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TOKYO, JAPAN

November 13, 2009

Document Control Desk
U.S. Nuclear Regulatory Commission
Washington, DC 20555-0001

Attention: Mr. Jeffrey A. Ciocco

Docket No. 52-021
MHI Ref: UAP-HF-09519

Subject: MHI's Response to US-APWR DCD RAI No. 460-3484 Rev. 0

Reference: 1) "Request for Additional Information No. 460-3484 Revision 1, SRP Section: 06.05.02 – Containment Spray as a Fission Product Cleanup System, Application Section: 6.5.2" dated 9/16/2009.

With this letter, Mitsubishi Heavy Industries, Ltd. ("MHI") transmits to the U.S. Nuclear Regulatory Commission ("NRC") documents entitled "Response to Request for Additional Information No. 460-3484 Rev. 1".

Enclosed 1 provides the response to the 1 question that is contained within Reference 1.

Please contact Dr. C. Keith Paulson, Senior Technical Manager, Mitsubishi Nuclear Energy Systems, Inc. if the NRC has questions concerning any aspect of the submittals. His contact information is below.

Sincerely,

Y. Ogata

Yoshiki Ogata,
General Manager- APWR Promoting Department
Mitsubishi Heavy Industries, LTD.

Enclosure:

1. Response to Request for Additional Information No. 460-3484 Revision 0

CC: J. A. Ciocco
C. K. Paulson

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Enclosure 1

UAP-HF-09519
Docket No. 52-021

Response to Request for Additional Information No. 460-3484
Revision 0

November 2009

RESPONSE TO REQUEST FOR ADDITIONAL INFORMATION

11/13/2009

US-APWR Design Certification

Mitsubishi Heavy Industries

Docket No. 52-021

RAI NO.:	**NO. 460-3484 REVISION 0**
SRP SECTION:	**06.05.02 – CONTAINMENT SPRAY AS A FISSION PRODUCT CLEANUP SYSTEM**
APPLICATION SECTION:	**6.5.2**
DATE OF RAI ISSUE:	**9/16/2009**

QUESTION NO.: 06.05.02-7

Background

RAI 06.05.02-1 (Reference 1) requested that the applicant explain the rise in pH of the RWSP water under accident conditions. The importance of such a calculation is to ensure that iodine dissolved in RWSP water does not revolatilize, which it could do if the pH is not maintained above 7. In fact, acceptance criterion II.1.G of SRP 6.5.2 requires that pH of 7 should be achieved before the onset of containment sprays. Staff concern was motivated by the statement in DCD 6.3.2.2.5 that the primary pH control chemical (NaTB) would not be fully dissolved until 12 h.

The applicant's response (Reference 2) claimed that the pH would be raised above 7 very early in the accident by dissolution of fission product cesium, which would exist primarily as the strong base CsOH. Specifically, it was stated that in about 1 h, sufficient CsOH would be released from fuel, escape the RCS, and be washed into the RWSP, so as to raise the pH in the RWSP above 7.

The staff attempted to confirm this effect using rough estimates for the concentrations of CsOH and boric acid, but the result was a calculated pH well below 7; hence, the staff requested that the applicant confirm their own calculation and supply all the important variables to NRC. (Reference 3) In response, the applicant gave a very lengthy and detailed description of pH calculations for the entire accident transient, including effects of radiolytic acid generation and addition of sodium tetra-borate (NaTB). (Reference 4)

The applicant did not actually perform a separate calculation which included only the effect of CsOH in RWSP water. However, the response did furnish information for the staff to perform a more accurate confirmatory calculation, which is described below.

We assume the data as taken from the sources listed:

Temperature = 100°C
Water density = 0.95838 (CRC Handbook of Chemistry and Physics)
Total water (RCS + RWSP) = 3.33×10^6 L (Reference 4)

Total Cs released to water (30% of core inventory) = 1170 mol (Reference 4)
Concentration of boric acid = 4200 ppm (Reference 4)

Assuming that all Cs is CsOH, concentrations of boric acid and CsOH are about 0.3885 m (molal) and 0.0003666 m, respectively. We neglect acid formation as this would only lower pH further. Using the methodology of the EPRI Guidelines (Reference 5), the pH of such a solution was calculated to be about 5.29. However, the EPRI model begins to lose accuracy for ionic strengths above 0.2 m, so we appropriated the model of Palmer et al (Reference 6). log−This model includes ionic strength effects, so the pH is actually defined as pH = $_{10}(a_{H+})$, where a_{H+} is the chemical activity. Using the concentrations listed above, the calculated pH was 5.12. Thus, the staff is unable to confirm the applicant's assertion that CsOH alone is capable of raising the pH of the RWSP to 7 or above.

