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"Boric Acid Corrosion of Oconee 1 Upper Tubesheet"

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Title BORIC ACID CORROSION OF OCONEE UNIT 1 UPPER TUBESHEET

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Reviewer is Independent.

Remarks:

This document presents the possible boric acid corrosion rate for the Oconee Unit 1 upper tubesheet exposed to reactor coolant as a result of a mis-drilled tubesheet hole. It was concluded that the tubesheet is structurally sound and is acceptable for the next cycle of operation.

***** This revision (01) is the NON-PROPRIETARY version of rev. 0. *****

1.0 Purpose

The purpose of this document is to determine the expected boric acid corrosion rate(s) of an Oconee Unit 1 steam generator tubesheet exposed to reactor coolant.

2.0 Background

During a steam generator tube removal operation at Oconee Unit 1, the upper tubesheet and cladding were inadvertently drilled to a maximum depth of 0.0805 inch into the tubesheet material. The maximum exposed area was determined by direct measurement and video estimation.

The tubesheet is made of a Mn-Mo-Ni alloy and is clad with Inconel. In the steam generator design, the tubesheet material was clad to avoid exposure to reactor coolant; therefore, concerns with boric acid corrosion exist. This document will present other instances in which carbon and low alloy steels were exposed to reactor coolant and the resulting/expected corrosion rates of these steels.

3.0 Corrosion of Carbon and Low Alloy Steels

Carbon and low alloy steels have been exposed to reactor coolant in several instances. In the following sections, descriptions will be given of several of these occurrences and the correction or acceptance of each situation.

3.1 Boric Acid Corrosion Studies

B&W Document 51-1200238-00[1] lists a number of events in which boric acid corrosion occurred as a result of coolant leakage. Carbon and low alloy steel components, from the RV head to closure studs, have corroded from boric acid exposure at various leak rates. Also, this document contains a summary of non-B&W research on the effects of boric acid corrosion on various materials. See Table 1 for a summary of the non-B&W research data.

3.2 ANO-1 Pressurizer Level Tap

A cracked and leaking pressurizer level tap nozzle at ANO-1 led to the exposure of the pressurizer material (carbon steel) to reactor coolant prior to the interim repair of the leaking nozzle. In an analysis of the ANO-1 interim repair, the following information was provided with regard to the various types of corrosion:

> <u>Crevice corrosion</u> is probably the most important consideration for the proposed interim fix. The environmental conditions in a crevice can, with time, become aggressive and cause local corrosion. B&W has conducted several studies on the environmental effects of a

crevice condition in a PWR environment, particularly in the OTSG tube-tube sheet crevice.

Test results indicate that iron oxide formation, the result of low alloy tube sheet corrosion in the tube-tube sheet crevice, plugged the leak path of the intentionally damaged tube. Under ambient conditions, the oxide became more tightly packed and appeared to more tightly plug the crevice.

In summary, our expectation is that minimal corrosion will occur in the level tap crevice. It is also expected that plugging of the crevice will occur through the formation and deposition of iron oxides. The gap between the new and old nozzles is expected to corrode somewhat, however, this should be limited to a few mils.

General corrosion will occur in the region between the end of the remaining portion of the level tap (old nozzle) and the new spool piece (new nozzle). However, general corrosion is not believed to be as great a concern as crevice corrosion, and as shown above, crevice corrosion should be limited to a few mils.

Pitting corrosion may also occur in the base metal within the gapped region. However, the depth of this localized corrosion is similarly expected to be limited to a few mils.

Galvanic corrosion may occur when two different metals in contact are exposed to a conductive solution. The larger the potential difference between the two metals, the greater is the likelihood of the occurrence of galvanic corrosion. Low alloy steel is more anodic that Inconel and would, therefore, be subject to galvanic attack when coupled and exposed to reactor coolant.

In studies performed in support of the reactor vessel cladding damage at Yankee Rowe, where low alloy steel was galvanically coupled to austenitic stainless steel, corrosion tests were conducted with A302 Grade B coupons and A302 Grade B coupons coupled to Type 304 stainless steel and exposed to a simulated PWR environment under deaerated conditions. Both coupons exhibited similar corrosion rates. Low alloy steel coupons coupled to Inconel 600 would probably exhibit less corrosion since Inconel is less cathodic to low alloy steels that stainless steel, as based on relative positions in the electromotive series.

