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Behaviour of reference electrodes in the monitoring of corrosion potential at high temperature

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Abstract

The main problem of corrosion potential measurements is the necessity to develop a reliable high temperature reference electrode. The aim of this work was to study the behaviour of three types of high temperature reference electrodes that have been developed for use in a BWR type reactor operating conditions. The reference electrodes were copper/copper(I) oxide with yttria-stabilized zirconia (YSZ) membrane; a silver/silver chloride couple and platinum. The application of these electrodes to corrosion potential monitoring is illustrated with several examples in different environments. The thermodynamic behaviour and stability of these sensors have been studied. Correlations between corrosion potential and water chemistry have been determined. © 1997 Elsevier Science S.A.

1. Introduction

Corrosion damage of nuclear materials in high temperature water environments can be frequently related to water chemistry. The importance of the specific environment and the associated oxidizing conditions on corrosion has long been recognized. Corrosion potential of a metal or alloy exposed to that aqueous solution is a key parameter for determining the material corrosion behaviour.

In making electrochemical potential (ECP) measurements at high temperatures, the main difficulty is in developing a reliable reference electrode. Design of high temperature reference electrodes was very important during '80s, and reference electrodes of many types and designs were developed, but each of them still has limitations in their uses. So, great care is required to assure that valid and useful data are being obtained.

The requirements, to obtain reliable data with a reference electrode, are: electrode potential independent of the environment; chemical and thermodynamic stability; reproducible measurements; electrode potential knowledge on a thermodynamic scale such as standard hydrogen electrode (SHE) and so on. Particular emphasis has been placed on the improvements of system integrity, reliability and materials stability.

In this study three types of reference electrodes have been fabricated with some modifications and improvements with respect to the electrodes found in literature data, as follows.

(1) Ag/AgCl electrode is a silver wire with electrodeposited silver chloride, enclosed in a solid Rulon chamber, filled with demineralized water (Fig. 1). Some silver chloride crystals are added in order to avoid changes in silver chloride solubility with temperature. As long as the solubility of silver chloride is known, the potential of the refer-

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ence electrode is easily calculated in a SHE scale, using the Nernst equation.

(2) Cu/Cu_2O electrode consists of a yttria-stabilized zirconia (YSZ) closed-end tube, filled with an internal junction of copper/cuprous oxide solid mixture (Fig. 2). It can serve as a membrane type electrode because there is a direct relationship between the conduction of oxygen ions through the ceramic and the pH in the adjacent aqueous phase (Niedrach, 1982). In this case, it would work as a membrane-type pH sensor and when the pH of the system is known and constant, it would act as a reference electrode.

(3) Platinum wire can be used as a reference, only when there is a stoichiometric excess of dissolved hydrogen concentration. Then this sensor acts as a reversible hydrogen electrode and when pH and

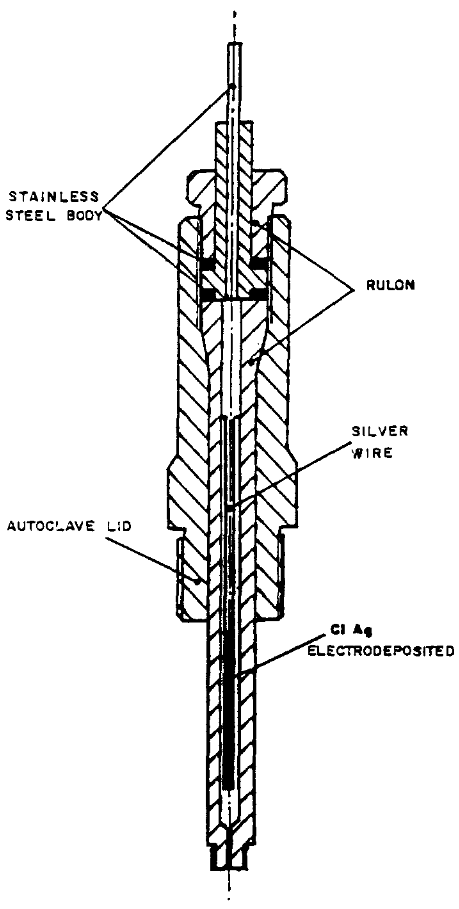

Fig. 1. Ag/AgCl reference electrode.

