pools. The PWR SFP water contains dissolved boron (approximately 2500 ppm) to reduce dilution of the reactor coolant during refueling. Boron is a moderator in PWR water. Both water chemistries are otherwise nearly identical such that the impurity concentrations are very low. The corrosion performance of Boral® in both PWR and BWR SFP service is compiled in a report.[1] One observation is that the PWR SFP water chemistry produces a thinner oxide film compared to the BWR SFP water chemistry at similar time/temperature immersion conditions; the presence of the oxide film or the corrosion of the aluminum cladding does not interfere with performance as a neutron absorber. In general, the aluminum cladding is susceptible to localized corrosion attack in the form of pitting; however, the very low impurity water does not cause significant pitting attack.

One observation with Boral® in SFP service is an incidence of blister formation. There are two potential impacts of blistering, (1) it may impact the free clearance to remove the fuel assemblies, and (2) it may displace water from the flux trap region reducing the ability of the water to thermolyze neutrons.[2] Of interest is the corrosion behavior of the core region of the Boral® which would be a relevant condition if the core were exposed due to blistering and the loss of the aluminum cladding blister dome.

The Zion Nuclear Power Plant (Zion), a PWR in Zion, Illinois, was decommissioned in 1998. Boral® panels were used as NAMs in the SFP and was the source of service-experienced material for testing. The Zion Plant started the dismantling process in 2011. The SFP racks were removed from the pool in 2015 and several Boral® panels were cut from the racks and sent to the Savannah River National Laboratory (SRNL) for characterization and testing. In total, the panels had about 22 years of service in the PWR SFP at normal water chemistry and temperature conditions.

The activities at SRNL included the characterization of the as-received Boral® panels and an investigation of their corrosion behavior at normal (nominal) and off-normal water chemistry and temperature conditions. The activities were tasked by the U.S. Nuclear Regulatory Commission (NRC) and a full description of the work has been published in a recent technical report[3]. The corrosion behavior of both the cladding and core components of the Boral® material have been investigated in this work to provide information to evaluate the performance of the Boral® material under long-term and under hypothetical, off-normal transient water chemistry and temperature conditions.

Corrosion testing involved both electrochemical and immersion testing performed on specimens prepared from selected Boral® panels. The specimen types included: i) cladding with a ground surface (fresh surface); ii) cladding that had a ground surface that was aged in the water solution to provide an oxide film; and iii) an exposed core surface. Tests were performed to obtain general corrosion rates and assess the susceptibility to localized forms of corrosion such as pitting. The electrochemical corrosion tests were performed at different temperatures to establish an Arrhenius correlation and determine activation energies for the corrosion mechanism. The samples were exposed to water chemistries ("simulants") that included: 1) a nominal composition that was prepared by averaging water quality data from Zion SFP; 2) a base composition using the SFP limits for water quality; and 3) an off-normal composition with impurity concentrations 100 times that of the base composition and judged to be well-bounding for a postulated transient where water chemistry control systems may be off-line for an extended period of time. Additionally, an immersion test was conducted with the core specimen type at high corrosive conditions (as determined by electrochemical tests) to directly evaluate mass loss that can be attributable to loss of boron carbide from the Boral® core.

EXPERIMENTAL PROCEDURE

Several Boral® panels were used for this study. The panels were cut into sections approximately 15 cm x 30.5 cm (6 in. x 12 in.) and shipped to SRNL. Some panels that had high levels of radioactive contamination were decontaminated using a dilute solution of nitric acid. Using a shear, 2 cm x 2 cm (0.79 in. x 0.79 in.) pieces were cut from the sectioned Boral® panels to provide specimens with a surface area of 4 cm^2 (0.62 in^2). The pieces were cleaned with distilled water and degreased with acetone. The pieces were further prepared and used for electrochemical and immersion testing.

Electrochemical testing

For electrochemical testing, each sample was electrically connected to a wire using silver epoxy and mounted using a two-part acrylic solution (VariDur from Buehler). A corrosion glass cell with 1 L (34 fluid ounces) volume capacity was used. The cell was placed on a hot plate with a connected thermocouple for heat control and contained approximately 500 mL (17 fluid ounces) of simulant. Two carbon graphite rods electrically connected by a cable served as the counter electrode. A saturated calomel electrode (SCE) was used as the reference electrode. The SCE was placed in a salt bridge to provide connection and separation from the heated solution to minimize disturbances in reference potential. A potentiostat (VSP by Bio-Logic Science Instruments) provided voltage and current operation for the tests. The ASTM standards for linear polarization resistance (LPR)[4], electrochemical impedance spectroscopy (EIS)[5], and cyclic potentiodynamic polarization (CPP)[6,7], were used for reference to establish the testing protocol and to check electrochemical instrumentation prior to testing.

A typical procedure for the electrochemical testing consisted of several sequential experiments. Initially, an open circuit potential (OCP) was measured until the potential of the sample equilibrated in the solution. This time varied from 2 to 7 hours. After the OCP was equilibrated to at least +/- 10 mV in 1 hour, LPR was performed over a potential range of +/- 25 mV with respect to the OCP at a rate of 0.167 mV/s. Next, the EIS experiment was performed to obtain the solution resistivity at high frequencies (i.e., > 1000 Hz) and polarization resistance to compare with the LPR experiments. The CPP experiment was conducted from -0.3 to 2 V vs. SCE at a rate of 0.167 mV/s to determine the susceptibility to localized corrosion and to obtain the Tafel constants needed to calculate corrosion rates. The corrosion rates were calculated based on ASTM G102.[8]

The sample preparation prior to the electrochemical experiments changed depending on the specimen type. For experiments using specimens with a freshly ground cladding surface and for the specimens tested after the oxide was allowed to grow on a freshly ground cladding surface, each specimen was ground using 600 grit SiC paper immediately prior to immersion in the test solutions. For the core specimen type, the cladding was removed on one side by peeling it off slowly using pincers prior to mounting - it was not ground and had an “as-peeled-back” surface finish. Exploratory testing to grind the cladding off to expose the core material tended to group (compact) the hard boron particles in the soft aluminum and increase the electrical resistance of the surface rendering the sample unusable for electrochemical testing.

