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Office of Nuclear Reactor Regulation  
U.S. Nuclear Regulatory Commission  
Washington, DC 20555

March 29, 2002

Re: Corrosion damage to RPV head at the Davis-Besse Nuclear Generating Station.

Dear Dr. Sheron,

I have read with considerable interest the NRC and newspaper accounts on the corrosion damage to the reactor pressure vessel head at the Davis-Besse Nuclear Generating Station. Having worked on defining corrosion processes in nuclear plants for the past thirty years, starting as an employee of Atomic Energy of Canada Ltd in the early 1970s, I offer below an explanation of why the damage occurred. My explanation is undoubtedly incomplete in detail, but I believe that the general facts are correct.

A number of years ago, under EPRI sponsorship, and using unique experimental techniques that were developed in my laboratory, my colleagues and I studied the properties of very concentrated boric acid/sodium hydroxide systems at temperatures up to 300 °C. (I am reluctant to call them "solutions", because 100 m B(OH)<sub>3</sub> is essentially wet boric acid powder). The property that we measured was the pH and, much to our surprise, we found that concentrated boric acid/NaOH systems are capable of generating very low pH values, as you will see from the attached publication. Indeed, pH values as low as 2 were found in some systems (see Figures 9 to 11). These highly acidic conditions are conducive to both general corrosion of carbon steel and stress corrosion cracking of Alloy 600 (so-called "acid cracking"). Accordingly, the scenario that I postulate is that a mechanism exists (possibly evaporation in a crevice at the head penetration) that results in the precipitation of boric acid, which, because it is wet, produces highly acidic local conditions, giving rise to accelerated attack. Given the observation of boric acid deposits in the damaged area, I believe that the above scenario is essentially correct. Indeed, ever since performing the work that is described in the attached paper in the late 1980s/early 1990s, I have often wondered if this little-appreciated property (low pH) of ultra-concentrated boric acid might become an issue in the operation of PWRs. This work has been largely overlooked, but it would seem that my concerns were not unfounded.

I hope that the above material and the attached paper are of interest in your deliberations on the cause of damage at the Davis-Besse reactor and the implications that it raises for other PWRs. Should you wish to discuss this work further, please contact me by telephone at (814) 863-7772 or by e-mail at [ddm2@psu.edu](mailto:ddm2@psu.edu) at your convenience.

Sincerely,

Digby D. Macdonald, Director  
Professor of Materials Science and Engineering

A020

Add: Brian Sheron

**Proceedings of the Fourth International Symposium on  
Environmental Degradation of Materials  
in Nuclear Power Systems—  
Water Reactors**

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# Measurement of pH in High Temperature Concentrated Solutions Simulating PWR Steam Generator Crevice Environments

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## Abstract

High-temperature sensors [Pt/H<sub>2</sub> and Hg/HgO/ZrO<sub>2</sub>(Y<sub>2</sub>O<sub>3</sub>)] have been used to measure pH as a function of temperature for 1 m NaOH, 1 m NaOH + 1 m Na<sub>2</sub>SO<sub>4</sub>, 1 m NaOH + 1 m Na<sub>2</sub>SO<sub>4</sub> + x m B(OH)<sub>3</sub> (x = 2, 5, 20, 50, 100), and 1 m NaOH + 1 m Na<sub>2</sub>SO<sub>4</sub> + 1 m NaCl at temperatures between 125° and 300°C. The ceramic membrane sensor was found to provide more consistent data than the hydrogen electrode. After a detailed analysis of the errors associated with the isothermal liquid junction potential of the reference electrode, the activity of water, and the partial pressure of hydrogen in the pressure vessel, and allowing for possible errors in the calculated pH values, we conclude that EPRI's MULTEQ chemistry code is capable of providing reasonable estimates of the pH of high-temperature aqueous solutions of the type that exist in PWR steam generators. The concentrated boric acid solutions were calculated (and observed) to yield acidic solutions with pH < 3 for x ≥ 50 m.

## Introduction

Concentrated electrolyte solutions are known to form in crevices under high heat transfer conditions and in other dry-out regions of nuclear steam generators, and these solutions pose a potential corrosion problem when the activity of hydrogen ion is high. A multicomponent system of particular interest is B(OH)<sub>3</sub>/NaOH/NaCl/H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O, because the components either are present in the bulk water as impurities (e.g., Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>) or are added for corrosion control (e.g., B(OH)<sub>3</sub> to control denting). Although the acidity of such systems can be estimated by using sophisticated computer codes (e.g., EPRI's MULTEQ), considerable uncertainty exists about the accuracy of the calculated pH because of poorly known activity coefficients and other factors. Accordingly, direct experimental determination of the pH would greatly contribute to validating the codes for application to concentrated, multicomponent systems.

In this study, we used Pt/H<sub>2</sub> and yttria-stabilized zirconia membrane (YSZ) electrodes to measure the pH of high-temperature/high-pressure concentrated aqueous solutions (Table 1) at temperatures from 125° to 300°C. The cell and electrodes were designed to allow precise pH measurements to be made under typical PWR steam generator conditions, and we assessed the accuracy of the pH measurements by a comprehensive error analysis. The measured values were compared with data calculated using MULTEQ. The reasonable agreement between the measured and calculated values ( $\Delta\text{pH} < \pm 1$ ) shows that the apparatus developed in this study is capable of yielding useful pH measurements in concentrated, high-temperature/high-pressure solutions and demonstrates the capability of MULTEQ for estimating the pH of simulated crevice environments. ♦

## Experimental

Two kinds of sensors were used in this study to measure the pH of the concentrated solutions listed in Table 1: Pt/H<sub>2</sub> hydrogen electrodes and Hg/HgO/ZrO<sub>2</sub>(Y<sub>2</sub>O<sub>3</sub>) ceramic membrane electrodes, with the potentials of both being measured against a Ag/AgCl, 0.1 m KCl external pressure balanced reference electrode (EPBRE). These electrodes have been used extensively in the past in our laboratory to measure the pH of dilute, high-temperature aqueous solutions (1-5), but to our knowledge, this study is the first attempt to measure the pH of concentrated solutions at elevated temperatures.