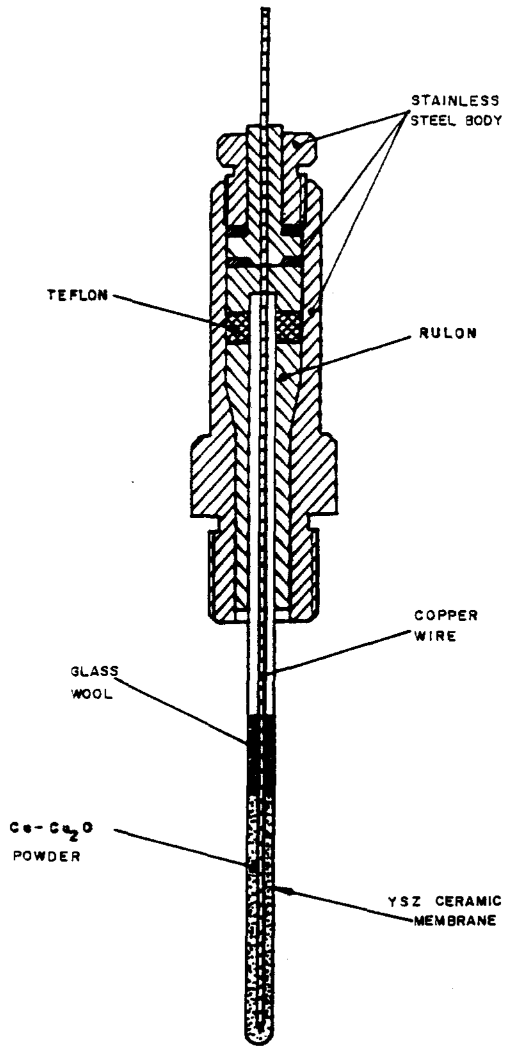

Fig. 2. Cu/Cu_2O reference electrode.

hydrogen partial pressure are constants it can be used as a reference electrode.

2. Experimental

The ECP measurements and various corrosion tests were performed in a testing facility, which simulates BWR conditions with high pressure—high temperature water (80 kg cm^{-2} and 280°C). The test assembly includes a one-litter stainless steel autoclave in which four electrodes can be fitted.

Table 1
Chemistry results

Gas concentration	Materials	Impurities (ppb)	σ (f) (μS cm^{-1})	σ (e) (μS cm^{-1})	$[O_2]$ (e)	T (°C)
200 ppb O_2	Inconel 600 AISI 316NG	—	0.10	0.29	114	277
		20 Cu^{2+}	—	0.36	130	277
		500 Cl^-	1.7	2.3	96	279
		20 SO_4^{2-} + 20 Cl^-	0.13	0.28	180	274
		100 $SO_4^=$	0.33	0.43	150	273
125 ppb H_2 + 20 ppb O_2	AISI 304 Inconel 600	—	0.07	0.26	2	282
		20 Cu^{2+} + 20 Cl^-	—	0.34	—	279
		20 Cl^-	0.13	0.45	—	278
		25 SO_4^{2-}	0.14	0.33	5	275
		25 SO_4^{2-}	0.15	0.41	2	279
		100 SO_4^{2-}	0.35	0.40	5	275

(f) is experimental data in the feedwater; (e) is experimental data in the effluent water.

Laboratory studies have been carried out under two simulated baseline environments: normal water chemistry (NWC): 200 ppb O_2; and hydrogen water chemistry (HWC): 125 ppb H_2 + 20 ppb O_2.

Corrosion potential measurements have been carried out for different materials: type AISI 304 austenitic stainless steel; type 316NG austenitic stainless steel and nickel base alloy, Inconel 600. The corrosion potentials were converted to SHE scale by adding the correction factor for each electrode. Comparisons between the corrosion potentials, obtained with the different electrodes, were made in order to study their reliability and to confirm the effect of impurities on corrosion potentials. In addition, electrode potentials were verified using a platinum electrode under HWC. Such measurements were used to assess the viability and behaviour of these sensors, comparing theoretical and experimental values.

