

## **Ag/AgCl Reference Electrode for Use in PWR Coolants**

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### **Abstract**

*To predict the corrosion behavior of metals the potential measurement is very important. our goal is the development of electrochemical corrosion potential (ECP) electrodes for condition monitoring and life management of secondary systems. The external pressure-balanced Ag/AgCl (0.1 M KCl) reference electrode was developed. The potential of Ag/AgCl electrode vs. SCE at ambient temperature was calculated and compared with the measured values, which showed good agreement with calculated values within  $\pm 1$  mV. The Ag/AgCl electrode performance test in reducing condition at low temperature was conducted. The Ag/AgCl electrode did not show any potential drift within one day of test period. The potential of Pt electrode was more positive than the predicted value. The causes of the difference may be the uncertainty of hydrogen fugacity value or temperature instability. But more analysis is need. The high temperature/high pressure autoclave test for Ag/AgCl reference electrode in reducing environment is planned.*

## 1. Introduction

The corrosion of metals in PWR operating water is the primary causes of the degradation and fouling of steam generator (SG), piping, and turbine. As the results of research about corrosion of metals in high temperature/high pressure (HT/HP) water, we can predict the corrosion behavior of metals as function of electrochemical corrosion potential (ECP) and pH. Based on these results, our goal is the development of ECP electrodes for condition monitoring and life management of secondary systems. Also, electrodes having advanced performance will be developed.

The purpose of reference electrode is to measure stable and reproducible potential to particular electrodes. A major problem in all high temperature electrochemical studies a aqueous system is choosing a suitable reference electrode[1]. General description for reference electrodes have been stated by Ives and Janz[2]. The designs and performances of reference electrodes for high temperature aqueous electrochemical studies are reviewed by Macdonald[1]. Many kinds of reference electrodes for high temperature system have been developed. For examples, hydrogen-hydrogen ion electrode is the most suitable reference electrode for high temperature aqueous work[1]. But in spite of many advantages, due to the problem of hydrogen fugacity measurement this electrode is not widely used except for thermodynamic studies. The silver-silver halide reference electrodes have been extensively studied[1]. Ag/AgCl reference electrode is well-defined, widely used, and very reliable electrode for high temperature work[3-9]]. But in high temperature and reducing environment, provided that the AgCl surface is not well protected, the decomposition rate of AgCl is very high[7]. To solve this problem the external reference electrode of which AgCl part was maintained in ambient temperature was developed. The electrode design with heat-shrinkable polytetrafluoroethylene (PTFE) body and a porous zirconia plug for liquid junction was established. The Ag/AgCl-Sapphire reference electrode by replacing PTFE with sapphire was developed and successfully applied to boiling water reactors[8]. And a buffered tungsten reference electrode also was

developed[10]. The main feature of this electrode is the potential stability in high reducing environments.

## 2. Experimental

### 2.1 Thermodynamic Calculation

When we measure the potential by using Ag/AgCl reference electrode in HT/HP systems, it is needed to transform the measured potential into the thermodynamically meaningful values. The potential to standard hydrogen electrode (SHE) scale is usually used. Therefore it is needed to know the potential difference between Ag/AgCl electrode and SHE at the temperature of interest. Fig. 1 shows the inter-relationship among Ag/AgCl electrode, SHE, and working electrode (WE). The observed potential by using the external Ag/AgCl electrode can be shown as follows.

$$\Delta E_{obs}^{Ex} = \Delta E_{SHE}(T) - \Delta E_{Ag/AgCl}(T) + \Delta E_{Th} \quad (1)$$

where,  $\Delta E_{obs}^{Ex}$  = the measured potential of an working electrode  $E - E_{Ag/AgCl}(25^\circ C)$   
 $\Delta E_{SHE}(T)$  = the potential of the working electrode against the SHE  
under the same conditions  
 $\Delta E_{Ag/AgCl}(T)$  = the isothermal potential of the Ag/AgCl electrode vs. the  
SHE at the temperature of interest  
 $\Delta E_{Th}$  = the potential of the thermal cell  $Ag - AgCl(25^\circ C) / KCl(M) /$   
 $Ag - AgCl(T)$