### pH Electrodes

**Pt Bead Electrode.** A platinum bead hydrogen electrode was used to sense the pH of a solution at a given hydrogen fugacity (partial pressure). The hydrogen fugacity in the pressure vessel was established using a Pd/25%Ag hydrogen diffuser with the hydrogen fugacity being taken as that on the dry side of the diffuser (Figure 1). In some cases, the diffuser itself was used as the pH sensor, as in our previous work (6,7) and, more recently, that of Nagy and Yonco (8).

**Ytria-Stabilized Zirconia (YSZ) Electrode.** Our previous work (1-5) on measuring the pH of high-temperature, dilute solutions with Hg/HgO/ZrO<sub>2</sub>(Y<sub>2</sub>O<sub>3</sub>) electrodes initially indicated that this sensor experiences a "boric acid error" [compare the alkaline error in glass electrodes (9)] and hence might not be suitable for measuring the pH of concentrated boric acid solutions. However, difficulties early in this program with the hydrogen diffuser (including cracking of the pressure vessel) led us to reconsider the ceramic membrane sensor, and ultimately most of the data reported here were obtained with this sensor.

YSZ sensors were constructed by filling about one inch of a closed end ZrO<sub>2</sub> (9% Y<sub>2</sub>O<sub>3</sub>) tube (5 in. long, 1/4 in. OD and 5/32 in. ID) with a ground mixture of Hg/HgO (Figure 2). A mild steel wire was embedded in this mixture to serve as an electrical contact, and the tube was backfilled with high-temperature epoxy to form a tight seal. The upper part of the sensor was sheathed in heat-shrink polytetrafluoroethylene (PTFE) and then introduced into a standard CONAX fitting.

**External Pressure Balanced Reference Electrode (EPBRE).** The potentials of the platinum bead electrode and the Hg/HgO/ZrO<sub>2</sub>(Y<sub>2</sub>O<sub>3</sub>) sensor were measured against a Ag/AgCl, 0.1 m KCl external pressure balanced reference electrode of the type shown in Figure 2 (10). The potential of the reference electrode was corrected to the standard hydrogen scale using the data of Macdonald et al. (10).

### Measurement Cell

All experiments reported in this work were performed in a 75-mL Type 316 stainless steel pressure vessel equipped with ports for the introduction of the pH sensors and reference electrode, a thermocouple, and a stainless steel capillary tube to a pressure gauge (Figure 4). The vessel was heated with two 900-W thin-cast (WATLOW) heaters controlled by a microprocessor controller (WATLOW Series 910).

## Potential Measurements

All potentials were measured using a Keithley 617 electrometer having an input impedance of  $2 \times 10^{14} \Omega$ . Measurements were continuously monitored by a Macintosh microcomputer through an IEEE 488 interface.

## Solutions

All solutions were prepared by weight using doubly distilled water and AR grade chemicals.

## Procedure

All measurements were performed at  $25^\circ\text{C}$  intervals within the temperature range  $125^\circ$  to  $300^\circ\text{C}$ . The potentials of the two pH sensors were continuously monitored at each temperature for 30 minutes or until they had become stable. Generally, the potential remained constant to within  $\pm 5$  mV over the monitoring period. At the two highest boric acid concentrations, the solutions formed hard glasses when they cooled; these glasses had to be chipped from the pressure vessel. Removal of the glass invariably resulted in destruction of the YSZ sensor and the reference electrode.

## Results and Discussion

### Reference Electrodes

The potential of the platinum bead hydrogen electrode and that of the  $\text{Hg}/\text{HgO}/\text{ZrO}_2(\text{Y}_2\text{O}_3)$  pH sensor measured against the EPBRE were corrected to the standard hydrogen scale (SHE) using the empirical relation derived by Macdonald et al. (3,10).

$$E_{\text{SHE}}(T) = E_{\text{OBS}} + 0.286637 - 1.003217 \times 10^{-3} \Delta T + 0.0174478 \times 10^{-5} \Delta T^2 - 0.3030048 \times 10^{-8} \Delta T^3 \quad (1)$$

where  $\Delta T = T - 298.15$  and  $T$  is the Kelvin temperature. This correction is accurate to about  $\pm 10$  mV at  $275^\circ\text{C}$  but is considered (3,10) somewhat more accurate at lower temperatures ( $\pm 5$  mV at  $100^\circ\text{C}$ ).

Because the solutions employed in this study were concentrated, significant isothermal liquid junction potentials were expected to exist across the junction between the internal solution of the reference electrode and the test environment. Therefore, it was necessary to estimate the liquid junction potential so that the measured potential could be accurately referenced to the standard hydrogen scale. As in previous work (4), we estimated the isothermal junction potential using Henderson's equation:

$$E_j = -\sum D_i [(m_i)_2 - (m_i)_1] \quad (2)$$

where the summation is performed over all charged species in the system and subscripts 1 and 2 designate the two sides of the junction. The  $D_j$  coefficients are given in terms of the molal concentrations ( $m_j$ ) and equivalent conductances ( $\lambda_j$ ) by

$$D_j = RT|z_j|\lambda_j / (z_j F \sum |z_j| \bar{m}_j \lambda_j) \quad (3)$$

where  $z_j$  is the ionic charge and  $\bar{m}_j$  designates the mean concentration between the two compartments.

Because we did not know the exact composition of the system (although we knew the stoichiometric concentrations), we adopted the following approximations to calculate the isothermal liquid junction potential:

1. All salts are completely dissociated.
2. The concentration of borate  $[B(OH)_4^-]$  is equal to the stoichiometric concentration of NaOH (1 m).
3. The concentration of hydrogen ion is equal to  $10^{-pH}$  where the pH is determined iteratively to converge on  $-\log(m_{H^+})$ .
4. The concentration of  $OH^-$  is equal to  $10^{-(pK_w - pH)}$  where  $pK_w = -\log(K_w)$  and  $K_w$  is the ionic product of water.