Immersion testing

For immersion testing, a layer of aluminum cladding was peeled off from one side to evaluate the potential loss of boron carbide from an exposed core specimen. A large glass vessel of 2 L (68 fluid ounces) capacity was filled with 1.5 L (51 fluid ounces) of solution and stirred to approximately 200 revolutions per minute for 12 days. The specimens were contained in specially designed glass baskets secured in the vessel by glass holders. A condenser was used with a chiller to prevent evaporation of the solution.

Four specimens were tested; three were exposed in the test solution and one was set aside (i.e. not exposed to the test solution) to act as a control specimen. The weights of the samples were measured prior to immersion in the solution using sequential drying in a vacuum oven to remove residual water from the core. The samples were washed with nitric acid after the test to remove the oxide without significantly attacking the aluminum-boron carbide core material. Then the samples were cleaned, dried and weighed to establish the mass loss or gain after the test.

Simulants

BWR and PWR SFP water chemistry solutions (simulants) were prepared to evaluate the effects of impurity species. The potentially aggressive species identified for evaluation included chloride, sulfate and fluoride based on historical Zion SFP chemistry records, EPRI guidelines for SFP water chemistry control limits and operating experience.[9-11] Three categories of SFP water chemistry solutions were evaluated and designated as “nominal”, “base” and “off-normal” for PWR and BWR SFPs resulting in a total of six simulants. The difference between the BWR and PWR simulants was that the PWR simulants contained boron added in solution as boric acid. The “nominal” simulant was based on an average historical concentration profile from the Zion SFP, the “base” simulant was based on the maximum limits of the SFP water chemistry guidelines, and the “off-normal” solution represented contaminant concentrations one hundred times higher than the water chemistry guidelines for the aggressive species. Table 1 shows the six simulants created for study. They are in ascending order of the concentration of the aggressive constituents.

Table 1
Water Chemistries of solutions used

Simulants	Boron Concentration, ppm	Concentration of aggressive species, ppm			pH
		Chloride	Sulfate	Fluoride	
1-PWR nominal	2500	0.012	0.006	0	4-5
2-BWR nominal	0	0.012	0.006	0	5-7
3-PWR base	2500	0.15	0.15	0.01	4-5
4-BWR base	0	0.15	0.15	0.01	5-7
5-PWR off-normal	2500	15	15	1	4-5
6-BWR off-normal	0	15	15	1	5-7

RESULTS

The test results are in subsections below for electrochemical and immersion tests. The electrochemical testing subsection includes the results of testing performed on specimens with freshly ground cladding surfaces, “aged” oxide surfaces, and as-peeled-back core surfaces. The immersion tests focused on a selected simulant that provided high corrosion rates in electrochemical tests with an exposed core.

Electrochemical Testing: Cladding Corrosion

Two conditions were tested at various temperatures: freshly ground surface cladding and cladding with an “aged” or oxidized surface generated by exposure over time while immersed in the test solution. The aging procedure produces a more representative oxidized surface condition for the samples rather than the as-received surface which was subjected to handling and decontamination treatments. The as-received oxide surface was initially studied, but the corrosion rates measured were higher than expected based on the estimates obtained from an analysis panel cross-sections. X-ray Diffraction measurements of the as-received panel specimens did not show an expected oxyhydroxide crystalline film (results not shown). It is suspected that thermal de-watering of the oxyhydroxide film occurred during panel retrieval from the Zion SFP and subsequent handling and surface preparations. De-watering of the oxyhydroxide film would degrade the passivating properties of the as-received surface film making it less representative of panels in the SFP. Alternatively, it was decided to produce a representative surface oxide condition by immersing the samples in the test solution and measure the corrosion rate change with exposure time.

Fresh surface

Fresh surface was obtained by grinding the surface of the sample with 600 grit SiC paper until a uniform surface was obtained. The grinding was done carefully since the cladding is very thin. The electrochemical experiments were performed in each of the six solutions at 25 °C (77 °F), 75 °C (167 °F) and 98 °C (208 °F). Figure 2 displays the corrosion rates derived from Tafel slopes obtained using CPP plots at a potential above and below 50 to 100 mV from OCP.[11] The following equation was used to calculate the corrosion rate using the corrosion current density i_{corr},

$$\mathrm{CR} = \mathrm{K}\ \frac{i_{\mathrm{corr}}}{\rho}\ \mathrm{EW} \tag{1}$$

where K is a constant equal to 3.27 x 10^{-3} mm g/μA cm yr, ρ is density in g/cm^3, EW is the equivalent weight (for Al 1100, the density and equivalent weight is 2.71 g/cm^3 and 8.99, respectively).