Potentials for the symmetrical thermocell  $Ag - AgCl(25^\circ C) / KCl / Ag - AgCl(T)$ ,  $E_{Th}$  have been determined by Macdonald et al.[11].  $E_{Ag/AgCl}(T)$  has been measured by Greeley et al.[12]. By using the measured thermocell potential and  $E_{Ag/AgCl}(T)$  Macdonald has constructed the polynomial equation showing the relationship between external Ag/AgCl electrode and  $E_{SHE}(T)$ .

$$\begin{aligned} \Delta E_{SHE}(T) &= \Delta E_{obs}^{Ex} + \Delta E_{Ag/AgCl}(T) - \Delta E_{Th} \\ \Delta E_{SHE}(T) &= \Delta E_{obs}^{Ex} + D_0 + D_1 \Delta T + D_2 \Delta T^2 + D_3 \Delta T^3 \end{aligned} \quad (2)$$

where,  $\Delta T = T - 25$

Table 1 shows the coefficients of Eq. (2), and Fig. 2 shows  $E_{SHE}(T)$  as the

function of temperature with Eq. (2). In Fig. 2, 'Extrapolated region' means that in this region it exceeds the experimental range.

## 2.2 Experimental Apparatus and Procedures

We adopted the external electrode design for Ag/AgCl reference electrode, which we named EREP(External Reference Electrode with PTFE). Fig. 3 shows the schematic diagram of the developing Ag/AgCl reference electrode, which is primarily based on Danielson's design[4]. The heat-shrinkable PTFE tube has the temperature limit, and the joint with zirconia liquid junction is loosened and the electrolyte leakage problems is caused. To mitigate this problem, it can be possible to insert the zirconia plug part into the Rulon adaptor and compress the adaptor with high pressure fitting. The procedures for making the electrode is briefly described as follows. 1/8" OD Ag rod doped with AgCl is inserted into the PTFE tube filled with the 0.1 M KCl. For high pressure application it is compressed with *Swagelok*<sup>®</sup> fittings and aluminium retainer is applied to prevent ejection of the silver rod. Ag/AgCl electrode should be cooled to maintain the ambient temperature. A glass wick which is wetted and then inserted into the electrode is also employed.

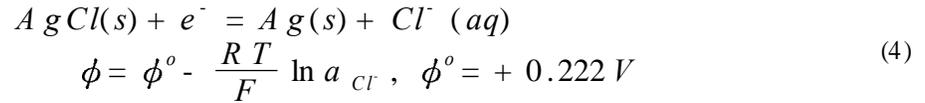
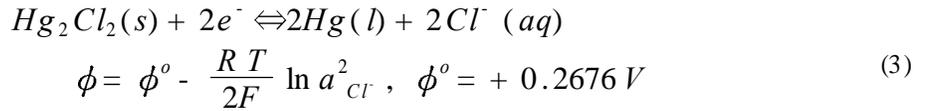
EREP performance test was carried out at low temperature. The testing EREP does not have the rulon adaptor. If the EREP passes in the low temperature test, it can be tested in high temperature autoclave. Fig. 4 shows the schematic diagram of experimental system. The potential variation of EREP and Pt electrode vs. saturated calomel electrode (SCE) was measured. The electric heater was located around the test glass cell and the potential variation with temperature also was measured. 0.01 M H<sub>3</sub>BO<sub>3</sub> and 0.01 M LiOH mixed solution was used. The test solution pH was 9.25 at 24.5 but by other work, pH is 10.62 at 25 [13]. The cause of the difference between measured value and reference value will be analyzed later.

At the aerated condition the potential was measured. And as the test solution was purged with 4% hydrogen and 96% argon continuously, the potential variation measured. The gas flow rate was maintained at about 150 cc/min through the experiment.

