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ALUMINUM OXIDE FILM THICKNESS
AND EMITTANCE (U)

By

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SAVANNAH RIVER LABORATORY, AIKEN, SC 29808

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EXECUTIVE SUMMARY

Aluminum reactor components which are not actively cooled could be subjected to high temperatures due to gamma heating after the core coolant level dropped during the ECS phase of a hypothetical LOCA event. Radiative heat transfer is the dominant heat transfer process in this scenario and therefore the emittance of these components is of interest. Of particular interest are the safety rod thimbles and Mark 60B blanket assemblies; for the K Reactor, these components have been exposed to low temperature ($< 55^{\circ}\text{C}$) moderator for approximately 1 year.

The average moderator temperature was assumed to be 30°C . The aluminum oxide film thickness at this temperature, after one year of exposure, is predicted to be $6.4\text{ }\mu\text{m} \pm 10\%$; this value is insensitive to exposure time. Dehydration of the film during the gamma heating accident would result in a film thickness of $6.0\text{ }\mu\text{m} \pm 11\%$.

The total hemispherical emittance for this film thickness ($f = 6\text{ }\mu\text{m}$) can be expressed as:

$$\epsilon_h(f=6\mu\text{m}, T) = (0.887) [1.492 - 2.886 \times 10^{-3}(T) + 3.047 \times 10^{-6}(T^2) - 1.18 \times 10^{-9}(T^3)]$$

where T is temperature in degrees Kelvin. The total hemispherical emittance is predicted to be 0.69 at 96°C , and decreases to 0.45 at 600°C . A one-sigma uncertainty of 11% is recommended for the total hemispherical emittance expression given above.

Some phenomena which would tend to yield thicker oxide films in the reactor environment relative to those obtained under experimental conditions were neglected and the predicted film thickness values are therefore conservative. The emittance values predicted for a given film thickness are also conservative. The conservativisms inherent in the predicted emittance are particularly relevant for uncertainty analysis of temperatures generated using these values.

1.0 INTRODUCTION

Aluminum reactor components which are not actively cooled could be subjected to high temperatures due to gamma heating after the core coolant level dropped during the ECS phase of a hypothetical LOCA event. Radiative heat transfer is the dominant heat transfer process in this scenario and therefore the emittance of these components is of interest. Of particular interest are the safety rod thimbles and Mark 60B blanket assemblies; for the K Reactor, these components have been exposed to low temperature ($\approx 30^{\circ}\text{C}$ avg. and 55°C max.) moderator for approximately 1 year.

This report summarizes the available literature on: (1) low temperature ($< 100^{\circ}\text{C}$) aluminum and aluminum alloy corrosion in distilled and/or deionized water, and (2) aluminum oxide film emittance as a function of temperature and film thickness. It is emphasized that this report is not intended to provide a complete and detailed description of these phenomena. Rather, the intent is to provide estimated values of film thickness and emittance for engineering analyses. Based on the literature data, recommended values for aluminum oxide film thickness and emittance under conditions of interest are developed. The uncertainties in these values are also evaluated. The approaches employed in this evaluation ensure conservatism in the resulting film thickness and emittance values.

Ondrejcin (1991) provided an initial evaluation of aluminum oxide film thickness and emittance. The results developed herein are based on additional literature data, particularly for aqueous corrosion at low temperatures ($< 50^{\circ}\text{C}$), and are recommended for use in the gamma heating accident thermal analysis.

2.0 ALUMINUM OXIDATION & FILM THICKNESS

Aluminum oxide film thickness data for the materials and conditions of interest in this evaluation have not been reported in the literature. Aluminum alloy data have been reported for higher temperatures and the exposure times of interest, and high-purity aluminum data are available in the temperature range of interest for short exposure times. These data are employed to generate predicted film thickness values over a range of temperatures and exposure times. The effects of variations in the corrosion environment are addressed to justify the application of the literature data to SRS reactor moderator conditions, and applicable data from SRS reactor components are compared to the predicted film thickness values. The uncertainty in the predicted film thickness values is assessed. The response of oxide films to the conditions expected during the gamma heating accident is also discussed. Lastly, a set of recommended film thickness values are presented.

2.1 Materials and Conditions of Interest

The safety rod thimbles and Mark 60B cladding are constructed of aluminum alloys Al-6063 and Al-1100, respectively (SRS 1977 and SRS 1983). The nominal composition and composition limits for the commercial and SRS reactor grades of these alloys are essentially the same (SRS 1989a). The reactor grade specifications are more restrictive on minor alloying elements which are strong neutron absorbers or yield activation products with high gamma decay energies (B, Cd, Co, Li and Zn); these differences are irrelevant with respect to corrosion behavior.

The thimbles and Mark 60B assemblies were charged to K Reactor in August and December of 1990, respectively. The Mark 60B assemblies are limited to 4 cycles of exposure (Ward 1979), which corresponds to approximately 4 years for a Mark 22 reactor charge at 30 to 50% of historical power (WSRC 1989). Aluminum components are replaced every 3 to 5 years of operation. Thus, exposure times on the order of 1 to 5 years are of interest.

Since the thimbles have been charged, the moderator temperature has been approximately 30°C, with increases up to 55°C for very short periods (Hovis 1991). For the purposes of this evaluation, a moderator temperature of 30°C was employed. The moderator chemistry

specifications are given in Table 1. In general, these limits have been met over the period of interest, August 1990 to the present (Stinson 1990).

2.2 General Low Temperature Aluminum Aqueous Corrosion ($T < 100^{\circ}\text{C}$)

The oxide present on aluminum surfaces in air is a thin amorphous film, typically less than a few hundred angstroms. Once exposed to water, the air-formed film dissolves and aluminum hydroxide precipitates. The initial film is composed of two layers: a thin amorphous barrier layer ($\approx 10 \text{ \AA}$), and a thicker outer layer of pseudoboehmite (metastable aluminum hydroxide). The outer pseudoboehmite layer transforms over time to boehmite ($\alpha\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$). Below approximately 90°C , bayerite ($\beta\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) crystallizes on top of the pseudoboehmite or boehmite layer. Above this temperature, bayerite is not formed and only the boehmite layer is present. The time required to nucleate and grow the bayerite layer decreases with decreasing temperature. Alwitt (1974) observed bayerite formation at 40°C for a 10 hour exposure, and reported that bayerite did not nucleate at all over this time period at 50 to 100°C . Hart (1957) reported that for a 1 week exposure, a solid bayerite layer was formed at 20 and 40°C , some bayerite growth occurred at 60°C , and that only a few bayerite crystals nucleated at 70 to 80°C . Draley and Ruther (1956b) observed bayerite formation up to 90°C for a 1 month exposure period, but at 100°C only boehmite was present. Thus, for the exposure periods of interest in this evaluation, a mixed film (boehmite and bayerite layers) would be expected at or below 90°C , and a uniform boehmite film would be expected above 90°C .

For exposure times in excess of a few weeks, aluminum oxide film growth generally follows a logarithmic rate law. Film formation kinetics for times less than a few weeks are not of practical interest in this evaluation; however, most of the aluminum aqueous corrosion literature deals primarily with this short term kinetic behavior. Descriptions of film growth for short exposure times over a range of temperatures are provided by Hart (1957), Altenpohl (1962), Vedder and Vermilyea (1969), Alwitt (1974). Alwitt (1976) provides an overview of the general features of aluminum oxidation, oxide film structure, and film growth kinetics.