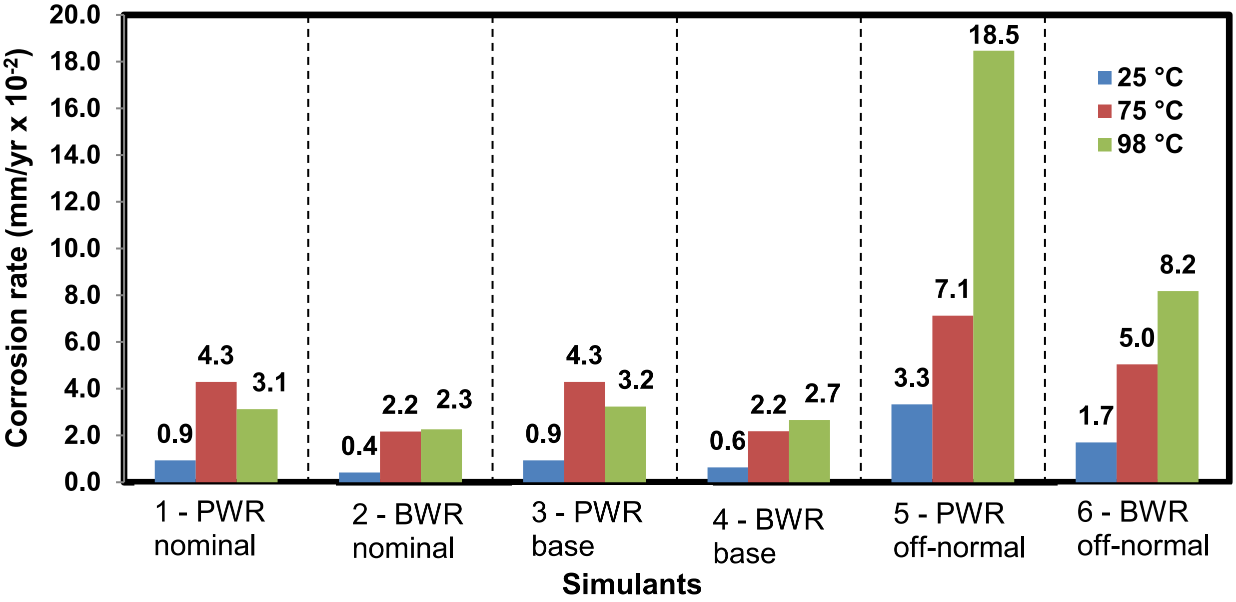


Figure 2: Corrosion rates of aluminum cladding in six simulants at three temperatures

The electrochemical testing performed on freshly ground cladding surfaces resulted in generally higher corrosion rates for the specimens tested in the simulated PWR water than the specimens tested in the simulated BWR water at each testing temperature. The corrosion rates for the ground specimens represent possible upper bound rates for these testing conditions since the protective oxides that form in the simulants have little time to develop during the electrochemical testing. Additionally, the corrosion rate generally increased with increasing test temperature.

Performing the electrochemical experiments at different temperatures allows the formation of an Arrhenius plot. An Arrhenius plot is often used to analyze the effect of temperature on the rates of electrochemical reactions (i.e., corrosion rates). The plot gives a straight line from which the activation energy can be determined. The Arrhenius equation is shown below in linearized form,

$$\ln i_{corr} = \ln A - \frac{E_a}{R\,T} \tag{2}$$

where i_{corr} is the corrosion current density (μA/cm^2); A is the pre-exponential factor which is an empirical relationship between temperature and corrosion rate; R is the gas constant and E_a is the activation energy, which is the minimum energy required to start the electrochemical reaction. In an Arrhenius plot, the ln i_{corr} vs. 1/T provides E_a/R as the slope of the line and ln A as the y-axis intercept. The Arrhenius plots for the fresh surface cladding are presented in Figure 3.

For the cladding, the Arrhenius plots resulted in almost equally linear parallel slopes indicating that the corrosion mechanisms were likely the same during the experiments. When comparing the nominal to the off-normal simulants, the slope for simulant 6 was slightly different than simulant 2 while simulants 5 and 1 had nearly identical slopes. The activation energies obtained for the simulants ranged from 17.6 to 23.0 kJ/mol (4.2 to 5.5 kcal/mol) and were consistent with the relative corrosion performance measured during the experiments (shown in Table 2) especially when comparing the off-normal conditions to the base and nominal conditions. When compared to the activation energies obtained for the core (Table 4), the activation energies for the freshly ground cladding and the core were similar indicating that aluminum corrosion is the dominant electrochemical reaction occurring.

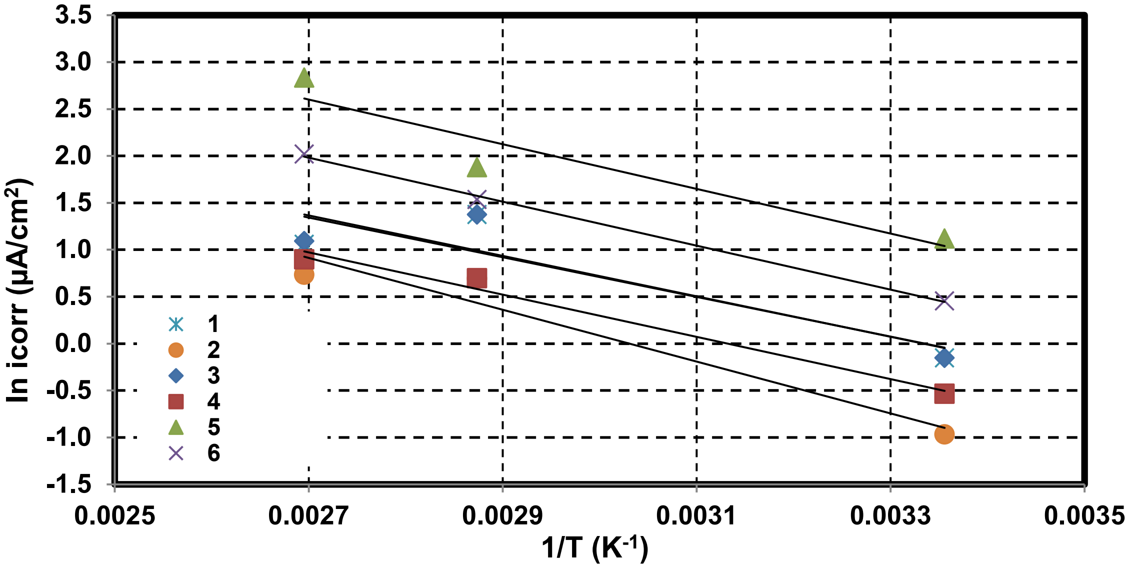
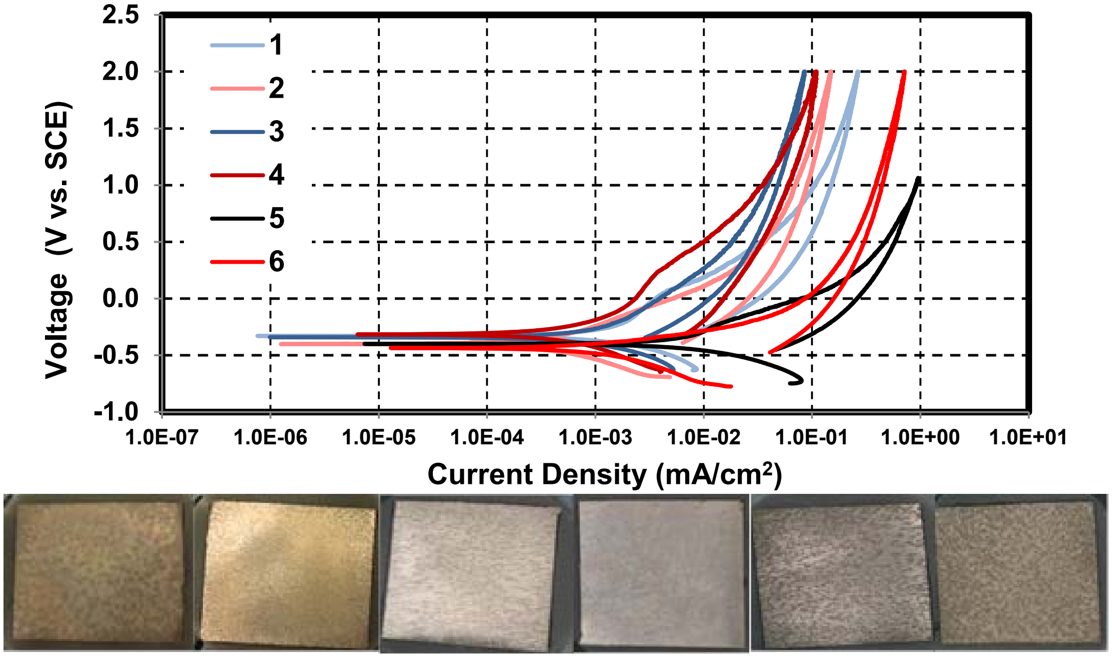