### 3. Results and Discussion

#### 3.1 EREP vs. SCE in the Saturated KCl Solution

The potential of EREP vs. SCE in the saturated KCl solution was measured. As a result, the measured value was 46 mV at 25 °C. The theoretical potential difference between Ag/AgCl electrode vs. SCE was calculated.



If we know the activity and concentration of chlorine ion, the half-cell potential can be calculated by Eq. (3) and (4). But it can be possible to calculate the potential with the mean ionic activity coefficient data. Table 2 shows the solubility of KCl and Table 3 shows the mean ionic activity coefficient of KCl.

$$\phi = \phi^\circ - 2.303 \frac{RT}{F} \log \gamma_{\pm} m \quad (5)$$

For SCE @ 25 °C ,

$$\begin{aligned} \phi &= 0.2676 - 2.303 \frac{(8.314)(298.15)}{96485} \log (0.590 \times 4.811) \\ &= 0.241 \text{ V} \end{aligned}$$

For SCE @ 12 °C ,

$$\begin{aligned} \phi &= 0.2676 - 2.303 \frac{(8.314)(285.15)}{96485} \log (0.5634 \times 4.27) \\ &= 0.246 \text{ V} \end{aligned}$$

For Ag/AgCl/Cl<sup>-</sup> (0.1m) @ 25 °C ,

$$\begin{aligned} \phi &= 0.222 - 2.303 \frac{(8.314)(298.15)}{96485} \log (0.768 \times 0.10) \\ &= 0.288 \text{ V} \end{aligned}$$

For Ag/AgCl/Cl<sup>-</sup> (0.1m) @ 12 °C ,

$$\begin{aligned}\phi &= 0.222 - 2.303 \frac{(8.314)(285.15)}{96485} \log(0.7697 \times 0.10) \\ &= 0.285 \text{ V}\end{aligned}$$

The calculated and predicted values are summarized in Table 3. The calculated values show good agreement with the predicted values within  $\pm 1$  mV.

### 3.2 EREP Performance Test

Fig. 5 shows the potential of EREP and Pt electrode vs. SCE with temperature variation. In Fig. 5, 'Ag/AgCl Temperature' means the wall temperature of the external Ag/AgCl electrode part exposed to air. And 'SCE Temperature' means the wall temperature of the SCE part exposed to air.

At the aerated condition, the potential of EREP vs. SCE was +51 mV and +283 mV for Pt electrode. After the solution was purged with 4% hydrogen gas, EREP potential showed no drift of potential and was maintained stably. The potential of Pt electrode was dropped drastically to the negative direction, and readily stabilized at -678 mV vs. SCE. We can calculate the potential of Pt electrode provided that the fugacity of hydrogen and pH of solution is known.

$$\begin{aligned}2H^+ + 2e^- &\Leftrightarrow H_{2(g)}, \quad E^o = 0.0 \text{ V} \\ E &= E^o - \frac{RT}{2F} \ln \frac{f_{H_2}}{a_{H^+}^2} \\ &= - \frac{RT}{2F} \ln f_{H_2} + \frac{RT}{F} \ln a_{H^+} \\ &= - 2.303 \frac{RT}{2F} \log f_{H_2} - 2.303 \frac{RT}{F} pH\end{aligned}\quad (6)$$

Above Eq. (4) the hydrogen fugacity can be calculated by below Eq. (5)[2].

$$\begin{aligned}f_{H_2} &= P_{H_2} e^{\frac{BP_{H_2}}{RT}} \\ P_{H_2} &= \text{Pressure of hydrogen, } J/cm^3 \\ R &= \text{Universal gas constant, } J/mol \cdot K \\ T &= \text{Temperature, } K \\ B &= \text{The second virial coefficient for hydrogen, } cm^3/mol\end{aligned}\quad (7)$$

The second virial coefficient, B can be also calculated by using Eq. (8)[2].