Pure aluminum (e.g. $> 99.5\%$ Al) is subject to significant grain boundary attack above approximately 40°C in distilled water. Altenpohl (1961) observed that the weight gain in boiling distilled water after 8 days was approximately the same for 99.45 and 99.85% pure

Al, but that for 99.99% pure Al was approximately twice as large, and the weight gain for 99.992% pure Al was almost 4 times as large. Severe grain boundary attack of 99.99% pure Al in boiling distilled water was also observed by Carlsen (1957). Kawasaki et al. (1962) reported that at 50°C, 99.99% pure Al was subject to intergranular attack only for a limited period; after a few days of exposure, a bayerite film completely covered the surface and the attack ceased. Conversely, a bayerite film was not formed at 90°C and intergranular attack continued throughout the 10 day exposure period. Hart (1957) found that over a 1 week exposure period, 99.995% pure Al was subject to severe grain boundary attack above 60°C, and limited attack down to 40°C. As with the study performed by Kawasaki et al. (1962), the attack observed at 40°C was apparently limited by the formation of an adherent bayerite film. In cases where significant grain boundary attack occurs, much of the oxidation does not take place uniformly across the surface, and the resulting weight change data cannot be used to predict film thickness. At or below approximately 40°C, grain boundary attack is very limited and the aqueous corrosion behavior of pure aluminum and aluminum alloys are similar.

Assuming that no corrosion product or aluminum is lost to the corroding medium and that the oxide film is uniform, then film mass may be computed directly from either weight gain (weight of specimen and oxide film) or loss (weight of specimen after removal of oxide film) measurements. This is generally the case below 70°C in stagnant systems and below 50°C in high flow rate systems. At higher temperatures, loss of corrosion product and/or aluminium requires that either (1) the film weight be measured directly (by stripping it off), or (2) both weight gain and loss data be available (film weight = weight gain + weight loss). If the film is of uniform composition and non-porous, then the film thickness may be computed directly from weight change data. The conversion factors for computing film thickness from weight change data under these assumptions are given in Table 2. The aluminum oxide and aluminum densities used to compute these conversion factors were taken from Newsome et al. (1960) and Icropera and DeWitt (1981). In reality, aluminum oxide films formed in aqueous environments are rarely of uniform composition, are often porous, and generally have some amount of water trapped in the film. The effect of non-uniform composition can be accounted for by estimating the fraction of the film mass due to each phase and adjusting the conversion factors accordingly; this does not introduce large errors since, as shown in Table 2, the conversion factors are not greatly different for the films of interest in this evaluation. The effect of porosity and water content are both

conservative (e.g. would lead to an underprediction of film thickness), as discussed in Sections 2.7 and 2.8.

2.3 Aluminum Alloys

The aqueous corrosion behavior of a range of aluminum alloys is similar (Dillon 1959). For the purposes of this evaluation, it was assumed that the oxide film thickness for Al-1100 and Al-6063 would be essentially the same.

The bulk of aluminum alloy corrosion data available for distilled water at temperatures less than 100°C are from a series of Al-1100 corrosion studies conducted at Argonne National Laboratory (Draley and Ruther 1956a, Draley and Ruther 1956b, Draley 1960, Draley et al. 1963, Draley et al. 1967, Mori and Draley 1967); the most directly applicable of these data are given in Draley et al. (1967). These experiments were conducted at 50, 70 and 95°C for exposures of up to 45 days. Distilled deionized water with a pH of 6.5 ± 0.2 and specific resistance of 1.4 ± 0.2 M Ω -cm was employed. Four specimens were loaded into a test chamber and a small flow rate of fresh water was continually fed through the chamber to maintain water chemistry; 18 cm³/min for the first 4 days, then 8 cm³/min for the remainder of the test. Both oxygen and helium saturated water were employed to examine the effect of oxygen concentration. The helium saturated water had an oxygen (O₂) concentration of 0.31-0.50 mg/liter for the 50 and 70°C tests, and 0.43-1.00 mg/liter for the 95°C tests; since the SRS reactor O₂ concentration is specified to be between 0.5 and 2 mg/liter, the helium saturated data are the most applicable. Weight gain measurements were taken by periodically removing and weighing the specimens, and weight loss data were based upon specimen dimension measurements made using an eddy current gauge. The weight loss data were logarithmic after 1 week of exposure. Very little oxide dissolution was observed at 50 or 70°C, and therefore the weight gain data follow the same trend. At 95°C, significant oxide and/or aluminum dissolution took place. The weight loss observed in these experiments can be expressed as:

$$W = A + B \cdot \ln(t) \quad (1)$$

where: W = Weight gain or loss (mg/dm²),
t = Exposure time (days), and
A, B = Empirical coefficients.

This expression implies that the coefficient 'A' is the weight change after 1 day of exposure (e.g. $\ln(1) = 0$). However, the logarithmic rate is not established until several days of

exposure have been accumulated and this coefficient is the extrapolated value at 1 day. The average value and relative standard deviation (based on 4 specimens for each test condition) of these coefficients are given in Table 3. Note that the data for helium and oxygen saturated water are similar. At 50 and 70°C, the specimens in helium saturated water had a slightly larger initial thickness and a slightly smaller growth rate, although for practical purposes the two data sets are identical. Although the trend is the same at 95°C, the differences between the data sets are larger; however, the predicted weight gains at 95°C for helium and oxygen saturated water are the same for 1 year of exposure. While the coefficients given in Table 3 were derived based on a 45 day exposure, the data reported by Draley et al. (1963) for oxygen saturated water at 70°C and exposure times of up to 500 days are in good agreement, so that these values may be employed for longer exposure periods.

The films formed at 50 and 70°C are expected to have both boehmite and bayerite layers. The data of Alwitt and Archibald (1973) and Alwitt (1974) suggest a boehmite film thickness of 2.5 to 3 μm . It therefore is reasonable to average the weight change conversion factors for boehmite and bayerite in order to compute film thickness for these data (e.g. 0.094 μm per mg/dm^2). At 95°C, bayerite film formation is not expected and the conversion factor for boehmite may be used directly. The resulting logarithmic film thickness expression is written as:

$$f = a + b \cdot \ln(t) \quad (2)$$

where: f = Film thickness (μm),
 t = Exposure time (days), and
 a, b = Empirical coefficients.

As with eqn.(1), the coefficient 'a' represents the extrapolated film thickness after 1 day of exposure. The coefficients based on the 50, 70 and 95°C data of Draley et al. (1967) are given in Table 4.

Takahashi et al. (1990) examined the corrosion of 99.99% pure Al in boiling distilled water and found that essentially no aluminum was lost to the aqueous environment for exposure periods of up to 1 hour. The 95°C data from Draley et al. (1967) show little oxide dissolution initially, but the fraction of Al lost to the solution increased with time and reached 15% after 45 days of exposure. As discussed earlier, the formation of a bayerite film essentially stops dissolution. This is consistent with physical expectations since the solubility of bayerite is much less than that of boehmite; at 25°C, the solubility of boehmite

is approximately a factor of 30 greater (Deltombe and Pourbaix 1958). Intercrystalline cracking of the outer bayerite film has been observed in a number of experiments (Hoxie 1960a and 1960b, Kawasaki et al. 1962). Cracking and subsequent healing of the bayerite film has been suggested as the primary film growth mechanism (Draley et al. 1963).