Figure 3: Arrhenius plot of aluminum cladding tested in six solutions

Table 2
Activation energies obtained from the Arrhenius plot for the aluminum cladding

Solutions	Activation Energy E_a, kJ/mol (kcal/mol)	Pre-exponential Factor A
1-PWR nominal	17.6 (4.2)	1155.6
2-BWR nominal	23.0 (5.5)	4324.7
3-PWR base	17.9 (4.3)	1320.0
4-BWR base	18.7 (4.5)	1152.7
5-PWR off-normal	19.8 (4.7)	8341.5
6-BWR off-normal	19.5 (4.7)	4065.9

CPP scans for the six solutions at 25 °C (77 °F) and for two solutions at 75 °C (167 °F) and 98 °C (208 °F) are shown in Figure 4 and Figure 5, respectively. At 25 °C (77 °F), a very active anodization behavior was observed for samples in all simulants with a small passive hump in the scan for the samples in simulants 1 and 4 (Figure 4). The OCP obtained ranged from -0.317 to -0.446 V vs. SCE. The CPP curves reached the 2 V limit during the scans, except for the CPP curve of solution 5, which met the threshold current density at approximately 1.06 V vs. SCE. The scans showed positive hysteresis, which indicates pitting susceptibility and, as observed in the pictures in Figure 4, all samples showed differing degrees of pitting. As expected, the pitting was more prevalent with larger pit diameters and greater apparent pit depths for samples exposed to simulants 5 and 6 than for samples exposed to simulants 1, 2, 3 and 4 as a result of the higher concentrations of chloride. At 75 °C (167 °F) and 98 °C (208 °F) (Figure 5), experiments were only performed for specimens exposed to simulants 1 and 2. At 75 °C (167 °F), the OCP obtained for simulant 1 was consistent the OCPs obtained at 25 °C (77 °F). All of the other OCPs obtained at 75 °C (167 °F) and 98 °C (208 °F) were more negative and in the range of -0.842 to -0.900 V vs. SCE. The lower OCPs resulted in an increment in the passive region (i.e., voltage change in which current remained at the same value after E_{corr} determination). As indicated in Figure 4 and Figure 5, the passive regions were larger for simulant 2 (BWR nominal) than simulant 1 (PWR nominal), especially for temperatures at 75 °C (167 °F) and 98 °C (208 °F). Positive hysteresis was observed in Figure 5, and the 2 V limit was reached for all the scans. The change in OCP to more active (i.e. more negative) values is believed to be caused by the transition of oxide crystalline structure from gibbsite/bayerite to boehmite, although there is not conclusive evidence. Pictures presented in Figure 5 show the appearance of localized corrosion which was more aggressive at 98 °C (208 °F) than at 75 °C (167 °F).



Solution 1 Solution 2 Solution 3 Solution 4 Solution 5 Solution 6

Figure 4: (top) CPP scans for fresh surface cladding exposed in solutions 1 to 6 at 25 °C and (bottom) after test pictures (The color differences between solutions 1 and 2 are due to lighting conditions)