The staff is concerned that applicant is not considering the buffering effect of boric acid in the RWSP due to formation of polyborate species (as described in References 5 and 6). Nowhere in Reference 4 is this effect described.

Requested Information

Describe in more detail the calculation that indicates fission product cesium raises containment water pH above 7. Describe how boric acid buffering is included in the calculation, and what equilibria are used for the various polyborate species.

References

1. "Request for Additional Information No. 234-2040 Revision 1, SRP Section: 06.05.02 - Containment Spray as a Fission Product Cleanup System, Application Section: Section 6.5.2" dated February 26, 2009. (ADAMS Accession No. ML0906102970)

2. Letter from Yoshiki Ogata, MHI, to NRC dated April 22, 2009; Docket No. 52-021 MHI Ref: UAP-HF-09199; Subject: MHI's Second Response to USAPWR DCD RAI No. 234 (ADAMS Accession No. ML0911804351)

3. "Request for Additional Information No. 416-2912 Revision 0, SRP Section: 06.05.02 - Containment Spray as a Fission Product Cleanup System, Application Section: 6.5.2" dated June 29, 2009. (ADAMS Accession No. ML091830408)

4. Letter from Yoshiki Ogata, MHI, to NRC dated July 28, 2009; Docket No. 52-021 MHI Ref: UAP-HF-09407; Subject: MHI's Response to US-APWR DCD RAI No. 416-2912 Rev. 0 (ADAMS Accession No. ML092110671)

5. Pressurized Water Reactor Primary Water Chemistry Guidelines, Vol. 1, Rev. 6, Electric Power Research Institute (December 2007).

6. D. A. Palmer, P. Benezath, D. J. Wesolowski, "Boric Acid Hydrolysis: A New Look at the Available Data," PowerPlant Chemistry 2(5), 261-4 (2000).

ANSWER:

Based upon a review of the calculations provided to date, there appears to be a problem concerning the boric acid-borate buffer equilibration calculation. By using a general method which takes speciation, mass and charge balances into account we have determined a consistent method for determining sump pH. The curve below indicates the results for a pool temperature of 100°C for both the initial method and for the modified method that includes the full boric acid-borate buffer equilibration calculation. The breaks in the curves can be explained by noting that the cesium release stops at 1.8 hours and the NaTB injection starts at 3.5 hours and continues until 15.5 hours.