Hoxie and Post (1962) exposed Al-1100 specimens to boiling, neutral, deionized water for times up to 1000 hours (≈ 42 days). They report film thickness values based on weight gain data; they do not provide detailed information on their method of converting weight gain to film thickness. The correlation given below is based upon their best-estimate film thickness curve at 10 and 42 days (1.1 and 1.7 μm):

$$f = 0.24 + 0.39 \cdot \ln(t) \quad (3)$$

As before, 'f' is the film thickness in μm and 't' is exposure time in days. The film thickness at 10 days (1.1 μm) is identical to that derived from the Draley et al. (1967) data. However, the film thickness growth rate is considerably larger so that the thickness predicted by eqn.(3) after 1 year of exposure is 42% larger than that based on the ANL data (eqn.(2) and Table 4). While this difference in growth rates was not expected, it is not physically inconsistent; a pure boehmite film is expected at both 95 and 100°C and the temperature increase may enhance diffusion to the degree required to account for the differences in the growth rates. It is also possible that the disagreement is due to differences in the conversion between weight gain and film thickness.

Cessna et al. (1964) report a 14 mg/dm² weight loss for Al-3003 exposed for 200 hours to distilled, aerated water at 77°C; at this temperature, bayerite would not be expected to nucleate inside the 200 hour exposure period. The corresponding uniform boehmite film thickness is 1.0 μm . This is slightly less than that based on the data of Hoxie and Post (1962) or Draley et al. (1967) for a 10 day exposure period (1.1 μm). It is considerably less than the 70°C values of Draley et al. (1967). As mentioned above, a boehmite film is expected, and therefore the film growth kinetics should be similar to those at higher temperatures. The data are therefore consistent with physical expectations.

2.4 Pure Aluminum

The available data for the low-temperature aqueous corrosion of high-purity aluminum in distilled and/or deionized water are summarized in Table 5. As mentioned earlier, high-

purity aluminum (>99.5%) is subject to intergranular attack at temperatures in excess of approximately 40°C. As a result, it is not possible to estimate film thickness values based on weight change data above this temperature. Two of data sets in Table 5 can, however, be used in this evaluation.

Alwitt (1974) reports a 88 mg/dm² weight gain for a 99.99% pure Al specimen exposed to distilled water at 40°C for 100 hours. The resulting film was composed of a boehmite layer approximately 2.5 to 3 μm thick and an outer bayerite layer (Alwitt and Archibald 1973 and Alwitt 1974). The conversion from Alwitt's weight gain data to film thickness is insensitive to the presumed film structure since the conversion factors for boehmite and bayerite are essentially the same (0.0604 vs. 0.0605). The calculated film thickness for a 88 mg/dm² weight gain is 5.3 μm.

Hart (1957) reports weight gain data for 99.995% pure Al in distilled water (2.5 MΩ-cm) over a 20 to 80°C temperature range for exposure periods of up to a few weeks. These measurements were made in both oxygen-rich (14-32 ppm) and oxygen-depleted (1.6 ppm) water. The oxygen-depleted data are most applicable to SRS moderator (0.5-2 ppm), although the data for both conditions are similar. The data at 20°C should be directly applicable since no intergranular attack was observed; the calculated film thickness at 20°C after 2 weeks of exposure is 7.0 μm. Hart reports a limited amount of intergranular attack at 40°C, so that these data are somewhat suspect. The calculated film thickness at 40°C after 1 week of exposure is 9.1 μm; this is significantly larger than the thickness based upon Alwitt's (1974) data (5.3 μm). It is probable that this difference is due to the intergranular attack observed by Hart. Altenpohl (1961) observed that the weight gain in boiling distilled water after 8 days of exposure for 99.992% pure Al was approximately 50% larger than that for 99.99% pure Al. The weight gain reported by Altenpohl may be exaggerated by experimental uncertainty, however the corrosion of super-purity aluminum is widely reported to be extremely sensitive to compositional variations. Based on these observations and the purity of the samples employed by Hart (99.995%) and Alwitt (99.99%), the increased weight gain reported by Hart at 40°C is reasonable. In any case, it is conservative to use the film thickness based upon Alwitt's data.

No long-term film growth kinetic data was identified for oxide films formed on high-purity aluminum at or below 40°C. The exposure periods employed by Alwitt (1974) and Hart (1957) were not sufficient to establish long-term growth rates. In the absence of

experimental data, it is a reasonable approximation to utilize the growth rate derived from the 50°C ANL data. The films formed at lower temperatures should have a slower growth rate since their initial thickness is larger. The growth rates were taken to be the product of the growth rate based on the 50°C ANL data and the ratio of the initial film thickness values [e.g. growth rate at 20°C = (growth rate at 50°C)*(initial thickness at 50°C)/(initial thickness at 20°C)]. The coefficients for the film thickness growth rate expression, eqn.(2), are given in Table 4 for 20 and 40°C.

2.5 Corrosion Environment Variables

Variations in the aqueous corrosion environment can impact the thickness of aluminum oxide films. The main corrosion environment variables (pH, corrosion product concentration, ionic species, water velocity, and radiation) are discussed below in terms of their impact on aluminum corrosion and the thickness of the resulting aluminum oxide film. The literature data does not offer a complete description of the role played in aluminum corrosion by these variables; it is possible, however, to deduce the basic trends.

2.5.1 pH

Troutner (1959) performed a large number of aluminum corrosion experiments in distilled water at 92°C for 2 week exposure periods over a pH range from 3.5 to 10. His data indicate that corrosion, based on weight loss measurements, appears to be only weakly dependent on pH over a range from approximately 4.5 to 7. Troutner attributed the dependence on pH to changes in solubility of the bulk oxide film. Outside this range, the solubility of boehmite increases substantially and, as a result, the measured weight loss increases. The increased solubility of the oxide prevents the formation of a protective film. In terms of film thickness, this implies that films formed outside the range from 4.5 to 7 may be comparatively thin. Draley and Ruther (1956b) report a minimum in aluminum corrosion at a pH of 6.5 at 50°C, and that the pH giving the minimum corrosion rate decreases with increasing temperature. At 50°C, their data show a nearly constant corrosion rate for pH values from 5 to 8; this is reasonably consistent with the 4.5 to 7 range in Troutner's (1959) data at 92°C. Alwitt (1976) reports little effect of pH on corrosion rates between 4 and 10 at 100°C. Vedder and Vermilyea (1969) report that pH has little effect on initial corrosion rates for pH values less than 10.

The solubility diagram constructed by Deltombe and Pourbaix (1958) for 25°C gives a minimum solubility at a pH of approximately 5.1; the Pourbaix diagram for bayerite indicates stability in the pH range from 4 to 8.5 at 25°C. Alwitt (1976) refers to data which give an oxide stability pH range of 4-10 at 25°C, and 3-7 at 100°C. Huddle (1956) concluded that a range of pH from 4-8 would have little effect on aluminum oxide dissolution at 100°C.