Other investigators have reported corrosion test results for galvanic corrosion between carbon and low alloy steels. Exposure of alloy steels coupled (welded) to stainless steels was carried out in near-neutral, high-purity water for 1000 hours at about 546°F in steam, steam-water, saturated water, and subcooled water containing from 0.1 ppm to 15 ppm oxygen and 2 ppm hydrogen in the steam and steam-water mixture. The chloride content of the water was less that 0.1 ppm. Visual, macroscopic, and metallographic investigations revealed no traces of galvanic, selective, or accelerated corrosion in or near weld zones of any of the welded specimens. Other investigators similarly found no evidence of galvanic corrosion when they tested 5% chromium steel and Type 304 stainless steel couples at 500°F for 85 days in water containing 35 ppm oxygen and 98 days in water containing 530 ppm oxygen.

In summary, galvanic corrosion is not expected to be a concern at ANO-1 using the proposed interim fix.

Hydrogen embrittlement is the degradation of a material's properties due to hydrogen interaction/diffusion. This type of embrittlement is observed most often in plastically deformed alloys in high pressure hydrogen environments and is characterized by loss of ductility and lowering of fracture stress. Carbon and low alloy steels, in a high strength condition, are especially susceptible to hydrogen embrittlement. Higher strength ferritic and martensitic stainless steels are also subject to hydrogen damage.

The Yankee Rowe reactor vessel and pressurizer have a unique type of cladding. The cladding is a sheet form of Type 304 stainless steel spot welded to the SA-302B and SA302-B nickel-modified low alloy steel. Both the reactor vessel and pressurizer have cladding defects. This resulted in extensive investigations on the potential effects of hydrogen on the base metal shells. In the instance of the pressurizer, the defect was cracking that occurred at the cladding spot welds. The cracks were postulated to penetrate into the shell material. It was shown that even under the worst conditions, the hydrogen levels in the base material, at a crack tip, would be far too low to be of concern.

Since the ANO-1 pressurizer is a carbon steel, hydrogen embrittlement is even of less concern in consideration of its lower yield strength and hardenability.

Summary -- Only minimal corrosion of the ANO-1 shell material was expected to occur during short-term exposure to the steam space environment.

3.3 Erosion-Corrosion

Single-phase erosion-corrosion of piping is restricted to carbon steel piping components that are essentially free from significant alloying. Small alloy additions, such as chromium and molybdenum, are significant in obviating the occurrence of erosion-corrosion.[2,3]

4.0 Expected Corrosion Rate(s) of Oconee Unit 1 Steam Generator Tubesheet

Based on the above information, the expected corrosion rates of the tubesheet material can be determined. There are two conditions under which the tubesheet will be exposed:

(1) Operating condition -- high temperature, RCS fluid, low oxygen concentration

(2) Shutdown condition -- low temperature, higher oxygen concentration, higher boron concentration.

In each of these conditions, based on the ANO-1 experience, the corrosion rate is expected to be low. For the operating condition, the temperature is high, and the tubesheet will be constantly wetted; thus leading to a low corrosion rate on the order of a few mils over the cycle, or less than one mil per year (<1 mpy). The shutdown condition is at a lower temperature and the environment is oxygenated. Corrosion of the tubesheet during shutdown is expected to be slightly higher that at operating condition, on the order of less than five mils per year (<5 mpy). A very conservative estimate would be 25 mpy. The alloy content of the tubesheet forging will aid in keeping the corrosion rate low.

5.0 Stress

The subject configuration results from the removal of a very small amount of tubesheet base metal. As discussed previously, corrosion occurring during the next fuel cycle may remove only a very small additional amount of base metal.

The structural adequacy of the tubesheet is justified by the design margin found in the stress report. Additionally, there is a large margin available for cyclic loadings as indicated by the maximum cumulative usage factor. It is obvious when considering the low number of cyclic loadings (transients) which will occur during the next fuel cycle, that the tubesheet cumulative usage factor will remain well within the code allowable.