Equivalent conductances were not available for  $B(OH)_4^-$ , but experimental data are available for the other species from the work of Quist and Marshall (11). Accordingly, we adopted the following values for  $\lambda_i$ :

$$\lambda_{H^+} = -2759.6378 + 17.5151 T - 0.028435 T^2 + 1.56794 \times 10^{-5} T^3 \quad (4)$$

$$\lambda_{OH^-} = -929.116 + 3.3085 T - 0.003754 T^2 - 7.326785 \times 10^{-6} T^3 \quad (5)$$

$$\lambda_{Na^+} = -85.971104 - 1.82398 T + 0.00726322 T^2 - 5.1394 \times 10^{-6} T^3 \quad (6)$$

$$\lambda_{HSO_4^-} = -226.5844 - 2.7298 T + 0.009087 T^2 - 6.4037 \times 10^{-6} T^3 \quad (7)$$

$$\lambda_{SO_4^{2-}} = -40.616 + 1.4136 T + 0.0076865 T^2 - 1.3204 \times 10^{-5} T^3 \quad (8)$$

$$\lambda_{Cl^-} = -150.66099 - 0.493813 T + 0.00554 T^2 - 4.396 \times 10^{-6} T^3 \quad (9)$$

where  $T$  is the Kelvin temperature. The equivalent conductance of  $B(OH)_4^-$  was taken to be equal to that for  $HSO_4^-$

$$\lambda_{B(OH)_4^-} = -226.5844 - 2.7289 T + 0.009097 T^2 - 6.4037 \times 10^{-6} T^3 \quad (10)$$

Isothermal liquid junction potentials calculated using the data listed above and equation (2) are summarized in Table 2.

### Hydrogen Electrode

The potential-determining reaction for the hydrogen electrode can be written as



which yields a Nernst potential of

$$E_{SHE} - E_j = -(2.303RT/2F) \log (P_{H_2}) - (2.303RT/F)pH \quad (12)$$

where  $P_{H_2}$  is the partial pressure (fugacity) of hydrogen. Rearrangement of equation (12) therefore yields

$$pH = F(E_j - E_{SHE})/2.303 RT - 1/2 \log (P_{H_2}) \quad (13)$$

where  $E_j$  is the liquid junction potential [equation (2)].

### YSZ Ceramic Membrane Electrode

As in our previous work (3), we write the Nernst equation for the Hg/HgO/ZrO<sub>2</sub>(Y<sub>2</sub>O<sub>3</sub>) pH sensor in the form

$$E_{SHE} - E_j = E^0 - [2.303RT/(2F)] \log a_{H_2O} - (2.303RT/F)pH \quad (14)$$

where the standard potential for the Hg/HgO internal reference is given by

$$E_{Hg/HgO} = 1.0540 - 14.177 \times 10^{-4} T + 9.193 \times 10^{-5} T \ln(T/298.15) + 3.5 \times 10^{-8} T^2 - 1.7996/T \quad (15)$$

where T is the Kelvin temperature and  $a_{H_2O}$  is the activity of water. The activity of water is defined as the ratio of the partial pressure of water above the solution to that above pure water at the same temperature. However, we lacked experimental data for  $a_{H_2O}$ , so we used values calculated from EPRI's chemistry code, MULTEQ (Table 3). The accuracy of these data is unknown.

$$pH = (F/2.303RT) (E_{Hg/HgO} - E_{SHE} + E_j) - 1/2 \log a_{H_2O} \quad (16)$$

In calculating the pH using either equation (13) or equation (16), we initialized the iterative procedure by first setting  $E_j = 0$ . This value was then used to estimate the liquid junction potential from equation (2), which in turn was used to calculate a new value of pH. The iterative procedure was repeated until convergence was achieved to 0.001 units in pH.

### Comparison of Measured and Calculated pH Values

Figures 5 through 12 summarize the pH data measured in this work and the values calculated by EPRI using MULTEQ. We estimate that the data measured with the Pt/H<sub>2</sub> electrodes are probably accurate to  $\pm 0.3$  at 125°C and to  $\pm 0.45$  at 300°C, and those measured with the YSZ electrode are accurate to  $\pm 0.35$  and  $\pm 0.5$ , respectively, at the same temperatures, depending upon the concentration. These uncertainties were established by differentiating equations (13) and (16) to yield

$$\delta \text{pH} = (F/2.303RT) \delta E + (1/2P_{\text{H}_2}) \delta P_{\text{H}_2} \quad (17)$$

$$\delta \text{pH} = (F/2.303RT) \delta E + (1/2a_{\text{H}_2\text{O}}) \delta a_{\text{H}_2\text{O}} \quad (18)$$

where  $\delta X$  is the estimated error in parameter X. Typically, the error in the measured potential is  $\pm 5$  mV, but when this value is corrected to the standard hydrogen scale, the error increases to  $\pm 15$  mV; the difference is due to the uncertainty ( $\pm 10$  mV) in the thermal liquid junction potential. The uncertainty in  $E_{\text{Hg}/\text{HgO}}$  has been estimated (3) from the thermodynamic data employed to be  $\pm 5$  mV. Finally, the error in  $E_j$  is difficult to estimate with precision because we do not know the accuracies of the  $\lambda_i$  values or know how applicable Henderson's equation is to concentrated solutions of the type employed here. Nevertheless, we estimated  $\delta E_j$  to be on the order of  $\pm 5$  mV for the dilute solutions and possibly as high as  $\pm 10$  mV for the more concentrated solutions. Accordingly, we estimated  $\delta E$  to vary between  $\pm 15$  mV and  $\pm 25$  mV for the Pt/H<sub>2</sub> electrodes and between  $\pm 20$  mV and  $\pm 30$  mV for the YSZ electrodes, with the higher values corresponding to the most concentrated solutions.