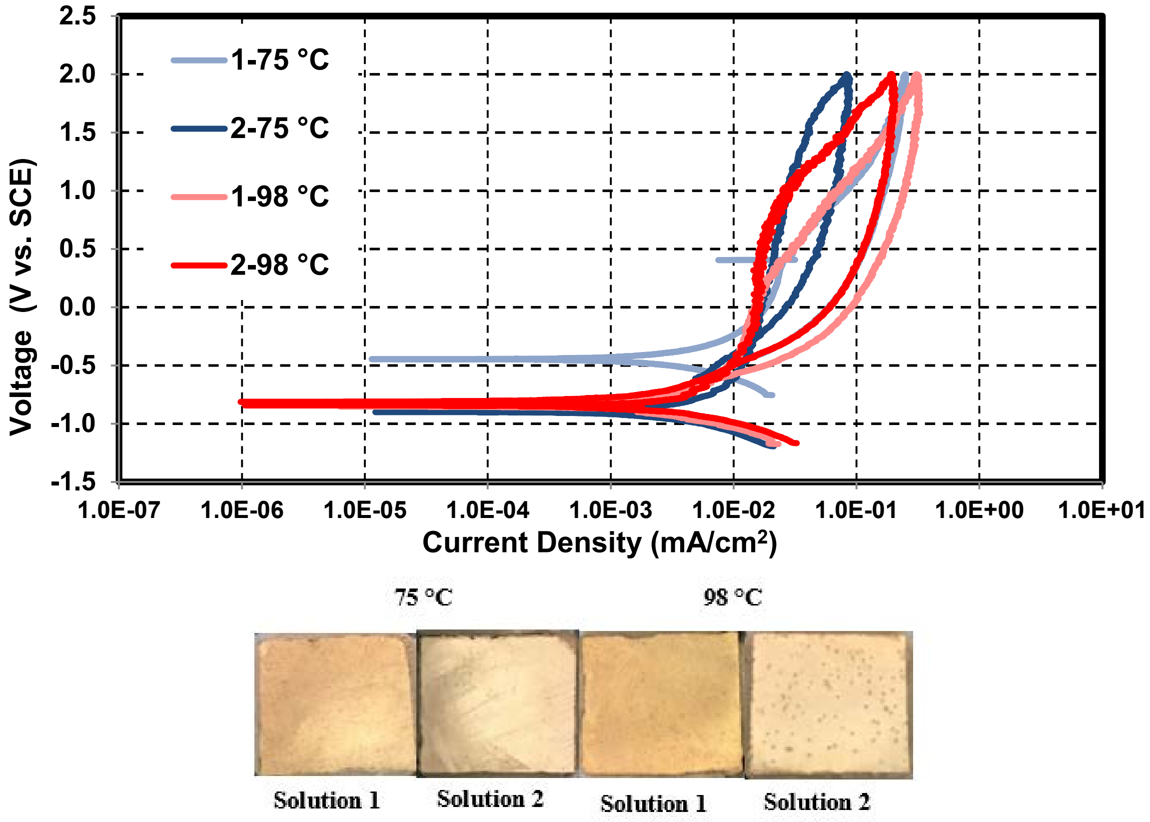


Figure 5: (top) CPP scans for fresh surface cladding exposed in solutions 1 and 2 at 75 °C and 98 °C and (bottom) after test pictures

"Aged" oxide surface

Two sets of tests were carried out on cladded samples to evaluate the impact of a surface oxide grown under typical SFP water conditions on the corrosion rates. Initially, it was observed that corrosion rates over time were different depending on whether the solution was refreshed intermittently during the test. Considering the large volume of the fuel pool water and the range of chemistries addressed in the test matrix, it was determined that a controlled solution refresh was representative of the pool exposure conditions. The two sets of test parameters adopted were PWR Simulant 3 and BWR Simulant 4 each at 40 °C (104 °F) with controlled solution refreshes during the test.

To understand the effect of maintaining a relatively constant immersion solution chemistry, corrosion tests were performed with solution monitoring and periodic solution changes when the chemistry exceeded a predetermined range. The electrochemical experiments consisted of running LPR and EIS experiments initially and weekly in a solution with refreshment to maintain conductivity to less than 12 μS/cm . To maintain low conductivity, a solution change-out was performed before the solution reached 12 μS/cm and at the completion of each electrochemical measurement interval.

Corrosion rate measurements were taken during the long-term exposure and are shown in Figure 6 and Figure 7. The PWR simulant 3 exposure shown in Figure 6 indicates that maintaining a consistent solution conductivity and pH results in a lower long-term corrosion rate. For example, at the end of the four-week exposure, the refreshed solution sample corrosion rate was 0.002 mm/yr (0.08 mils per year (mpy)) compared to the non-refreshed solution sample corrosion rate of 0.010 mm/yr (0.39 mpy). The refreshed condition is considered more representative (compared to the non-refreshed) of the chemistry in a well maintained SFP and, thus, representative of the expected temperature dependent corrosion rates for the Boral® clad. The data also supports a general conclusion that for both the PWR and BWR base conditions (simulants 3 and 4) the longer-term corrosion rate at 40 ˚C (104 °F) is about 0.002 to 0.003 mm/yr (0.08 to 0.12 mpy).

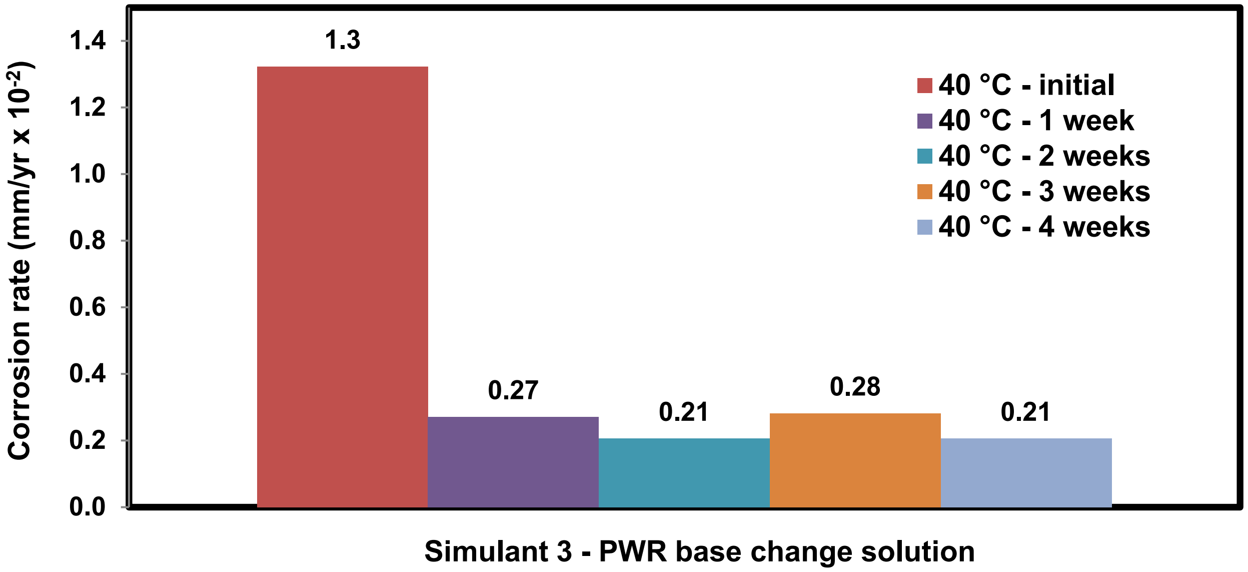


Figure 6: Weekly corrosion rates in PWR Simulant 3 at 40 °C with periodic change of solution.