Therefore, it is concluded that the tubesheet, with locally exposed base metal, is structurally adequate for operation during the next fuel cycle.

6.0 Conclusions

The estimates given in Section 4.0 (1.0 and 5.0 mpy for operating condition and shutdown condition, respectively) are based on the corrosion rates discussed above. The methods of corrosion expected at the Oconee Unit 1 tubesheet will be similar to those expected in the ANO-1 pressurizer base metal. Based on the above results, the state of the Oconee Unit 1 upper tubesheet is acceptable for the next cycle of operation.

7.0 References

1. Ouellette, C.A., Update of Boric Acid Corrosion Events, B&W Document 51-1200238-00, July 31, 1990.

2. Jones, R., et al., Single Phase Erosion-Corrosion of Carbon Steel Piping, Electric Power Research Institute, Palo Alto, CA, February, 19, 1987.

3. Bignold, G.J., et al., Erosion-Corrosion in Nuclear Steam Generators, CEGB Report No. RD/L/N 133/80, Central Electricity Research Laboratories, Surrey, England, January, 1981.

TABLE 1
(Ref. 5)

BORIC ACID CORROSION DATA OBTAINED BY NON-B&W RESEARCH

Test Material	Exposure Time (hours)	Solution Chemistry (ppm)	Flow Rate	Test Temperature (^{o}F)	Corrosion Rate (in/yr)	Notes
SA-193 B7 (Cr-Mo alloy)	500	1000 B as H_3BO_3 at $600^{o}F$	0.05 gph	175	0.833	SS fixture; Ref. 31
				350	0.431	
SA-540 B23 Class 4 (Cr-Ni-Mo alloy)	500	1000 B as H_3BO_3 at $600^{o}F$	0.05 gph	175	0.815	SS fixture; Ref. 31
				350	0.841	
SA-540 B24 Class 3 (Cr-Ni-Mo alloy)	500	1000 B as H_3BO_3 at $600^{o}F$	0.05 gph	175	0.265	SS fixture; Ref. 31
				300	0.722	
				350	1.29	
				400	1.69	
SA-540 B24 Class 3 (Cr-Ni-Mo alloy)	500	1000 B as H_3BO_3 at $600^{o}F$	0.05 gph	175	0.66	Low alloy steel fixture; Ref. 31
				350	0.664	
Cr-ion Implanted low alloy steel	500	1000 B as H_3BO_3 at $600^{o}F$	0.05 gph	175	1.542	Low alloy steel fixture; Ref. 31
TiN plasma coated low alloy steel	500	1000 B as H_3BO_3 at $600^{o}F$	0.05 gph	175	0.753	Low alloy steel fixture; Ref. 31
Enamel-coated low alloy steel	500	1000 B as H_3BO_3 at $600^{o}F$	0.05 gph	175	2.032	Low alloy steel fixture; Ref. 31
Solid Film Lubricated low alloy steel	500	1000 B as H_3BO_3 at $600^{o}F$	0.05 gph	175	1.65	Low alloy steel fixture; Ref. 31
SA-533 Grade B	70	723 B as H_3BO_3 1.8 Li; 0.4 N_2H_4	N/A	350	0.0171	Beaker test; Ref. 27
SA-508 Class 2	70	723 B as H_3BO_3 1.8 Li; 0.4 N_2H_4	N/A	350	0.0168	Beaker test; Ref. 27

TABLE 1 (CONTINUED)