$$B = 17.42 - 314.7 T^{-1} - 211100 T^{-2}, [cm^3/mol] \quad (8)$$

The Pt electrode potential can be calculated under the condition of 4% hydrogen and the solution pH of 9.25 at 25 .

$$\begin{aligned} f_{H_2} &= (0.04 \text{ atm}) \exp \frac{(13.97 \text{ cm}^3/mol)(0.04 \times 0.1013 \text{ J/cm}^3)}{(8.314 \text{ J/mol} \cdot \text{K})(298.15 \text{ K})} \\ &= 0.04 \text{ atm} \end{aligned}$$

Eq. (8) is substituted with the calculated fugacity value and the potential can be calculated.

$$\begin{aligned} E &= - 2.303 \frac{(8.314)(298.15)}{2(96485)} \log 0.04 - 2.303 \frac{(8.314)(298.15)}{96485} (9.25) \\ E &= - 0.506 \text{ V} \end{aligned}$$

The measured potential is more positive than the predicted value by 69 mV. The unstability of solution temperature and the uncertainty of hydrogen fugacity can be the causes of the difference. EREP potential was changed corresponding to the solution temperature variation. It is thought that the effect of the thermal liquid junction potential appears. From Eq. (8), the potential is proportional to the solution temperature. As the temperature increase, the potential goes to more negative side. In the reducing environment, EREP shows no potential drift within test period of about one day. But the temperature was not maintained at constant value.

#### 4. Conclusion

The external pressure-balanced Ag/AgCl (0.1 M KCl) reference electrode was developed. The potential of Ag/AgCl electrode vs. SCE at ambient temperature was calculated and compared with the measured values, which showed good

agreement with calculated values within  $\pm 1$  mV. EREP performance test in reducing condition at low temperature was conducted. EREP did not show any potential drift within one day of test period. The potential of Pt electrode was more positive than the predicted value. The causes of the difference may be the uncertainty of hydrogen fugacity value or temperature instability. But more analysis is need. The HT/HP autoclave test for EREP in reducing environment is planned.

### **Acknowledgement**

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Table 1. The coefficients for the polynomial equation for  $E_{SHE}(T) - E_{obs}^{Ex}$  [11].

M (mole/kg)	$D_0$	$10^3 D_1$	$10^5 D_2$	$10^8 D_3$
0.010	0.343185	- 1.005690	0.054081	- 0.549061
0.102	0.286637	- 1.003217	0.017447	- 0.303004

Table 2. Solubility of KCl[14].

Temp. ( )	Solubility (g/ 100g of H <sub>2</sub> O)
0	28.07
12	31.81
25	35.87

Table 3. Mean Ionic Activity Coefficient of KCl(aq)[14].

Molality (mol/kg)	Temperature		Comment
	25	12	
0.1	0.768	0.7697	
4.0	0.578	0.5603	
4.27	0.582	0.5634	KCl solubility @ 12
4.5	0.585	0.5661	
4.811	0.590	0.5705	KCl solubility @ 25
5.0	0.593	0.5731	

Table 4. Potential difference between Ag/AgCl (0.1 M KCl) and SCE.

Temperature	Potential (V)			
	SCE	Ag/AgCl	pre.	meas.
25	0.241	0.288	0.047	0.046
12	0.246	0.285	0.039	0.040 ± 0.001

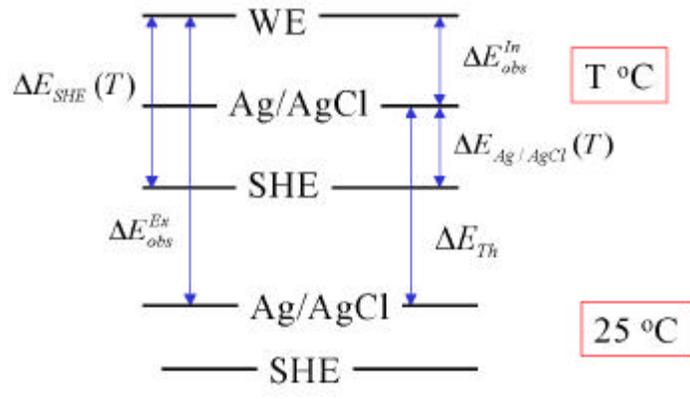


Figure 1. Schematic view showing potential relationship among SHE, Ag/AgCl electrode, and working electrode with temperature[5].