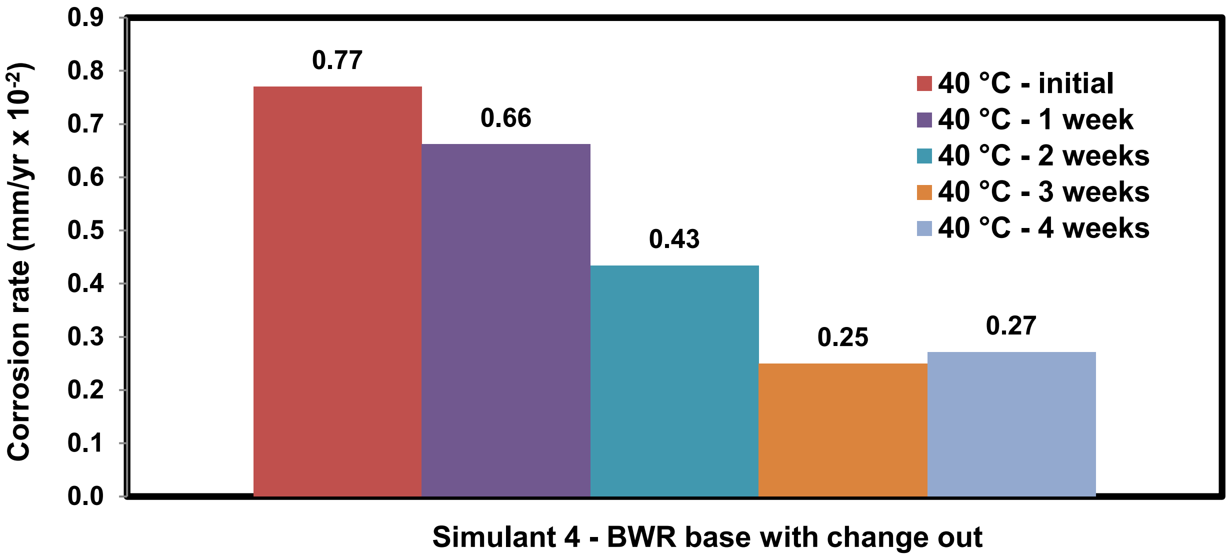


Figure 7: Weekly corrosion rates in BWR Simulant 4 at 40 °C with periodic change of solution.

Using the data generated for the “aged” oxide sample corrosion rates, an equation for predicting the metal loss of the cladding with exposure was derived using the following assumptions:

Activation energy = 17.9 kJ/mol (4.3 kcal/mol) (based on the activation energy for the PWR fresh surface base simulant.

Since the tests for the “aged” surface were limited to one temperature, the activation energy cannot be calculated from the data set. However, for this calculation it is assumed that the activation energy from the fresh surface tests apply (a conservative assumption). The nominal corrosion rate of 0.002 mm/yr (0.08 mpy) as measured at the end of the exposures is adopted as the corrosion rate at 40 °C (104 °F).

Using the calculated activation energy (Table 2), the Arrhenius equation (equation 2) can be adjusted based on the corrosion rate since the corrosion rate is proportional to i_{corr}. For the “aged” clad surface, the pre-exponential factor calculated is,

$$A = \text{corrosion rate}/\ e^{-Ea/RT} = (0.002\ \text{mm/yr})/e^{-17900/8.314/313} = 1.94 \qquad (3)$$

Table 3 lists several conditions for which the extent of clad corrosion was predicted for an “aged” surface using the calculated pre-exponential factor for the PWR base simulant.

Table 3
Example results of calculations for long term corrosion of the Boral® clad in base PWR simulant based on the activation energy for a freshly ground surface (a conservative assumption)

Temperature, °C (°F)	Time, days	Corrosion, µm	Corrosion, mils
25 (77)	30	0.12	0.004
98 (208)	30	0.48	0.019
25 (77)	365	1.40	0.055
40 (104)	365	1.98	0.078
98 (208)	365	5.82	0.229

Electrochemical Testing: Core corrosion

Figure 8 shows the corrosion rates obtained for the four simulants at three temperatures. To determine the corrosion rate for the core, the LPR data was adjusted assuming that aluminum is the only component that it is corroding and that the surface area was composed of 60 % aluminum and 40 % boron carbide particles, as determined by quantitative metallography. Thus, the surface area of the active sample was reduced to 60% of the sample size for the LPR-determined corrosion rate. Since the corrosion rate determined via LPR is inversely proportional to the sample surface area, the resulting corrosion rates are higher than if the total sample surface area was used.

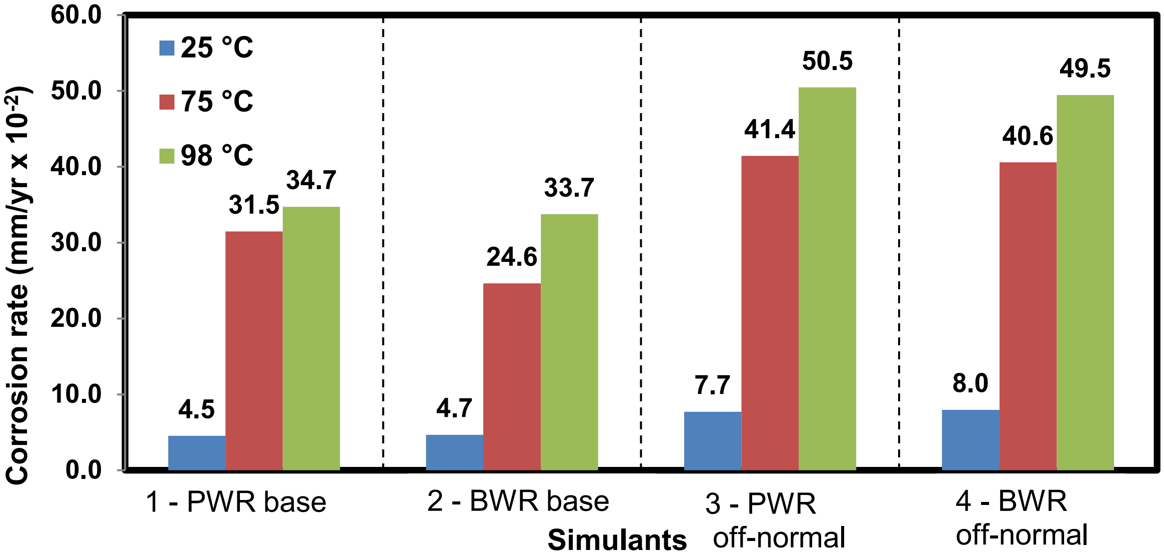


Figure 8: Corrosion rates of cermet core in four simulants at three temperatures

As expected, corrosion rates increased with increasing temperature and with the concentration of species in the solutions. At room temperature, the corrosion rates were about 0.045 to 0.080 mm/yr (1.8 to 3.2