The experimental data employed in this evaluation were generated using distilled water (pH $\approx$ 6.5). The operating limit for moderator pD is 5 to 5.2 and the technical standard requires that pD be maintained between 4.5 and 8. The SANSO data (SRS 1989b) from August of 1990 through September of 1991 show that pH (inline measurements) has been maintained between 4 and 6.5 (Stinson 1990), the corresponding pD range is 4.4 to 6.9 (Baumann and Ondrejcin 1990). Based on the experimental data and evaluations discussed above, pH variations in this range should have a negligible effect on corrosion and the experimental corrosion data in distilled water should be directly applicable to moderator conditions.

2.5.2 Corrosion Product Concentration

Increasing aluminum hydroxide or aluminum ion concentration in the aqueous medium should increase the rate at which film formation occurs, suppress film dissolution, and lead to a thicker film; the available experimental data support this conclusion.

Draley et al. (1963) showed that increasing the water refreshment rate decreased the weight loss of Al-1100 at 70°C and attributed this effect to the concentration of corrosion products in the water; higher corrosion product concentrations led to more severe corrosion. Their data show that very low refreshment rates gave weight changes 20% larger than those obtained at higher refreshment rates. Increased corrosion was also observed when the number of specimens in the test chamber was increased. The main effect was on the initial amount of corrosion; the corrosion rate appeared to be insensitive to corrosion product concentration for exposure periods ranging from 10 to 100 days. This is consistent with physical expectations; the initial stages of film formation are governed by the nucleation and spread of the oxide film. Increased corrosion product concentrations in the water should increase the rate at which these processes take place and yield a larger initial film thickness. Altenpohl (1962) concluded that films developed in the presence of dissolved hydroxides are formed more quickly, but are less protective than films formed in "clean" water. Once

the film covers the surface and thickens, the effect of corrosion product concentration should decrease. However, film growth may still be enhanced by high corrosion product concentrations; Kawasaki et al. (1962) observed that bayerite films were able to grow at 70°C without corrosion of the aluminum substrate via precipitation of aluminum oxide from the water.

The presence of turbidity in the reactor moderator demonstrates that the aluminum hydroxide concentration is at or near saturation. Bayerite, boehmite, and gibbsite have all been identified as components in reactor turbidity (Hoxie 1960a and 1960b). The data discussed above indicate that films formed in the reactor should have a larger initial thickness than predicted based on the experimental data employed in this evaluation. In addition, since bayerite films would be expected at the temperatures of interest and these films have been shown to grow via aluminum oxide precipitation, it is expected that film growth rate would be increased as well.

Hoxie (1960a and 1960b) report that an Al-Li target slug irradiated in C Reactor developed a 0.50 mil ($\approx 13 \mu\text{m}$) bayerite film. The temperature at which the film was formed was not reported; however a bulk moderator temperature of 50 to 70°C is expected. In addition, Hoxie does not give any information pertaining to the method employed to measure film thickness or the uncertainty associated with the reported value. The film thickness correlation based upon the ANL data give a film thickness of $4.4 \mu\text{m}$ for one year of exposure at 70°C. Some of the difference in these film thickness values could be due to radiation or moderator flow rate, as discussed below, but it suggests that the aluminum hydroxide concentration in the moderator enhances film growth.

2.5.3 Ionic Species Concentration

Troutner (1959) examined the effect of a number of ions at concentrations up to 100 ppm on aluminum corrosion at 92°C for exposure periods up to 2 weeks. He reports that most of the ions had no effect beyond that expected due to the change in solution pH. Only phosphate and citrate ions were observed to have a direct effect on the corrosion rate, with phosphate inhibiting corrosion and citrate enhancing it. Troutner attributed these effects to a modification of the oxide film in the case of phosphate ions, and to complexing of aluminum by citrate. Troutner reported that chloride, nitrate, sulfate, and peroxide ions at concentrations up to 100 ppm had no effect on corrosion. Experiments conducted by Vermilyea and Vedder (1970) indicated that phosphate and silicate ions at a concentration of

10^{-3} M ($\approx$ 100 ppm) strongly inhibited aluminum corrosion at 100°C by preventing hydroxide formation. Chlorate, chloride, nitrate and nitrite ions at this concentration were reported to have little influence on corrosion rate; sulfate and oxalate ions had a moderate inhibiting effect. Takahashi et al. (1990) also examined the effects of silicate, phosphate, and citrate ions on aluminum corrosion.

The concentration limits for the major ionic species in the moderator are given in Table 1. At these concentration levels (< 1 ppm), none of these species are expected to have a significant effect on aluminum. Ions not listed on Table 1 may be present in the moderator, but at sufficiently low concentrations so as not to exert a significant influence on corrosion.

2.5.4 Water Velocity

Kawasaki (1962) found that the films formed in high flow rate systems were both thicker and less protective than those formed at lower flow rates. For example, a flow rate of 6 m/s gave an oxide film on Al-1100 at 70°C which was almost three times as thick as that formed at a flow rate of 0.07 m/s, while the total weight loss at 6 m/s was approximately 8 times that at 0.07 m/s. Dillon (1959) reported that the oxide films formed in flowing water were more porous and hence less protective than those formed in static systems. Troutner (1959) attributed the lower corrosion rate in static systems to the increased concentration of aluminum ions near the oxide surface suppressing film dissolution. Other literature data support these conclusions.

The experimental data employed in this evaluation were generated in static or very low flow rate systems; the films formed in flowing moderator should therefore be thicker than predicted based on these data. The thick oxide film formed on C Reactor target slug discussed in Section 2.5.2 may be partially due to the presence of flowing water.

2.5.5 Radiation Fields

Although the effect of radiation on aluminum oxide films was not examined in this evaluation since the components of interest are unirradiated at the current time, it is expected that the presence of radiation would tend to increase oxide film thickness. The thick oxide film formed on C Reactor target slug discussed in Section 2.5.2 may be partially due to the radiation field inside the reactor core. This effect could play a role in film growth kinetics once K Reactor is restarted and the aluminum components are subject to a radiation field.

2.5.6 Net Effect of Corrosion Environment Variables

The discussions given above demonstrate that pH and ionic species concentration should not influence the film thickness corrosion rates in the moderator relative to the experimental data employed in this evaluation. The aluminum hydroxide concentrations, water velocity, and radiation fields present in the SRS reactors would all tend to give thicker oxide films than those predicted based upon the experimental data employed in this evaluation. The combined magnitude of these effects is difficult to predict.

2.6 SRS Low-Temperature Film Thickness Data

Two sets of film thickness measurements have been made at SRS which are directly applicable to this evaluation (Caskey and DeWitt 1990). Mark 14 fuel assemblies from the Process Development Pile (PDP), a zero-power reactor physics facility, were included in the P-11 charge in 1972 (Temple 1972). The tubes had been immersed approximately 100 times in 20-22°C water for a total exposure time of 250 hours over a 16 month period; the pH and conductivity of the water were 6.3-7.3 and 1.2-4.0 $\mu\text{mho/cm}$, respectively (Ondrejcin 1972). The tubes were dried on 4 occasions by (1) circulating dried ambient air over the tubes for 16 hours, or (2) by circulating 120°C air for 8 hours followed by 16 hours in dried circulating ambient air. Otherwise, the tubes were stored in 100% relative humidity air. Film thickness measurements were performed on 4 fuel tubes at 3 axial locations and 2 circumferential positions (24 measurements). The reported values ranged from 1.3 to 8.9 μm (Ondrejcin 1972). The average and relative standard deviation for these measurements is $5.3 \mu\text{m} \pm 38\%$. The large uncertainty is partially due to the use of a measuring device with an accuracy of approximately $\pm 2 \mu\text{m}$. Draley et al. (1963) demonstrated that, for short exposure times, withdrawing aluminum specimens from a water environment and reinserting them decreased the resulting film thickness relative to the value achieved if the specimens were immersed continually for an equivalent exposure time. Presumably, this is because the film must re-hydrate upon exposure prior to accumulating appreciable growth. Thus, the film thickness on the fuel tubes should be less than that achieved with 250 hours of continuous exposure. The film thickness correlation based upon the data from Hart (1957) for high-purity aluminum in 20°C distilled water gives a thickness of 7.5 μm for 250 hours of continuous exposure, which is 42% larger than the average value measured by Ondrejcin (1972). This level of agreement is

acceptable given the discontinuous nature of the exposure accumulated by the Mark 14 fuel assemblies.