The uncertainty  $\delta P_{\text{H}_2}$  is estimated to be  $\pm 10\%$  of the partial pressure, because it was difficult to establish equilibrium across the hydrogen diffuser. Accordingly, we set  $\delta P_{\text{H}_2}/P_{\text{H}_2} \sim 0.1$ . A similar uncertainty is estimated for  $\delta a_{\text{H}_2\text{O}}/a_{\text{H}_2\text{O}}$ , although we do not have any experimental data for an independent check of this estimate. For the most concentrated solutions, the uncertainty in the value for  $\delta a_{\text{H}_2\text{O}}/a_{\text{H}_2\text{O}}$  could be considerably higher than 0.1; it could approach  $\pm 0.25$  ( $\delta a_{\text{H}_2\text{O}} = \pm 0.1$ ,  $a_{\text{H}_2\text{O}} \sim 0.2$ ) for solutions with boric acid concentrations above 10 m.

The data for the two highest boric acid concentrations, particularly for the 100 m B(OH)<sub>3</sub> system, are badly scattered. In neither case is the boric acid completely soluble at ambient temperature, but available data (12) show that the solubility increases rapidly as the temperature is raised. However, we had no way to determine whether the solid was completely dissolved at the highest experimental temperature, so it is possible that the system remained in two phases over the entire temperature range. To minimize the effect of incomplete boric acid dissolution, we performed one experiment in which we first heated the solution to 300°C and then measured the pH as the pressure vessel cooled (Figure 11). Good agreement was obtained between the measured and calculated pH at temperatures for 175°C < T < 275°C, but at lower temperatures, the measured pH diverged rapidly in the positive direction from the calculated values. This behavior is consistent with the formation of a glass, which we represent by the reactions



Thus, reaction of the mono boric acid species to form the glass causes the borate/boric acid equilibrium, reaction (19), to shift to the right, which releases hydroxide ion and increases the pH. We have chosen to write reaction (19) in terms of formation of a "metaborate" glass. The glass that forms is more likely to consist of a mixture of borate chains and sheets formed by six-membered rings. In any event, polymerization of the free boric acid entities will result in the release of hydroxide as described by reaction (20) and hence in the observed increase in pH.

Poor agreement was observed between the pH calculated for the 5 m B(OH)<sub>3</sub> solution and that measured with the YSZ electrode, although good agreement was obtained with one of two runs performed with the hydrogen electrode (Figure 8). However, the three runs performed using the ceramic membrane pH sensor gave consistent results that diverged by no more than ±0.2 pH units but were as much as 2 pH units more positive (alkaline) than the calculated values. We do not currently have an explanation for this observation.

Comparison of the measured and calculated data in Figures 5 through 12 indicates that the YSZ ceramic membrane electrode provides more consistent pH values than does the Pt/H<sub>2</sub> electrode. The large scatter observed in the data obtained with the hydrogen electrode is attributed to the difficulty in establishing an equilibrium partial pressure of hydrogen in the pressure vessel by means of the Pd/25%Ag diffuser. The main problem appears to be the difficulty in preventing hydrogen escaping from the vessel, probably by diffusion through seals and possibly through the vessel walls. Accordingly, the pH values calculated from the measured voltage and the assumed partial pressure of hydrogen using equation (13) could be greatly in error. On the other hand, the pH values calculated from the YSZ sensor are highly susceptible to uncertainty in E<sub>j</sub> (as is the hydrogen electrode), so the level of agreement between calculated and measured pH values found in this work is probably as good as can be expected. We should note that the calculated values themselves could also contain significant error because of uncertainties in equilibrium constants, poor definition of ion-pairing phenomena, and uncertainties in the activity coefficients of ionic and neutral species. Finally, both the calculated and experimental data show that the pH of the concentrated boric acid solution is quite low (pH < 3 for x ≥ 50), so B(OH)<sub>3</sub> concentrated into crevices by boiling in operating steam generators is expected to form highly acidic and possibly aggressive environments.

### Summary and Conclusions

Pt/H<sub>2</sub> and Hg/HgO/ZrO<sub>2</sub>(Y<sub>2</sub>O<sub>3</sub>) ceramic membrane electrodes have been used to measure pH versus temperature data for 1 m NaOH, 1 m NaOH + 1 m Na<sub>2</sub>SO<sub>4</sub>, 1 m NaOH + 1 m Na<sub>2</sub>SO<sub>4</sub> + x m B(OH)<sub>3</sub> (x = 2, 5, 20, 50, 100), and 1 m NaOH + 1 m Na<sub>2</sub>SO<sub>4</sub> + 1 m NaCl at temperatures between 125° and 300°C. These pH values were compared with data calculated using EPRI's chemistry code, MULTEQ. Allowing for the considerable uncertainties that exist in the isothermal liquid junction potential, the pressure of hydrogen in the pressure vessel (established by using a Pd/25%Ag diffuser), and the activity of water, particularly for the more concentrated solutions, the measured and calculated pH values agree reasonably well. Those measured using the YSZ

electrode were more consistent than those obtained using the hydrogen electrode. Even though considerable uncertainties may exist in the calculated values, because of errors in measured dissociation constants and calculated activity coefficients, and because of the poor definition of ion pairing phenomena, the generally reasonable agreement observed in this study between the calculated and experimental pH values greatly increases our confidence in the ability of MULTEQ to model the chemistry of high-temperature concentrated solutions of the type that exist in crevices in pressurized water reactor (PWR) steam generators. The concentrated boric acid solutions were calculated and observed to yield  $\text{pH} < 3$  for  $x \geq 50$ .