mpy) and increased to rates exceeding 0.246 mm/yr (9.7 mpy) at temperatures over 75 °C (167 °F). The corrosion seemed to be exacerbated by galvanic effects associated with interactions between the inert boron carbide particles and the aluminum powder that comprise the cermet core.

Arrhenius plots are shown in Figure 9 for the core exposed in simulants 3 through 6 at three temperatures. It is noted that similar corrosion rates were measured for the material in simulants 5 and 6 (off-normal) and, likewise, similar values were obtained from simulants 3 and 4 (nominal). Linear regression showed similarities in the slopes denoting similar electrochemical reactions. Activation energies for the core were calculated from the slope and ranged from 24.0 to 27.3 kJ/mol (5.7 to 6.5 kcal/mol). Table 4 lists the calculated activation energies.

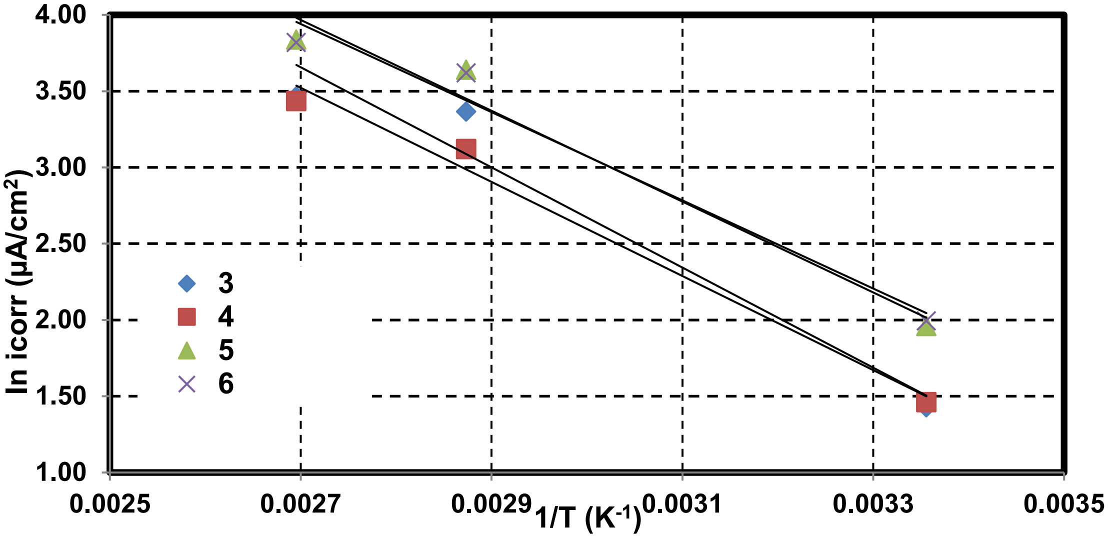


Figure 9: Arrhenius plot of core tested in four solutions

Table 4
Activation energies obtained from the Arrhenius plot for the core

Solutions	Activation Energy E_a, kJ/mol (kcal/mol)	Pre-exponential Factor A
3-PWR base	27.3 (6.5)	273758.0
4-BWR base	25.6 (6.1)	140084.3
5-PWR off-normal	24.7 (5.9)	163734.2
6-BWR off-normal	24.0 (5.7)	126247.6

Using the calculated activation energies, pre-exponential factors (Table 4) and the measured corrosion rates (Figure 8), the penetration depth can be calculated. For example, using the PWR base (simulant 3) data, the thickness loss can be calculated for the core specimen. Table 5 lists values of thickness loss due to corrosion calculated based on the i_{corr} in PWR base water (simulant 3) of the core using equation 1. The amount of corrosion at 40 °C (104 °F) represents what might be observed after a year of exposure of the core to the nominal test conditions while the amount of corrosion at 98 ºC (208 °F) represents the potential performance at an elevated temperature for shorter durations of 7 days and 30 days. These rates and values are listed for information only and reflect a more severe condition because, as shown with the case of “aged” oxide, the corrosion rate is expected to decrease with exposure time and oxide build-up and they do not consider potential mitigating responses for the 98 °C (208 °F) case. To develop more accurate values for modeling the corrosion of the core, further testing to develop a steady state corrosion rate is required.

Table 5
Calculated Corrosion Rate of the Cermet Core in PWR Base Water

Time days	Temperature °C (°F)	Corrosion* µm	Corrosion* mils
365	40 (104)	83.2	3.3
7	98 (208)	8.2	0.3
30	98 (208)	35.2	1.4

* Based on an Al:boron carbide surface area ratio of 60:40

Immersion Testing

The electrochemical testing resulted in low corrosion rates for the Boral® materials in very aggressive water solutions at high temperatures. These findings were used to select the immersion testing conditions which included immersing the as-peeled-back core surface specimens in simulant 5 at 98 °C (208 °F) to substantiate the electrochemical testing results. Specimens with the as-peeled-back/de-clad core surface were tested to evaluate the potential for boron carbide loss.

Four specimens were prepared for immersion testing. The cladding side was polished to 600 grit to start with a fresh surface free of oxide (back side of sample), then it was rinsed in nitric acid and heated in a vacuum oven at 230 - 240 °C (446 - 464 °F) for drying. The drying can vary in time from 1 to 18 hours. Figure 10 shows pictures of the specimens prior to immersion.