Stanaland and Eberhard (1985) examined nine Mark 31A target slugs clad with Al-1100 which had been exposed to shutdown conditions in L Reactor for 2 years. They report oxide film thickness values of 0.1-0.2 mils (2.5-5.1 μm); no data are given on the experimental technique employed or the uncertainties associated with these data. Presumably, the moderator temperature during this L Reactor shutdown period was similar to that during the current K Reactor shutdown (e.g. approximately 30°C). Interpolating between the predicted film thickness at 20 and 40°C gives a film thickness of 6.4 μm for a 2 year exposure. This level of agreement is acceptable in the absence of accurate information on the moderator temperature during the L Reactor shutdown and the measurement technique and uncertainties associated with the data reported by Stanaland and Eberhard (1985).

Thus, the film thickness measurements on the Mark 14 and 31A assembly cladding are in general agreement with the predictions of the 20 and 40°C film thickness correlations and serve to increase confidence in the methodologies employed.

2.7 Uncertainty Evaluation

There are three main sources of uncertainty in the aluminum oxide film thickness relationships developed here: variance in corrosion rates under a specific set of corrosion conditions, differences between the corrosion conditions of interest and those employed in the experiments, and relationship between weight change and film thickness.

The uncertainty introduced by variance in corrosion rates under a specific set of corrosion conditions may be addressed by considering the weight loss data of Draley et al. (1967). The total relative uncertainty in weight loss values computed using eqn.(1) can be expressed as (Tsoulfanidis 1983):

$$\sigma_{\frac{W}{W}}^r = \frac{\sigma_{\frac{W}{W}}^a}{\frac{W}{W}} = \frac{1}{\frac{W}{W}} \sqrt{(\bar{a} \sigma_a^2 + [\ln(t)]^2 (\bar{b} \sigma_b^2)} \quad (4)$$

where σ^a and σ^r are the absolute and relative standard deviations and the other symbols have the same meaning as in eqn.(1). Based on the mean and standard deviation values

given in Table 3, the relative standard deviation in weight loss for a 1 year exposure in helium and oxygen saturated water at 50-70°C computed using this approach ranges from 1.8 to 4.5%. As mentioned earlier, the weight change data reported in Draley (1963) for exposure periods of up to 500 days are in general agreement with those given in Table 3, which are based on exposure periods of less than 45 days. Draley (1963) report that the weight change for specimens exposed to the same test conditions may vary by as much as 10%, which implies a standard deviation on the order of 5%. The 95°C weight loss data of Draley et al. (1967) give a standard deviation of approximately 10%. The low temperature data of Hart (1957) also have an uncertainty of about 10%. Based on these considerations, an uncertainty of 10% appears reasonable.

As discussed in Section 2.5, any differences between the corrosion conditions of interest and those employed in the experiments either will have a negligible effect or increase film thickness. Therefore, it is not appropriate to consider these effects in assigning an uncertainty to the predicted film thickness.

The conversion between the experimental weight change data and film thickness yields bounding thickness values since credit was not taken for porosity effects. That is, any porosity in the film would result in a larger film thickness for a given weight change. Similarly, the water content of the film need not be considered in deriving the uncertainty since the experimental specimens were dried prior to measurement. Thus, the computed film thickness values are bounding and it is not appropriate to consider these effects in deriving their uncertainty.

The total uncertainty associated with the predicted film thickness values is therefore taken to be 10%.

2.8 Response of Film to Gamma Heating Accident Conditions

The recommended film thickness values correspond to the film as it exists in the aqueous environment. Under the conditions predicted for the gamma heating accident, the aluminum components would be in a steam environment; their temperature would increase up to a maximum, power-dependent, value within 15 to 30 minutes, and then slowly cool. The maximum temperatures of interest for the aluminum components in the gamma heating accident are 400 to 600°C. Extended exposure to these temperatures would dehydrate

bayerite or boehmite films and produce γ - Al_2O_3 . Two effects must be considered: phase changes of the film due to dehydration, and the reaction between aluminum and water trapped in the film or made available via dehydration.

Bayerite may decompose over a range from approximately 120 to 250°C to either boehmite or γ - Al_2O_3 (Newsome et al. 1960). Temperature increase rates in excess of 1°C/min and moist environments promote decomposition to boehmite; it is assumed that this decomposition path would be followed during the gamma heating accident. Boehmite decomposition to γ - Al_2O_3 can occur over a range of temperatures from approximately 200 to 500°C, the degree of decomposition depending primarily on the heating rate and time at temperature (Newsome et al. 1960). Kollie et al. (1991) observed partial dehydration of a boehmite film held for 4 hours at 204°C, and complete dehydration after 4 hours at 482°C. For the conditions predicted for the gamma heating accident, complete dehydration of the film would be expected. The room temperature densities of bayerite, boehmite, and γ - Al_2O_3 are 2.53, 3.01, and 3.2 gm/cm³ (Newsome et al. 1960); therefore phase changes upon dehydration will result in a contraction of the film. It is expected that this contraction will cause micro-cracking.

The water of hydration lost during decomposition of bayerite or boehmite can react with aluminum to produce additional oxide. Alwitt (1971a) observed that fully hydrated anodic aluminum oxide films only lost 40% of their water of hydration upon heating at 600°C for 2 hours; hydrated anodic aluminum oxide films are essentially equivalent to boehmite. Therefore, 60% of the water of hydration reacted with the aluminum substrate to produce additional Al_2O_3 . Bernard and Randall (1960) report that 1/3 to 1/2 of the water of hydration of boehmite films formed at 80 to 100°C reacts with additional aluminum when heated to 600°C for 1 hour. The reaction of water with aluminum will produce hydrogen gas. Since this occurs over a fairly short time, micro-cracks and gas bubbles will be formed in the resulting film.

To compute the thickness change expected during the gamma heating accident, it is assumed that complete dehydration occurs and that 1/2 of the water of hydration reacts with aluminum to form additional oxide. In addition, it is assumed that the resulting film develops a porosity of 10% as a result of micro-cracking and the development of hydrogen bubbles. A film composition of 1/2 bayerite and 1/2 boehmite was assumed in converting weight gain data to film thickness for exposures at or below 70°C. For consistency, this

same composition was assumed in calculating the film thickness response to dehydration. A net film thickness reduction of 6% is computed with the assumptions given above. The uncertainty in this value is estimated to be 1/2 the porosity correction (5%), so that the net film thickness reduction is $6\% \pm 0.3\%$.