Moreover, different types of impurities and concentrations were added to evaluate the effect on the material corrosion based on corrosion tests and ECP measurements. Chemical additives used in this study include Na_2SO_4, ClNa and $CuCl_2$. Concentrations and chemical conditions are presented in Table 1. During a run, conductivity, level of dissolved oxygen and temperature were continuously monitored in the feed and the outlet waters. It must be pointed out that the addition of impurities, within the ppb range, did not change the solution pH and the variation of water conductivity was found to be no more than 1 μS cm^{-1}.

3. Results and discussion

3.1. Platinum electrode

This electrode showed a reversible behaviour in chemistry with hydrogen addition. However, some irreversibility has been observed with high levels of oxygen or with electroactive species which can be reduced more easily than protons. So it is necessary to use another high temperature reference electrode which is insensitive to redox changes.

3.2. Silver electrode

In the first electrode design there was a final chamber in order to avoid possible chloride contaminations of the solution. However, it has been proved that the above introduced a liquid junction potential drop. So, in the last measurements under NWC, this chamber was eliminated and the

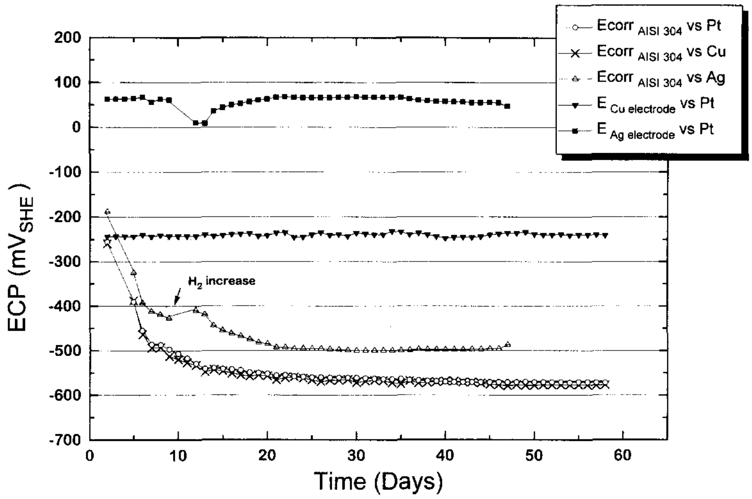

Fig. 3. Corrosion potential of AISI 304 SS and electrode potentials under HWC + 100 ppb SO_4^{2-}.

results were improved without any difference in the potential measured with the copper electrode. In addition, the electrolyte lost (Cl^-) from the electrode has not been detected during the experiments.

The Ag/AgCl electrode has exhibited some problems in the accuracy of the electrode potential. This potential can vary between 130 and 190 mV_{SHE}, according to different authors (Leibovitz, 1982; Indig and Weber, 1983; Taylor, 1991), because of the uncertainty of AgCl solubility data at high temperature. In this study, the electrode potential was 130 mV_{SHE} in most cases, only decreasing in some measurements under HWC. This may be due to moderate concentrations of hydrogen diffusing through the Rulon wall and causing a secondary reaction to occur with the silver chloride:

$$H_2 + 2AgCl_{(S)} \leftrightarrow 2Ag + 2Cl^- + 2H^+$$

In the above case, there is a lower electrode potential which generates an increase in the corrosion potential measured (Indig, 1990), as shown in Fig. 3, in which there was an accidental increase in hydrogen concentration which decreased the electrode potential and increased the corrosion potential.

3.3. Copper electrode

A reversible behaviour has been exhibited by this electrode, because electrode potential measured with a platinum electrode has shown good stability, accuracy and reproducibility. In addition, corrosion potential measurements made with this electrode showed the same variations and the same values as those obtained with the platinum electrode, so this also suggested reversible behaviour, independent of chemistry impurities. Moreover, reproducibility has been achieved when the same material and chemical environment have been used, as, for example, is shown in Fig. 4. The best characteristics of this electrode were its easy and reproducible construction and its high strength in the absence of contaminants.