#### Acknowledgement

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#### References

1. S. Hettiarachchi, P. Kedzierzawski, and D. D. Macdonald, *J. Electrochem. Soc.*, **132**, 1866 (1985).
2. S. Hettiarachchi and D. D. Macdonald, *J. Electrochem. Soc.*, **131**, 2206 (1984).
3. D. D. Macdonald, S. Hettiarachchi, and S. J. Lenhart, *J. Solution Chem.*, **17**, 719 (1988).
4. D. D. Macdonald, P. Butler, and D. Owen, *Can. J. Chem.*, **51**, 2590 (1973).
5. D. D. Macdonald and D. Owen, *Can. J. Chem.*, **51**, 2747 (1973).
6. D. D. Macdonald, P. R. Wentreck, and A. C. Scott, *J. Electrochem. Soc.*, **127**, 1745 (1980).
7. D. D. Macdonald, C. Scott, and P. R. Wentreck, unpublished data, Project RP1168-1, Electric Power Research Institute, Palo Alto, CA, 1978/1979.
8. Z. Nagy and R. M. Yonco, *J. Electrochem. Soc.*, **133**, 2232 (1986).
9. Hubert T.S. Britton, *Hydrogen Ions*, Vol. 1, Chap. 7 (D. Van Nostrand Company, Inc., London, 1955).
10. D. D. Macdonald, A. C. Scott, and P. R. Wentreck, *J. Electrochem. Soc.*, **126**, 908 (1979).
11. A. S. Quist and W. L. Marshall, *J. Phys. Chem.*, **69**, 2984, (1965).
12. H. Stephen and T. Stephen, editors, *Solubility*, Vol. 1 (Macmillan, New York, 1963).

Table 1  
TEST SOLUTIONS

Solution No.	Composition	No. of Tests
1	1 m NaOH	2
2	1 m NaOH + 1 m Na <sub>2</sub> SO <sub>4</sub>	2
3	1 m NaOH + 1 m Na <sub>2</sub> SO <sub>4</sub> + 2 m B(OH) <sub>3</sub>	2
4	1 m NaOH + 1 m Na <sub>2</sub> SO <sub>4</sub> + 5 m B(OH) <sub>3</sub>	5
5	1 m NaOH + 1 m Na <sub>2</sub> SO <sub>4</sub> + 20 m B(OH) <sub>3</sub>	3
6	1 m NaOH + 1 m Na <sub>2</sub> SO <sub>4</sub> + 50 m B(OH) <sub>3</sub>	1
7	1 m NaOH + 1 m Na <sub>2</sub> SO <sub>4</sub> + 100 m B(OH) <sub>3</sub>	2
8	1 m NaOH + 1 m Na <sub>2</sub> SO <sub>4</sub> + 1 m NaCl	2

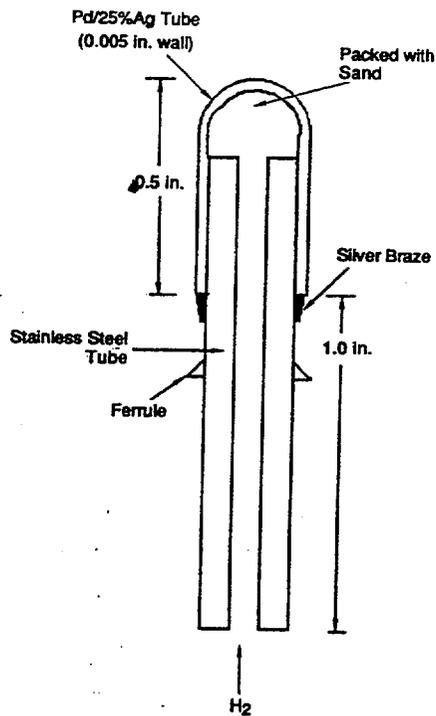
Table 2  
ESTIMATED LIQUID JUNCTION POTENTIALS (mV)

Solution	Temperature (°C)							
	125	150	175	200	225	250	275	300
1	15.6	15.8	15.6	15.2	14.8	14.2	13.3	12.3
2	10.7	10.3	9.7	9.0	8.1	7.0	5.6	3.8
3	9.4	9.5	9.6	9.7	9.6	9.4	9.2	8.8
4	8.5	9.0	9.5	10.0	10.5	10.9	11.1	11.2
5	7.5	8.4	9.4	10.4	11.5	12.5	13.6	14.7
6	7.2	8.2	9.3	10.5	11.8	13.0	14.3	15.6
7	7.0	8.2	9.3	10.6	11.9	13.2	14.6	16.0
8	7.1	6.8	6.4	6.0	5.4	4.7	3.9	2.9

Table 3  
ACTIVITY OF WATER

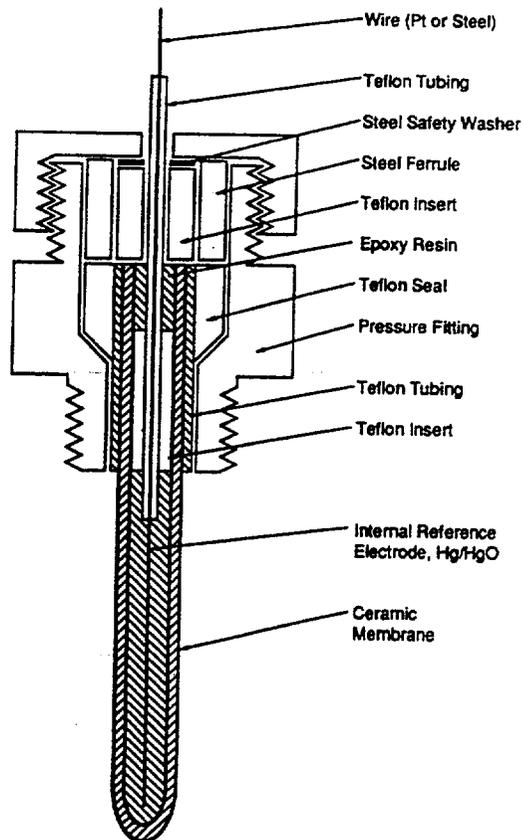
Solution No.	Temperature (°C)							
	125	150	175	200	225	250	275	300
1	0.968	0.968	0.968	0.970	0.971	0.972	0.973	0.975
2	0.930	0.932	0.934	0.936	0.939	0.942	0.946	0.952
3	0.930	0.931	0.933	0.936	0.939	0.943	0.949	0.958
4	0.894	0.894	0.895	0.895	0.895	0.895	0.896	0.898
5	0.670	0.667	0.663	0.657	0.650	0.642	0.633	0.625
6	0.375	0.368	0.360	0.349	0.336	0.322	0.307	0.394
7	0.142	0.135	0.128	0.119	0.109	0.099	0.089	0.081
8	0.894	0.897	0.900	0.904	0.908	0.913	0.919	0.928