BORIC ACID CORROSION DATA OBTAINED BY NON-B&W RESEARCH

Test Material	Exposure Time (hours)	Solution Chemistry (ppm)	Flow Rate	Test Temperature (°F)	Corrosion Rate (in/yr)	Notes
SA-508/SA-533 weld	70	723 B as H_3BO_3 1.8 Li; 0.4 N_2H_4	N/A	350	0.0161	Beaker test; Ref. 27
SA-533 Grade B	392.5	1000 B as H_3BO_3 at 600°F	0.05±0.02 gpm	650	0.9660 1.1626 0.8106 1.0414	Capillary samples; corrosion rate is maximum for test; Ref. 27
	369.0	1000 B as H_3BO_3 at 600°F	0.10±0.02 gpm	650	1.0683 0.9359	
	392.5	1000 B as H_3BO_3 at 600°F	0.05±0.02 gpm	650 not heated 650 not heated	0.5580 0.3571 0.5133 0.3794	Deposit samples; Ref. 27
	369.0	1000 B as H_3BO_3 at 600°F	0.10±0.02 gpm	650	0.5698 0.6172	
SA105 Grade B	4	79,400 B as H_3BO_3	N/A	220	7.25	Beaker test; Ref. 27
	6	26,200 B as H_3BO_3	N/A	220	1.63	
	27	26,200 B as H_3BO_3	N/A	220	0.396	
	24	22,000 B as H_3BO_3	N/A	220	0.752	
	96	22,000 B as H_3BO_3	N/A	220	0.241	
SA533 Grade B	6	26,200 B as H_3BO_3	N/A	220	1.416	Beaker test; Ref. 27
	27	26,200 B as H_3BO_3	N/A	220	0.305	
	24	22,000 B as H_3BO_3	N/A	220	0.651	
	96	22,000 B as H_3BO_3	N/A	220	0.358	

TABLE 1 (CONTINUED)

BORIC ACID CORROSION DATA OBTAINED BY NON-B&W RESEARCH						
Test Material	Exposure Time (hours)	Solution Chemistry (ppm)	Flow Rate	Test Temperature (^{o}F)	Corrosion Rate (in/yr)	Notes
A193 Grade B7	71.5	4,000 B as H_3BO_3		352	0.05	**Ref. 8**
	72.5	4,000 B as H_3BO_3		352	0.042	
	24.33	4,000 B as H_3BO_3		212	0.432	
	23.3	4,000 B as H_3BO_3		212	0.124	
	71.5	H_3BO_3+LiOH to pH 7.3		352	0.054	
	72.5	H_3BO_3+LiOH to pH 7.3		352	0.046	
	24.33	H_3BO_3+LiOH to pH 7.3		212	0.112	
	24.75	H_3BO_3+LiOH to pH 7.3		212	0.125	
	74.67	H_3BO_3+LiOH to pH 7.3		212		
	146.67	H_3BO_3+LiOH to pH 7.3		212	0.118	
	146.67	H_3BO_3+LiOH to pH 7.3		212	0.13	
	74.67	H_3BO_3+LiOH to pH 7.3		212	0.126	

TABLE 1 (CONTINUED)

BORIC ACID CORROSION DATA OBTAINED BY NON-B&W RESEARCH						
Test Material	Exposure Time (hours)	Solution Chemistry (ppm)	Flow Rate	Test Temperature (°F)	Corrosion Rate (in/yr)	Notes
SA508 Class 2	6	26,200 B as H_3BO_3	N/A	220	0.911	Beaker test; Ref. 27
	27	26,200 B as H_3BO_3	N/A	220	0.214	
	24	22,000 B as H_3BO_3	N/A	220	0.519	
	96	22,000 B as H_3BO_3	N/A	220	0.238	
A-4135	336	8,750 B as H_3BO_3		70	0.0055	Ref. 8
	672	8,750 B as H_3BO_3		70	0.0041 0.0042	
	336	22,750 B as H_3BO_3		140	0.029 0.0303	
	672	22,750 B as H_3BO_3		140	0.025 0.028	
	336	8,750 B as H_3BO_3 + KOH to pH 7.3		70	0.000024 0.000011	
	1344	8,750 B as H_3BO_3 + KOH to pH 7.3		70	0.000033 0.000031	
	336	22,750 B as H_3BO_3 + KOH to pH 7.3		140	0.000011 0.0000092	
	672	22,750 B as H_3BO_3 + KOH to pH 7.3		140	0.00024 0.000049	
	1344	22,750 B as H_3BO_3 + KOH to pH 7.3		140	0.0034 0.0038	
A-4130	71.58	4,000 B as H_3BO_3		600	0.0256 0.0279 0.0254 0.0219	Ref. 9