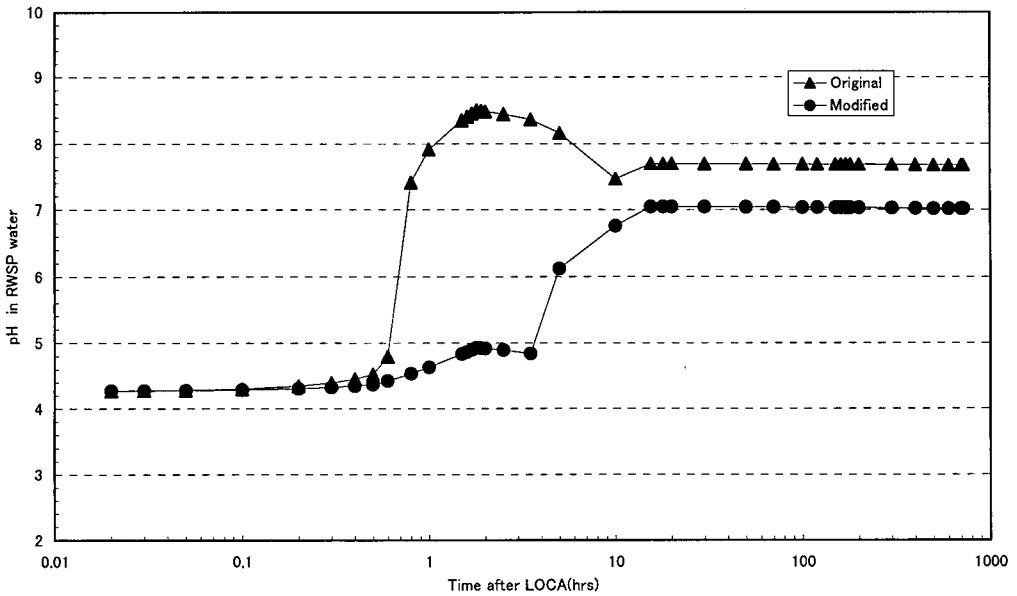

Figure 06.05.02-7-1 Variation of recirculation water pH with time at 100°C (modified)

It can be shown that either increases in the availability of NaTB or reductions in the initial boron concentration will cause the modified curve to shift upward further reducing the time until a pH of at least 7 is determined. A pH of 7 yields vapor fraction of less than 0.3% of the I_2 in the water while a pH of 6 releases 1.4% (Beahm, 1991). Thus even at early times there would be little release and in the long term, as required by NUREG-0800, the pH would be greater than 7 for this scenario.

The effect of introducing 18tons (=39700lbm) of NaTB over 12 hours starting at 3.5 hours is shown in the following figure. Note that a pH of 7 is established approximately 15 hours after the start of the accident. In this analysis it was assumed that the RWSP contained the initial volume of water, the accumulator release and most of the RCS water for a total volume of 3330 m^3.

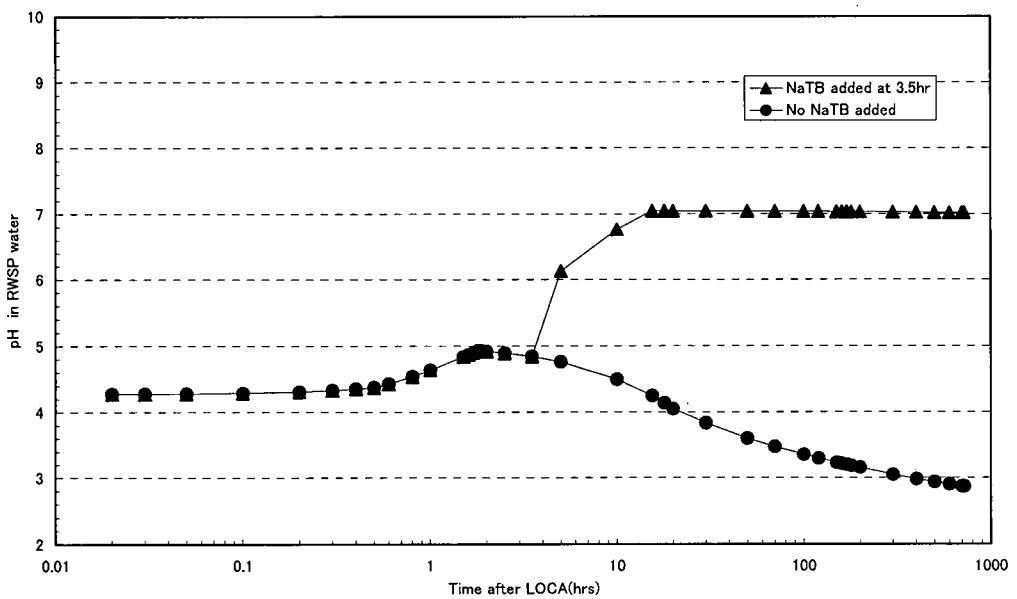

Figure 06.05.02-7-2 Buffer effect on pH at 100°C

Model Description:

Species:

Cations: H^{+1}, Na^{+1}, Cs^{+1}
Anions: OH^{-1}, $B(OH)_4^{-1}$, $B_2(OH)_7^{-1}$, $B_3(OH)_{10}^{-1}$, $B_4(OH)_{14}^{-2}$, I^{-1}, NO_3^{-1}, Cl^{-1}
Neutral: H_3BO_3, CsOH, HNO_3, HCl, HI, $Na_2B_4O_7$, H_2O

Dissociation Reactions:

$H_2O \Leftrightarrow H^{+1} + OH^{-1}$
$H_3BO_3 + OH^{-1} \Leftrightarrow B(OH)_4^{-1}$
$2\ H_3BO_3 + OH^{-1} \Leftrightarrow B_2(OH)_7^{-1}$
$3\ H_3BO_3 + OH^{-1} \Leftrightarrow B_3(OH)_{10}^{-1}$
$4\ H_3BO_3 + 2\ OH^{-1} \Leftrightarrow B_4(OH)_{14}^{-2}$

$CsOH \Rightarrow Cs^{+1} + OH^{-1}$
$HCl \Rightarrow H^{+1} + Cl^{-1}$
$HNO_3 \Rightarrow H^{+1} + NO_3^{-1}$
$HI \Rightarrow H^{+1} + I^{-1}$
$Na_2B_4O_7 + 7\ H_2O \Rightarrow 2\ Na^{+1} + 2\ B(OH)_4^{-1} + 2\ H_3BO_3$

Equilibrium Relationships:

$$K_w = [H^{+1}][OH^{-1}]$$

$$Q_{11} = \frac{[B(OH)_4^{-1}]}{[H_3BO_3][OH^{-1}]}$$

$$Q_{21} = \frac{[B_2(OH)_7^{-1}]}{[H_3BO_3]^2[OH^{-1}]}$$

$$Q_{31} = \frac{[B_3(OH)_{10}^{-1}]}{[H_3BO_3]^3[OH^{-1}]}$$

$$Q_{41} = \frac{[B_4(OH)_{14}^{-2}]}{[H_3BO_3]^4[OH^{-1}]^2}$$

Mass Balances:

TOTNa = $[Na^{+1}]$
TOTB = $[H_3BO_3] + [B(OH)_4^{-1}] + 2[B_2(OH)_7^{-1}] + 3[B_3(OH)_{10}^{-1}] + 4[B_4(OH)_{14}^{-2}]$

Charge Balance:

$[H^{+1}] + [Na^{+1}] + [Cs^{+1}] = [OH^{-1}] + [B(OH)_4^{-1}] + [B_2(OH)_7^{-1}] + [B_3(OH)_{10}^{-1}] + 2[B_4(OH)_{14}^{-2}] + [NO_3^{-1}] + [Cl^{-1}] + [I^{-1}]$

Equilibrium Coefficients

Boric Acid (Bergmann, 1985)

$\log Q11 = 1573.21/T + 28.6059 + 0.012078 \times T - 13.2258 \log T$
$\log Q21 = 2756.1/T - 18.7322 - 0.00033 \times T + 5.835 \log T$
$\log Q31 = 3339.5/T - 7.85 - 0.00033 \times T + 1.497 \log T$
$\log Q42 = 12820/T - 134.33 - 0.00033 \times T + 42.105 \log T$
T: absolute temperature (K)

Water (Bergmann, 1985)

$\log K'_w = -4.098 - 3245.2/T + 2.2362 \times 10^5/T^2 - 3.9847 \times 10^7/T^3 + (13.957 - 1262.3/T + 8.5641 \times 10^5/T^2) \times \log(\rho w)$
T: absolute temperature (K)
ρ_w: water density (gm/cc)
K'_w : aqueous dissociation constant ((moles/kg-H_2O)^2)
$K_w = K'_w \rho_w^2$ ((moles/liter)^2)

Water Properties

Density (Bergmann, 1985)

$\rho_w = A/B$
$A = 1 + 0.1341489\ TB^{1/3} - 3.946263 \times 10^{-3}\ TB$
$B = Vc - 0.3151548\ TB^{1/3} - 1.203374 \times 10^{-3}\ TB + 7.489081 \times 10^{-13}\ TB^4$
$TB = (374.11 - t)$
$Vc = 3.1975\ (cm^3/g)$
t = Temperature (°C)

References :

Beahm, E.C., C.F. Weber, and T.S. Kress, "Iodine Chemical Forms in LWR Severe Accidents", NUREG/CR-5732, 1991.

Bergmann, C.A. et. al., "The Role of Coolant Chemistry in PWR Radiation-Field Buildup", EPRI NP-4247, 1985.

Impact on DCD

There is no impact on the DCD.

Impact on COLA

There is no impact on the COLA.

Impact on PRA

There is no impact on the PRA.