Rearrangement of equation (14) therefore yields the pH as



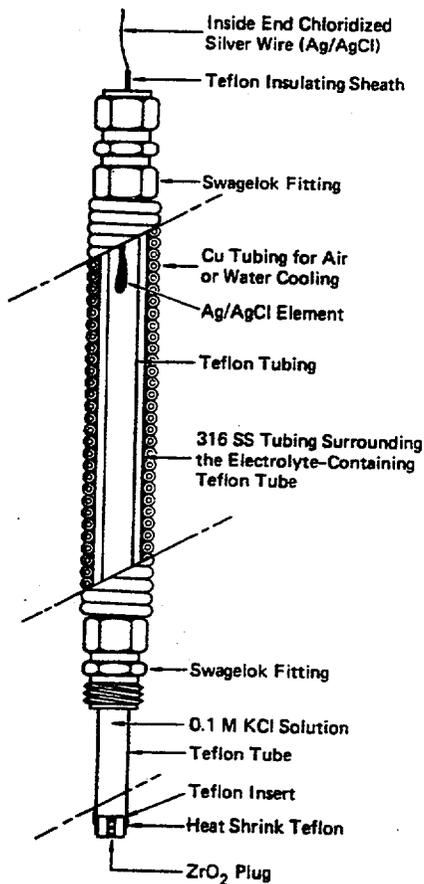
RA-6117-1

Figure 1. Design of Pd/25%Ag Hydrogen Diffuser



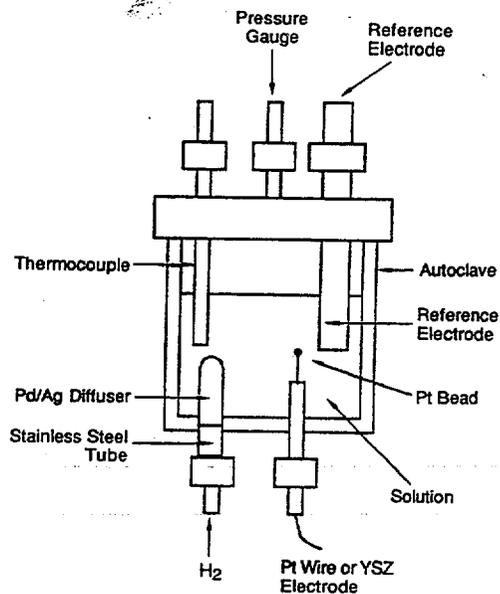
RA-M-320583-13

Figure 2. Ytria-Stabilized Zirconia pH Sensor Assembly



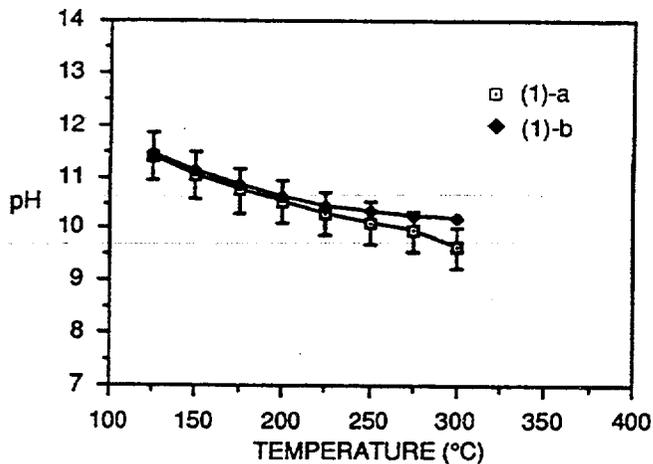
RA-320583-11A

Figure 3. External Pressure-Balanced Reference Electrode Assembly



RA-6117-2

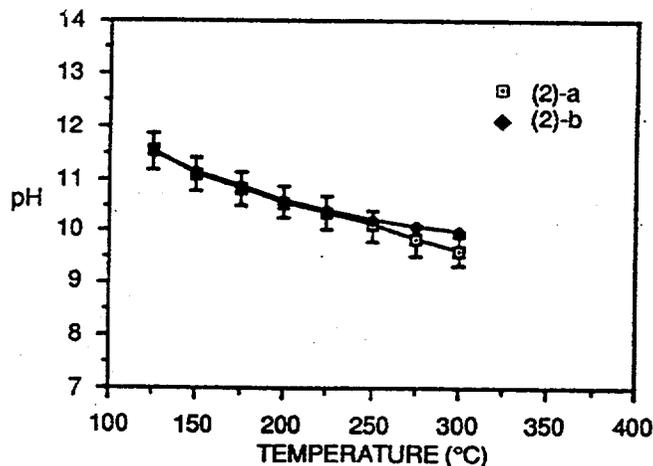
Figure 4. Schematic of test cell showing electrode configuration for measuring the pH of concentrated solutions at elevated temperatures.



RA-6117-3

Figure 5. Plots of pH versus temperature for 1 m NaOH solution.