2.9 Recommended Film Thickness Values

Table 4 gives coefficients for the logarithmic film thickness correlation at temperatures ranging from 20 to 100°C; a 10% uncertainty is assigned to the film thickness values computed using these coefficients. The initial film thickness values at 20 and 40°C are based on the high-purity aluminum data of Hart (1957) and Alwitt (1974), respectively; the growth rates at these temperatures are based on the 50°C data of Draley et al. (1967) and the ratio of the initial film thickness values (as discussed in Section 2.4). The coefficients given for 50, 70 and 95°C are based primarily on the data reported by Draley et al. (1967), but are supported by other ANL data as well (as discussed in Section 2.3). The significance of the growth rate differences at 95 and 100°C is discussed in Section 2.3.

The coefficients given in Table 4 are judged to be applicable for exposure times from a few weeks up to 5 years. The predicted film thickness values over this period are illustrated in Figure 1; the key data employed to derive the film thickness expressions at each temperature are noted in the legend. The resulting film thickness values are conservative since no credit was taken for the increased film thickness expected due to the high aluminum hydroxide concentration in the moderator, moderator flow, or radiation effects. Film thickness values at temperatures between those given in Table 4 should be computed by interpolation. The film thickness correlation for 30°C is therefore:

$$f = 6.0 + 0.068 \cdot \ln(t) \quad (5)$$

where 'f' is the film thickness in μm and 't' is exposure time in days. A 6% reduction in film thickness should be employed to account for dehydration during the gamma heating accident; the uncertainty in the film thickness reduction due to dehydration is estimated to be 5% (e.g. $6\% \pm 0.3\%$). The thickness of a film formed at 20°C and subsequently dehydrated would therefore be:

$$f = 0.94 \cdot [6.0 + 0.068 \cdot \ln(t)] \quad (6)$$

The net uncertainty in the film thickness after dehydration is the root-mean-square of the relative uncertainties in the hydrated film thickness and the film thickness reduction term (Tsoulfanidis 1983); this gives a net one-sigma uncertainty of 11% on film thickness. The film thickness predicted using eqn.(6) is illustrated in Figure 2; 2-sigma uncertainty bands are also given in the figure.

For the safety rod thimble and Mark 60B cladding, which were charged to the reactor in August and December of 1990, respectively, and have been exposed to moderator at an average temperature of 30°C, the oxide film thicknesses as of the end of November of 1991 are predicted to be 6.42 and 6.40 μm , respectively; these values are essentially identical since the oxide film grows extremely slowly after several weeks of exposure at this temperature. Accounting for dehydration gives a film thickness of 6.0 μm ($\pm 11\%$).

3.0 EMITTANCE OF ALUMINUM OXIDE FILMS

The total hemispherical emittance as a function of temperature is required to allow thermal analyses of aluminum reactor components under the conditions predicted for the gamma heating accident. Kollie et al. (1991) give total hemispherical emittance data for a 25 μm boehmite film as a function of temperature up to approximately 500°C. Brannon and Goldstein (1970) give total normal emittance data for an anodized aluminum oxide film at 96°C as a function of film thickness up to 86 μm . The dependence of emittance on temperature and thickness shown by these data sets are employed to construct a total hemispherical emittance correlation applicable to the oxide thickness and temperature range of interest.

3.1 *Dependence of Emittance on Temperature*

Kollie et al. (1991) measured the total hemispherical emittance of a 25 μm boehmite film before and after dehydration. The film was developed on an aluminum component of the TSR-II reactor at Oak Ridge National Laboratory over a 25 year period. As mentioned in Section 2.8, Kollie et al. report partial dehydration of the boehmite film after 4 hours at 204°C, and complete dehydration after 4 hours at 482°C. The uncertainty reported by Kollie et al. decreases from $\pm 4.8\%$ at 20°C down to $\pm 1.8\%$ at 500°C. They correlated the emittance data for the 25 μm boehmite film prior to dehydration as:

$$\epsilon_h(f=25\mu\text{m}, T) = 1.1808 - 9.75309 \times 10^{-4}(T) + 2.9687 \times 10^{-7}(T^2) \quad (7)$$

where: ϵ_h = Total hemispherical emittance,
f = Film thickness, and
T = Temperature (K).

The data employed to construct this fit extend up to 200°C, and agree with the values generated by the fit to within 1.6%. The emittance after complete dehydration of the oxide film was correlated by Kollie et al. as:

$$\epsilon_h(f=25\mu\text{m}, T) = 1.30779 - 1.83452 \times 10^{-3}(T) + 1.0950 \times 10^{-6}(T^2) \quad (8)$$

The data employed to construct this fit extend up to 500°C. The data and correlation predictions agree to within 0.7%. Kollie et al. (1991) report that the correlation agrees to within 3% with emittance data reported by Weaver (1963) for a 25 μm anodized aluminum

oxide film. The lower bound alumina emittance recommended by Touloukian and DeWitt (1970a) are slightly higher than the data employed to construct eqn.(8); this is physically consistent since a 25 μm alumina film on an aluminum substrate would be expected to have a slightly lower emittance than pure alumina. Equation (8) gives increasing emittance values beyond approximately 575°C; this trend is not in agreement with the bulk of the data given in Touloukian and DeWitt (1970a). Accordingly, the Kollie et al. correlation was modified by taking a linear extrapolation above 700 K. The resulting two-region fit for total hemispherical emittance is given below:

$$\epsilon_h(f=25\mu\text{m}, T) = \begin{array}{ll} 1.30779 - 1.83452 \times 10^{-3}(T) + 1.0950 \times 10^{-6}(T^2) & T < 700 \text{ K} \\ 0.77124 - 3.0152 \times 10^{-4}(T) & T \geq 700 \text{ K} \end{array} \quad (9)$$

These expressions were combined into a single third-order polynomial fit applicable to up to 600°C, given below:

$$\epsilon_h(f=25\mu\text{m}, T) = 1.492 - 2.886 \times 10^{-3}(T) + 3.047 \times 10^{-6}(T^2) - 1.18 \times 10^{-9}(T^3) \quad (10)$$

The relative standard deviation of eqn.(10) with respect to data generated every 10°C from 100 to 600°C using eqn.(9) is less than 0.2%, so that eqn.(10) may be employed directly without introducing significant error. Based on the uncertainty and standard deviation reported by Kollie et al. (1991), the agreement of their data with that reported by Weaver (1963), and the magnitude of the data relative to those recommended by Touloukian and DeWitt (1970a), a total uncertainty of 5% was assigned to eqn.(10). The values predicted by the correlations developed by Kollie et al. for the boehmite and dehydrated films are shown in Figure 3 along with values generated using eqn.(10). Since the data of Kollie et al. were generated with a film produced by low-temperature aqueous corrosion of aluminum and subsequently dehydrated, it is expected that the temperature dependence predicted by eqn.(10) should be directly applicable to this evaluation.

3.2 Dependence of Emittance on Film Thickness

Equation (10) gives the emittance of a 25 μm dehydrated aluminum oxide film. However, film thicknesses on the order of 6 μm are of interest in this evaluation. It is therefore necessary to introduce a film thickness correction factor to eqn.(10) which adjusts the predicted total hemispherical emittance to account for reduced film thickness.