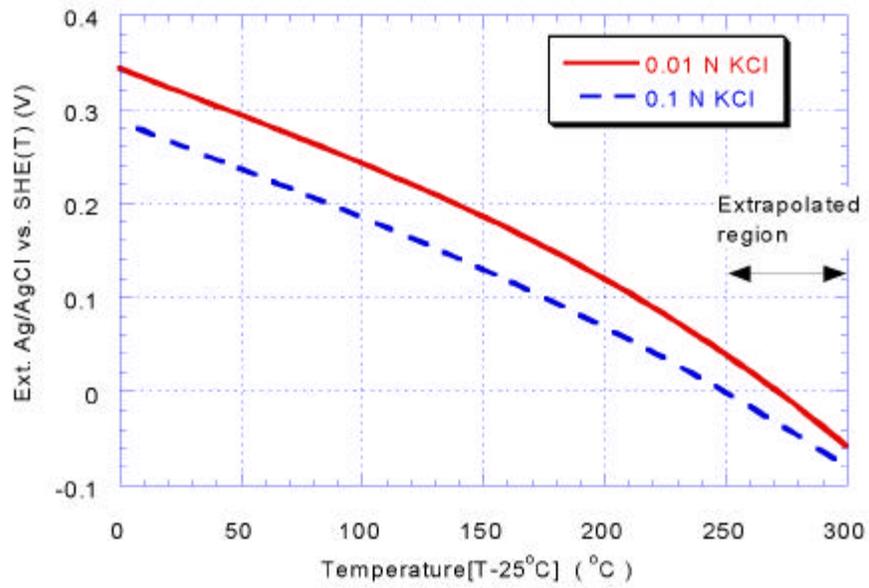
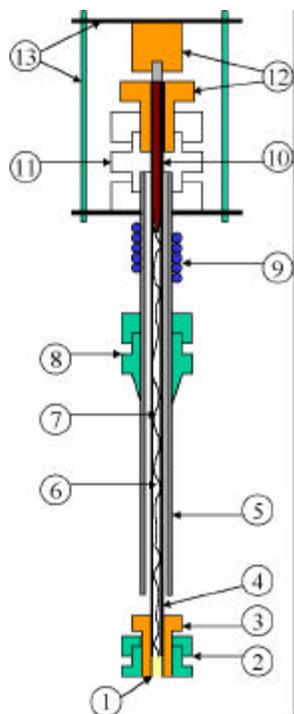


Figure 2. Potential of external pressure-balanced Ag/AgCl (0.1 M KCl) electrode vs. SHE(T). (Replotted from Ref. [5])



#	Materials Description	Dimension or Composition	Comment
1	Zirconia liquid junction	3 mm dia.	
2	Swagelok Union Fitting	1/4"	
3	Rulon adapter		
4	Heat-shrinkable PTFE		
5	SS tube	1/4" OD	316SS
6	Electrolyte	0.1 M KCl	
7	Glass wick		
8	Swagelok Female Adapter		
9	Cooler		
10	Ag/AgCl electrode	1/8" Dia.	
11	Swagelok Union Fitting	1/4"	
12	Rulon Adapter		
13	Restrainer	Al plate & threaded rod	

Figure 3. Schematic diagram and part list of EREP.