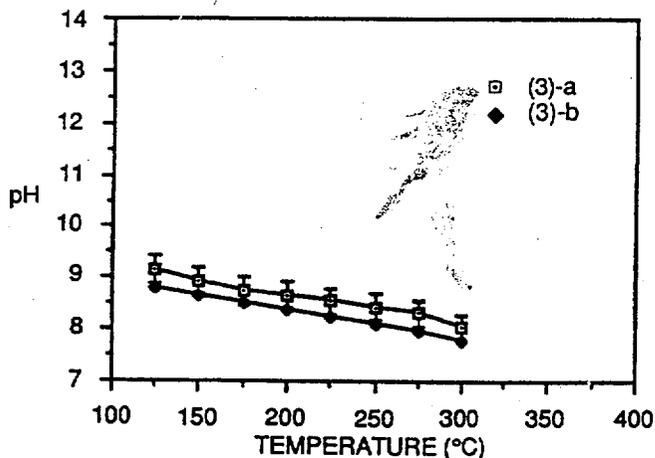
(1)-a: Measured using Hg/HgO/ZrO<sub>2</sub>(Y<sub>2</sub>O<sub>3</sub>) electrode.  
 (1)-b: Calculated using MULTEQ.



RA-6117-4

Figure 6. Plots of pH versus temperature for 1 m NaOH + 1 m Na<sub>2</sub>SO<sub>4</sub> solution.

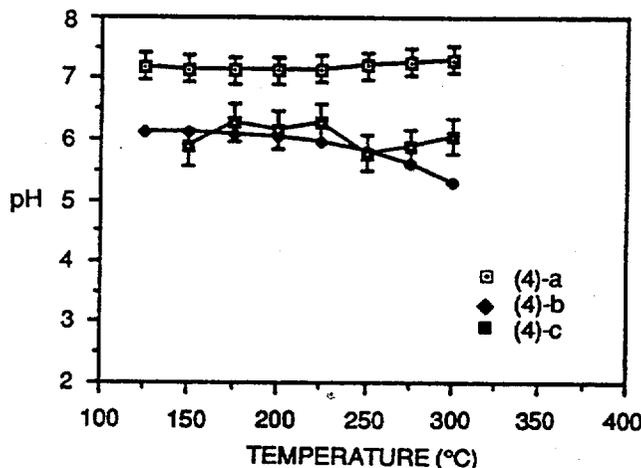
(2)-a: Measured using Hg/HgO/ZrO<sub>2</sub>(Y<sub>2</sub>O<sub>3</sub>) electrode.  
 (2)-b: Calculated using MULTEQ.



RA-6117-5

Figure 7. Plots of pH versus temperature for 1 m NaOH + 1 m Na<sub>2</sub>SO<sub>4</sub> + 2 m B(OH)<sub>3</sub> solution.

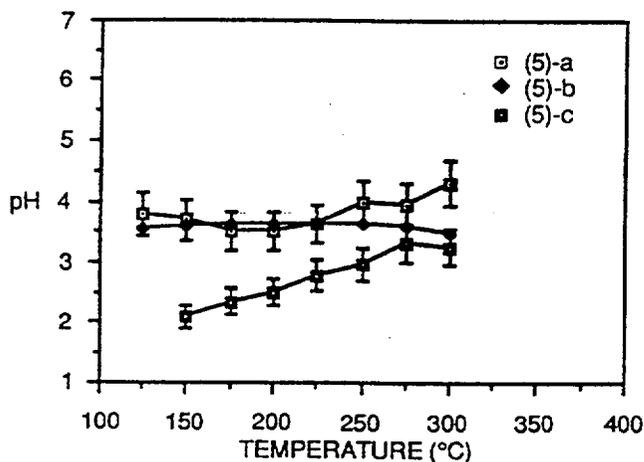
(3)-a: Measured using Hg/HgO/ZrO<sub>2</sub>(Y<sub>2</sub>O<sub>3</sub>) electrode.  
 (3)-b: Calculated using MULTEQ.



RA-6117-6

Figure 8. Plots of pH versus temperature for 1 m NaOH + 1 m Na<sub>2</sub>SO<sub>4</sub> + 5 m B(OH)<sub>3</sub> solution.

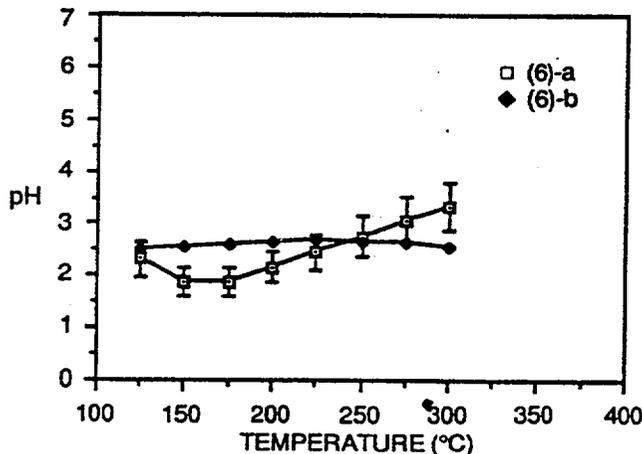
(4)-a: Measured using Hg/HgO/ZrO<sub>2</sub>(Y<sub>2</sub>O<sub>3</sub>) electrode.  
 (4)-b: Calculated using MULTEQ.  
 (4)-c: Measured using Pt/H<sub>2</sub> electrode.



RA-6117-7

Figure 9. Plots of pH versus temperature for 1 m NaOH + 1 m Na<sub>2</sub>SO<sub>4</sub> + 20 m B(OH)<sub>3</sub> solution.

(5)-a: Measured using Hg/Hg/ZrO<sub>2</sub>(Y<sub>2</sub>O<sub>3</sub>) electrode.  
 (5)-b: Calculated using MULTEQ.  
 (5)-c: Measured using Pt/H<sub>2</sub> electrode.