Figure 10: Pictures of Boral® coupons with one face de-clad prior to immersion

The weight was recorded in triplicate after the sample was rinsed in nitric acid and vacuum dried. The process was continued until the weight change was below 0.0006 g maximum.
Table 6 lists the weights in triplicate prior to immersion.

Table 6
Weight of coupons initially and prior to immersion after drying

Samples	Initial weight, g	Post-treatment weight prior to immersion (in triplicate), g			Average weight, g	Standard deviation, g
1	1.8748	1.8314	1.8315	1.8319	1.8316	0.0003
2	1.9644	1.9235	1.9238	1.9238	1.9237	0.0002
3	1.9663	1.9229	1.9235	1.9236	1.9233	0.0004
4	1.9673	1.9100	1.9105	1.9106	1.9104	0.0003

Samples 1 through 3 were immersed in the solution while sample 4 acted as a control and was left separated inside the hood. The initial and final pH's and conductivities of the solutions were recorded at room temperature. Aliquots of the solution were taken at day 1, day 5 and day 9 to measure the pH and conductivity at room temperature. Table 7 lists the pH and conductivities measured during the duration of the test.

Table 7
pH and conductivity measurements of Solution 5 during immersion test

Measurements	Initial	Water samples (20 mL approx.)			Final
		1st day	5th day	9th day	
pH	4.89	5.21	5.55	5.67	5.81
Conductivity, µS/cm	97.0	94.1	99.7	102.3	105.2

Figure 11 shows the specimens after the test. The three samples that were immersed showed rust spots, but other than that the samples were relatively similar than before immersion. The rust appears to be from iron impurities that were present in the cladding and may have been corroded by the off-normal water condition. The samples appear darker than initial pictures (Figure 10), but that is due to lighting conditions at the time the pictures were taken. Table 8 shows the weight obtained post-immersion and after nitric acid rinsing and vacuum drying in triplicate to record weight changes.

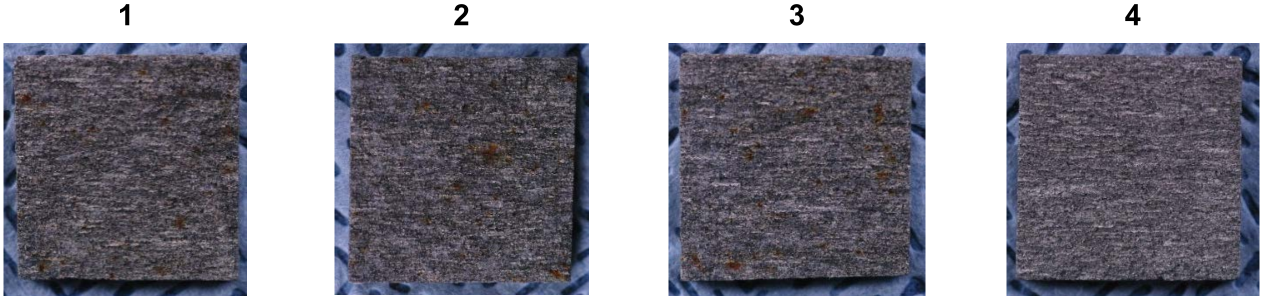


Figure 11: Pictures of Boral® coupons with one face de-clad after immersion

Table 8
Weight of coupons post immersion and weight change results

Samples	Weight post Immersion, g	Post-treatment weight after immersion (in triplicate), g			Average weight, g	Standard deviation, g	Weight change, mg
1	1.8750	1.8347	1.8354	1.8349	1.8350	0.0004	3.4
2	1.9732	1.9272	1.9277	1.9277	1.9275	0.0003	3.8
3	1.9623	1.9279	1.9280	1.9277	1.9279	0.0002	4.5
4	1.9175	1.9095	1.9095	1.9085	1.9092	0.0006	-1.2

During the test, the coupons did not show signs of particle dislocation or loss. Even after rinsing several times, in 5 minutes intervals with nitric acid, particles remained visually intact in the core. There was a small weight gain observed in the samples immersed. A possible explanation is that water may be absorbed into the core porous structure aided by immersion at almost water boiling conditions, in which drying at maximum temperature of 240 °C (464 °F) in a vacuum oven for up to 18 hours may not be sufficient time and temperature to remove. In comparison, the control sample (i.e., unexposed) exhibited slight weight loss (reflected in table by a negative sign) due to cleaning with nitric acid and/or measurement uncertainty. Based on the small weight gains obtained, it can be concluded with confidence that there was no boron loss after exposure for 12 days at 98 °C (208 °F) in any of the samples.

CONCLUSIONS

Electrochemical experiments performed on cladding and core components of Boral® showed an increase in corrosion rate with temperature from 25 to 98 °C (77 to 208 °F). The testing in the nominal and base simulants showed similar corrosion rates but testing in the off-normal simulants resulted in corrosion rates a factor of 1.9 times higher by comparison. For the exposed core material surface, corrosion rates ranging from 0.246 to 0.505 mm/yr (9.7 to 19.9 mpy) were obtained compared to 0.022 to 0.185 mm/yr (0.85 to 7.3 mpy) obtained for freshly ground cladding surfaces at 75 °C (77 °F) and 98 ºC (208 °F). These corrosion rates are representative of an oxide-free surface and are expected to decrease over time with the formation and growth of an oxide layer that protects the material from further corrosion. "Aged" oxide experiments were performed with increasing immersion times while maintaining good water quality (conductivity less than 12 μS/cm). The results showed that corrosion rates significantly decreased with time for PWR and BWR base simulants and after four weeks, the corrosion rate was approximately 0.002 mm/yr (0.08 mpy).

Immersion testing to measure specimen mass loss verified the electrochemical tests. The electrochemical testing conditions that showed the highest corrosion rate (simulant 5-PWR off-normal at 98 °C (208 °F), 0.185 mm/yr (7.3 mpy)) was selected as the condition to perform the immersion test for 12 days. After, 12 days, there was no apparent loss in boron carbide from the exposed core (no significant mass loss); the only observed change was the formation of rust spots inferring that some iron contaminants may have corroded. The results indicate that the Boral® core would not corrode significantly even under off-normal water chemistry and temperature conditions for up to well over a week of exposure.

DISCLAIMER

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