The only literature data which give the emittance of aluminum oxide films spanning the range of thicknesses required ($\approx 4 - 25 \mu\text{m}$) are reported by Brannon and Goldstein (1970). They give total normal emittance data for anodized aluminum oxide films at 96 and 190°C for thickness values from near zero up to 86 μm . Their data for film thicknesses less than 15 μm are shown in Figure 4; their emittance value at 25 μm (0.84) is also shown for comparison. Other data sets reported in the literature for the total normal emittance of anodized aluminum oxide films are also shown in Figure 4, along with the temperature at which the measurement was made. Some of the data shown in the figure were taken directly from the compilation of Touloukian et al. (1972). Weaver (1963) measured total hemispherical emittance. Gubareff et al. (1960) reports calculated and measured hemispherical to normal emittance ratios of 0.94 and 0.985; Incropera and DeWitt (1981) give a range of 0.95 to 1.0 for this ratio. Weaver's (1963) hemispherical data were converted to the normal emittance values shown on Figure 4 using a ratio of 0.95. Figure 5 is taken from Gubareff et al. (1960) and gives additional emittance vs. film thickness data for anodized aluminum oxide films.

The emittance of oxide films is not only dependent on temperature and thickness, but also on film composition and microstructure (porosity, particle size, etc.). It is therefore difficult to directly compare the emittance data shown in Figures 4 and 5; the oxide films employed to produce these data were generated using a wide variety of methods. However, it is clear that the relationship between oxide film thickness and emittance shown by Brannon and Goldstein's (1970) data is in general agreement with the bulk of the literature data.

Film thicknesses from approximately 2 to 10 μm are of interest for the purposes of this evaluation. Brannon and Goldstein's emittance data for film thickness values of 2.4, 3.6, 7.1 and 9.1 μm were used to develop the third-order polynomial fit given below:

$$\epsilon_n(f, 96^\circ\text{C}) = 0.02241 + 0.2767(f) - 3.526 \times 10^{-2}(f^2) + 1.538 \times 10^{-3}(f^3) \quad (11)$$

where: ϵ_n = Total normal emittance, and
f = Oxide film thickness (μm).

This correlation is, obviously, only applicable inside the range of data employed to construct it (2.4 - 9 μm). The correlation predictions and Brannon and Goldstein's data are shown in Figure 6. Based on the scatter in their data and the comparison with other

literature data, the uncertainty of Brannon and Goldstein's data is judged to be approximately 5%. Section 2.9 gives a recommended nominal film thickness of 6 μm with an uncertainty of 11%. Varying the value of 'f' in eqn.(11) by $\pm 11\%$ about 6 μm gives a normal emittance range of ± 0.014 . The uncertainty in the emittance at 96°C and 6 μm due to the film thickness uncertainty is taken to this value (± 0.014) divided by the normal emittance at 6 μm (0.745), or 1.9%. The uncertainty in eqn.(11) is taken to be the root mean square of the uncertainty in Brannon and Goldstein's data (5%) and that due to the uncertainty in film thickness (1.9%); this gives a value of 5.3%. Note that the contribution from the uncertainty in film thickness is relatively minor since the slope of the emittance vs. film thickness curve is small at 6 μm .

Using eqn.(11), the ratio of the total normal emittance of an oxide film of thickness 'f' to that for a 25 μm film (0.84) can therefore be written as:

$$\epsilon_r(f; 25\mu\text{m}, 96^\circ\text{C}) = (1.19) [0.02241 + 0.2767(f) - 3.526 \times 10^{-2}(f^2) + 1.538 \times 10^{-3}(f^3)] \quad (12)$$

The uncertainty in eqn.(12) is taken to be the root mean square of the uncertainty in eqn.(11) and that for the 25 μm film emittance (5%); this gives a value of 7.3%. The relative emittance expression given as eqn.(12) is based on 96°C emittance data. At higher temperatures, the emitted energy distribution shifts towards shorter wavelengths (Touloukian and DeWitt 1970b); this would tend to increase the value of ϵ_r since the depth of penetration of emissions from the aluminum substrate would decrease. However, as discussed by Brannon and Goldstein (1970), the absorptivity of aluminum oxide decreases as shorter wavelengths; this would tend to decrease ϵ_r . Brannon and Goldstein's data at 96 and 190°C do not show any significant difference with respect to the relative emissivity of thin and thick films (e.g. ϵ_r), so that these effects are either minor or are of the same magnitude over this temperature range. Therefore, the thickness correction given as eqn.(12) is recommended for all temperatures [e.g. $\epsilon_r(f, 96^\circ\text{C}) = \epsilon_r(f)$], as shown below:

$$\epsilon_r(f; 25\mu\text{m}) = (1.19) [0.02241 + 0.2767(f) - 3.526 \times 10^{-2}(f^2) + 1.538 \times 10^{-3}(f^3)] \quad (13)$$

Taking into account the assumption of temperature independence, an uncertainty of 10% is assigned to eqn.(13).

3.3 Recommended Emittance Values and Uncertainty

The total aluminum oxide hemispherical emittance as a function of temperature and film thickness can be expressed as the product of eqns.(10) and (13), as shown below:

$$\epsilon_h(f,T) = \epsilon_r(f;25\mu m) * \epsilon_h(25\mu m,T)$$

or,

$$\epsilon_h(f,T) = (1.19) * [0.02241 + 0.2767(f) - 3.526 \times 10^{-2}(f^2) + 1.538 \times 10^{-3}(f^3)] \quad (14) \\ * [1.492 - 2.886 \times 10^{-3}(T) + 3.047 \times 10^{-6}(T^2) - 1.18 \times 10^{-9}(T^3)]$$

where: f = Oxide film thickness (μm),
 T = Temperature (K),
 $\epsilon_r(f;25\mu m)$ = Ratio of emittance of a film of thickness 'f' to that at 25 μm ,
 $\epsilon_h(25\mu m,T)$ = Total hemispherical emittance of a 25 μm film as a function of temperature, and
 $\epsilon_h(f,T)$ = Total hemispherical emittance.

The uncertainty in eqn.(14) is taken to be the root mean square of the uncertainties in eqns.(10) and (13), 5 and 10%, respectively, which gives a net one-sigma standard deviation of 11%. The total aluminum oxide hemispherical emittance as a function of temperature for a film thickness of 6 μm is therefore:

$$\epsilon_h(f=6\mu m,T) = (0.887) [1.492 - 2.886 \times 10^{-3}(T) + 3.047 \times 10^{-6}(T^2) - 1.18 \times 10^{-9}(T^3)] \quad (15)$$

Emittance values generated using eqn.(15) are shown in Figure 7 along with 2-sigma uncertainty bands. The total hemispherical emittance is predicted to be 0.69 at 96°C, and decreases to 0.45 at 600°C.

The effect of radiation damage to the oxide film was not addressed in this evaluation. It is expected that radiation damage would increase emittance by introducing lattice disorder. However, the magnitude of this effect is difficult to predict.

4.0 EFFECT OF POST-RESTART CONDITIONS

The bulk moderator temperature at 50% of historical reactor power ranges from 50 to 70°C (WSRC 1989). The temperature at the metal-film interface will be slightly higher than the bulk moderator temperature since a limited amount of heat is produced via neutron and gamma interaction with the component. It is therefore possible that a slight increase in growth rate would occur relative to that predicted for the current 30°C moderator temperature. However, since the incremental growth which would be accumulated is very small relative to the current film thickness, it is anticipated that the increased growth rate would be inconsequential. It is also possible the the film thickness growth rate after restart could increase substantially due to radiation. However, the magnitude of this effect can not be deduced from the available data. The film thickness values given in Section 2.9 are therefore recommended.