RA-6117-8

Figure 10. Plots of pH versus temperature for 1 m NaOH + 1 m Na<sub>2</sub>SO<sub>4</sub> + 50 m B(OH)<sub>3</sub> solution.

(6)-a: Measured using Hg/HgO/ZrO<sub>2</sub>(Y<sub>2</sub>O<sub>3</sub>) electrode.  
 (6)-b: Calculated using MULTEQ.

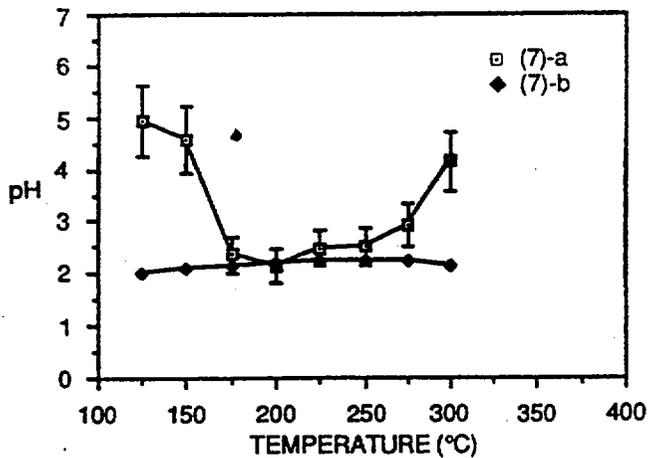


Figure 11. Plots of pH versus temperature for 1 m NaOH + 1 m Na<sub>2</sub>SO<sub>4</sub> + 100 m B(OH)<sub>3</sub> solution.  
 (7)-a: Measured using Hg/HgO/ZrO<sub>2</sub>(Y<sub>2</sub>O<sub>3</sub>) electrode.  
 (7)-b: Calculated using MULTEQ.

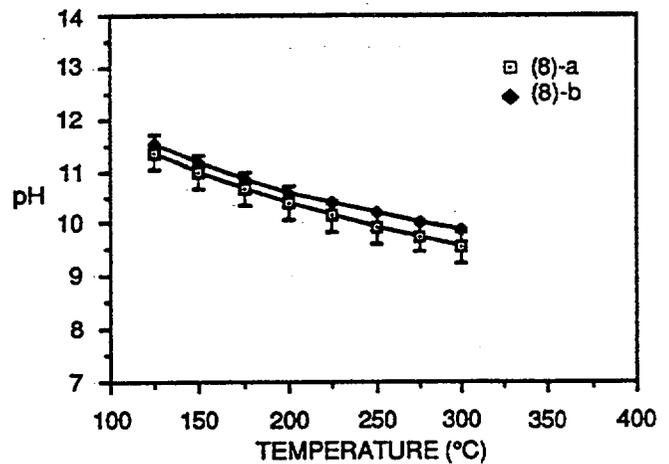


Figure 12. Plots of pH versus temperature for 1 m NaOH + 1 m Na<sub>2</sub>SO<sub>4</sub> + 1 m NaCl solution.  
 (8)-a: Measured using Hg/HgO/ZrO<sub>2</sub>(Y<sub>2</sub>O<sub>3</sub>) electrode.  
 (8)-b: Calculated using MULTEQ.

### DISCUSSION

Presenting Author: D. Macdonald

Questioner: P. Andresen, GE, R&D

Question/Comments: In most of your solutions above ~10m, the activity of water plays an important role. Can you comment on (1) the possible circular error in your use of MULTEQ calculated activity of water and (2) loss of water to the vapor space or through the seals, etc. of your autoclave.

Reply: (1) You are quite correct. However, the water activities predicted by MULTEQ are typical of concentrated solutions so that any error is within the limits of uncertainties claimed.

(2) We minimized the vapor space as much as possible to minimize the error. Furthermore, water is strongly bound to borate (as indicated by the water activity) so that the error from this source is probably not too large.

### DISCUSSION

Presenting Author: D. Macdonald

Questioner: J. Atkinson, CEGB-CERL

Question/Comments: Can the yttria stabilized zirconia electrode be manufactured in a miniature form suitable for insertion into cracks or crevices.

Reply: We have tried to make miniature electrodes but with little success so far. I believe that the development of such electrodes should be an activity of high priority.

### DISCUSSION

Presenting Author: P. Paine

Questioner: T. Beineke, Combustion Engineering, Inc.

Question/Comment: How many cycles of concentration were used in the MULTEQ calculations?

Reply: Since the laboratory system is a water solid system no concentration factors were used in these calculations. Dr. Beineke correctly implies that with the boric acid volatility from a crevice, MULTEQ or any other computer code would be hard pressed at the present to calculate the SRI measured pHs.

### DISCUSSION

Presenting Author: D. Macdonald

Questioner: P. Gonzalez, Ontario Hydro

Question/Comments: The H<sub>3</sub>BO<sub>3</sub> pH that was measured was quite low, 2-5. How could this be related with the apparent inhibiting effect of H<sub>3</sub>BO<sub>3</sub> on the denting process?

Reply: I believe that inhibition of steel in concentrate boric acid is due to the formation of a passivating compound between iron and borate, although to my knowledge this has never been confirmed.

## DISCUSSION

Presenting Author: P. Paine

Questioner: J. Gorman, Dominion Engineering, Inc.

Question/Comment: What concentrations of boric acid can be expected to occur in steam generator crevices?

Reply: Equilibrium boric acid concentrations will depend on crevice pH (presence of NaOH and KOH as well as acidic species), boric acid volatility, reactions to produce precipitated Na and Fe borates, bulk water boric acid concentrations feeding the crevices and locally available crevice superheat ( $T_{pri} - T_{sat}$ ). We don't expect a uniform concentration of boric acid to form in the crevice, but measurements have been made of solid borate compounds by several techniques indicating that solubility was exceeded on a local basis. Corrosion rates have been reduced in laboratory tests to levels that imply a pH reduction of 3 pH units in the presence of concentrated NaOH.