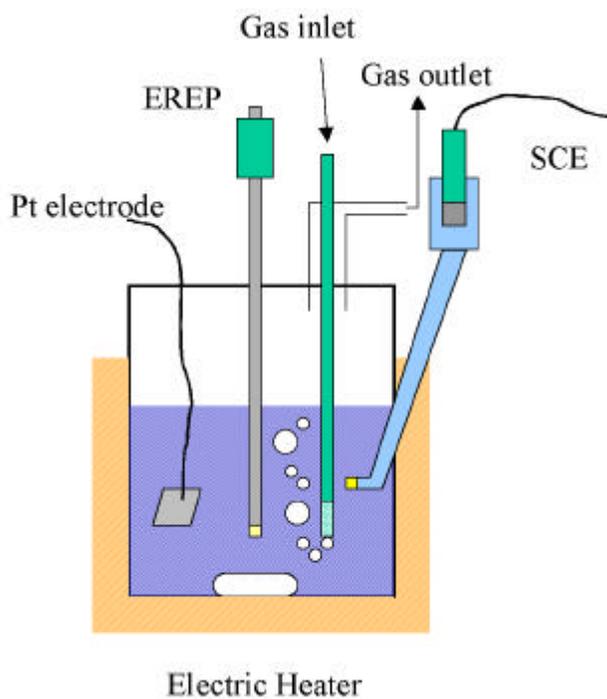


Figure 4. Experimental apparatus for EREP test in reducing environment.

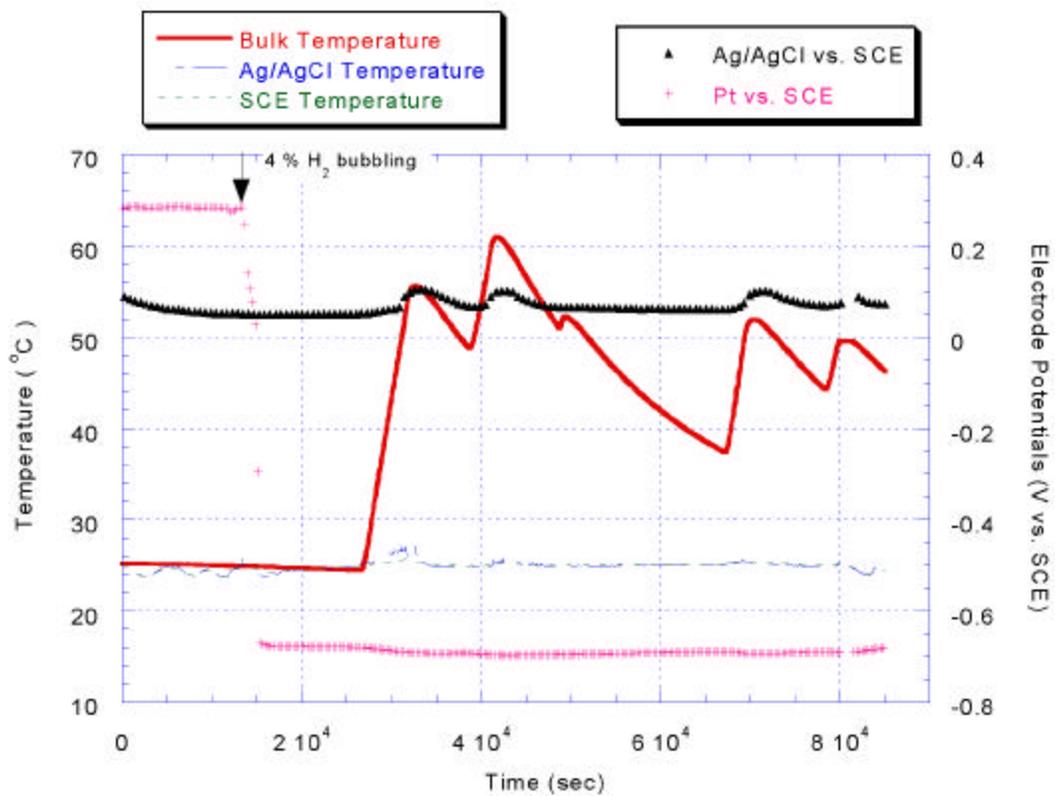


Figure 5. Potential of EREP and Pt electrode vs. SCE with temperature variation.