5.0 CONCLUSIONS

Literature reviews of the low temperature aqueous corrosion of aluminum in distilled and/or deionized water and of the emittance of aluminum oxide films were conducted. Based on an analysis of the literature data, aluminum oxide film thickness and emittance values were recommended for the conditions of interest. An evaluation of the uncertainty in the recommended values was performed. It is emphasized that the approaches adopted in this evaluation were conservative; credit is not taken for several phenomena which would be operative in the reactor environment and would increase both the aluminum oxide film thickness and emittance.

The safety rod thimbles and Mark 60B blanket assemblies have been exposed to 30°C moderator for approximately 1 year. An oxide film thickness of 6.4 μm is calculated for these conditions. Under the conditions predicted for the gamma heating accident, complete dehydration of the film is expected and the resulting film thickness is estimated to be 6.0 μm . An 11% one-sigma standard deviation is assigned to this value. A temperature and film thickness dependent total hemispherical emittance expression was constructed. For a 6.0 μm thick oxide film, the total hemispherical emittance at 96°C is predicted to be 0.69 at 96°C; the predicted value at 600°C is 0.45. The total one-sigma standard deviation in emittance for at this film thickness is 11%.

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Table 1 SRS Reactor Moderator Chemistry Specifications
(Baumann and Ondrejcin 1990).

Quantity	Tech. Standard	Operating Limit
pD	4.5 - 8.0	5.0 - 5.2
Conductivity ($\mu\text{mho/cm}$ at 25°C)	< 3.5 (3.5 - 5.1 for 1 day max. ^[a])	1.9 - 3.0 (0.3 - 3.0 ^[b])
Turbidity (ppm)	-----	< 0.5
Nitrate (ppb)	-----	500 - 630 ^[b]
Nitrite (ppb)	-----	< 30
Chloride (ppb)	-----	< 30
Sulfate (ppb)	-----	< 50
Oxalate (ppb)	-----	< 50
Peroxide (ppb)	-----	< 1000

[a] During reactor operation.

[b] During layup; nitrate limits would also change.

Table 2 Conversion Factors for Weight Change Data.

Oxide of Interest	Weight Change to Film Thickness Conversion (μm per mg/dm^2)		
	Weight Loss	Weight Gain	Film Weight
Bayerite	0.114	0.0605	0.0395
Boehmite	0.0738	0.0604	0.0322

Table 3 Al-1100 Weight Loss Data (Draley et al. 1967).

Water Condition and Temperature	Intercept ('A') [at 1 day]		Slope ('B') [for time in days]	
	Average (mg/dm^2)	Rel. Standard Deviation (%)	Average ($\text{mg}/\text{dm}^2/\text{day}$)	Standard Dev. (%)
Helium-Saturated				
50°C	37.43	4.9	1.14	9.4
70°C	38.48	1.7	1.51	6.1
95°C	11.17	14	2.46	13
Oxygen-Saturated				
50°C	36.60	2.1	1.36	3.4
70°C	37.55	1.6	1.56	5.0
95°C	5.72	36	3.40	19

Table 4 Constants for Film Thickness Growth Rate Expression.

Temperature (°C)	Intercept ('a') [at 1 day]	Slope ('b') [for time in days]	Constants Based on Data from
20	6.9	0.054	Hart (1957)
40	5.1	0.081	Alwiit (1974)
50	3.5	0.11	Draley et al. (1967)
70	3.6	0.14	Draley et al. (1967)
95	0.91	0.099	Draley et al. (1967)
Boiling	0.24	0.39	Hoxie & Post (1962)

Table 5 High-Purity Aluminum Aqueous Corrosion Data.

Reference	Aluminum Purity (%)	Temp. (°C)	Water Descr.	Exposure Time	Variable Measured	Value Reported
Altenpohl (1961)	99.992	Boiling	Distilled	8 days	Film Mass	4.2 μm
	99.99		"		($t=A*W/\rho$)	2.8 μm
	99.85		"			1.2 μm
	99.45		"			1.1 μm
Alwitt (1971b)	99.99	Boiling	Distilled + Deionized	1/2 hour	Weight Loss Film Thickness	4.0 mg/dm^2 0.47 μm
Alwitt and Archibald (1973)	99.99	40	Distilled	1 - 4 days	Film Thickness (SEM)	2.8 μm
Alwitt (1974)	99.99	40	Distilled	100 hours	Weight Gain	88 mg/dm^2
				8 hours	Film Thickness	1.2 μm
				16 hours	(SEM)	1.8 μm
				1 - 4 days		2.5 μm
Bernard & Randall (1961)	>99.986	80-100	0.8 $\text{M}\Omega\text{-cm}$	10 min.	Metal Loss	2.4 mg/dm^2
		100		4 hours		6.5 mg/dm^2
Bernard & Randall (1960)	>99.986	100	Distilled	2 min.	Metal Loss	1.6 mg/dm^2
				30 min.		3.6 mg/dm^2
Burger & Cheseldine (1960)	99.99	Boiling	Distilled	5 min.	Film Weight	190 mg/dm^2
				30 min.		310 mg/dm^2
				60 min.		370 mg/dm^2
Hart (1957)	99.995	20	Distilled (2.5 $\text{M}\Omega\text{-cm}$)	2 weeks	Weight Gain	115 mg/dm^2
		40		1 week		150 mg/dm^2
		60		1 week		140 mg/dm^2
		80		1 week		42 mg/dm^2
Kawasaki et al. (1962)	99.99	52	Distilled + Deionized (5 $\text{M}\Omega\text{-cm}$)	100 hours	Weight Gain	84 mg/dm^2
		60				86 mg/dm^2
		71				89 mg/dm^2
		81				121 mg/dm^2
		90				62 mg/dm^2
Leidheiser & Das (1975)	99.994	Boiling	not reported	100 min.	Weight Gain	9.5 mg/dm^2
Takahashi et al. (1990)	99.99	Boiling	Doubly Distilled	1 hour	Weight Loss	7 mg/dm^2
					Film Weight	20 mg/dm^2
Vedder & Vermilyea (1969)	> 99.99	70	Distilled (2 $\text{M}\Omega\text{-cm}$)	4 hours	Weight Gain	13 mg/dm^2
		Boiling		4 hours		20 mg/dm^2
		50		14 hours		34 mg/dm^2
		70		14 hours		48 mg/dm^2

Figure 1 Aluminum Oxide Film Thickness Correlations.

Figure 2 Thickness of Aluminum Oxide Film Formed at 30°C and Subsequently Dehydrated (Nominal and ± 2 Sigma Range).

Figure 3 Total Hemispherical Emittance Correlations for 25 μ m Aluminum Oxide Films.

Figure 4 Total Normal Emittance vs. Aluminum Oxide Film Thickness.

Figure 5 Emittance vs. Film Thickness Data Compiled by Gubareff et al. (1960).

Figure 6 Total Normal Emittance vs. Aluminum Oxide Film Thickness Data and Correlation.

Figure 7 Total Hemispherical Emittance of Al-Oxide Film Formed at 30°C and Subsequently Dehydrated (Nominal and ± 2 Sigma Range).

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