With regard to chemical and thermodynamic viability of this electrode, the thermodynamic of YSZ membrane has been extensively studied by different authors (Macdonald et al., 1990) and (Niedrach and Stoddard, 1985). Macdonald et al. concluded that this sensor did not exhibit a thermodynamic behaviour, because Cu(II) can be formed from the internal Cu_2O when a sensor is cycled. Considering this, and because available thermodynamic data were limited, the powder

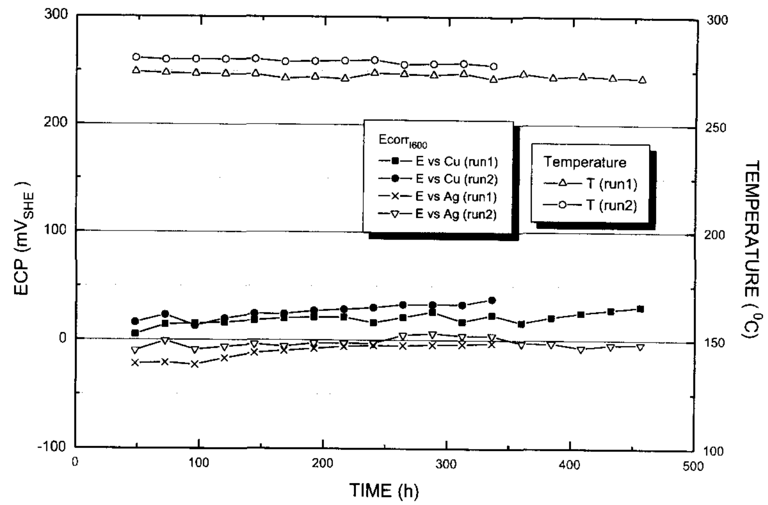

Fig. 4. Reproducibility of Inconel 600 corrosion potentials under NWC + 100 ppb SO_4^{2-}.

mixture was analyzed by electron spectroscopy for chemical analysis (ESCA), both before and after electrode use. In all cases, Cu(II) was not found, indicating a reversible behaviour, according to the results of Niedrach and Stoddard (1985).

3.4. Corrosion potential measurements

Usually, corrosion potentials were equal and reproducible, independent of the electrode used, as it is possible to observe in Fig. 5 under HWC and Fig. 6 under NWC. Therefore, this suggests that the reference electrodes are reliable and have chemical stability, apart from the exceptions mentioned above. In addition, the designs yielded reproducible results and were free from seal failure.

The reference electrodes seem to provide reliable data, thus making it possible to study the effect of water chemistry on the corrosion potential. Corrosion potential measurements for different materials, such as stainless steel type AISI 304, AISI 316NG, and Inconel 600 were made under different chemistries. An increase in corro-

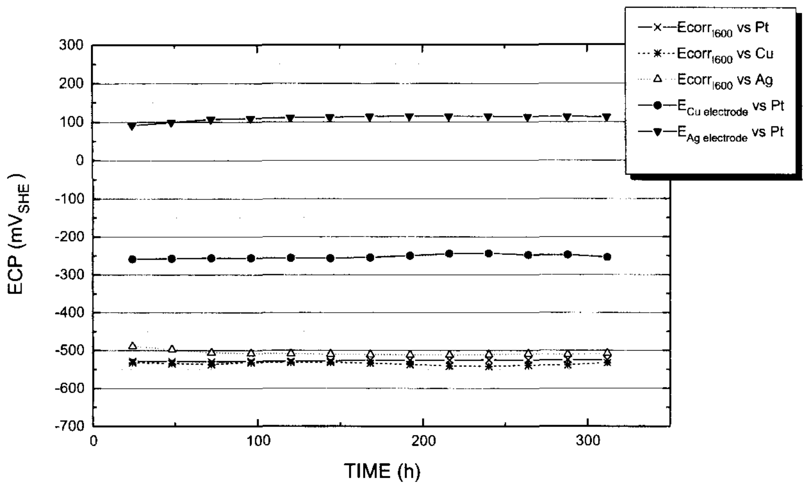

Fig. 5. Corrosion potential of Inconel 600 and electrode potentials under HWC + 100 ppb SO_4^{2-}.

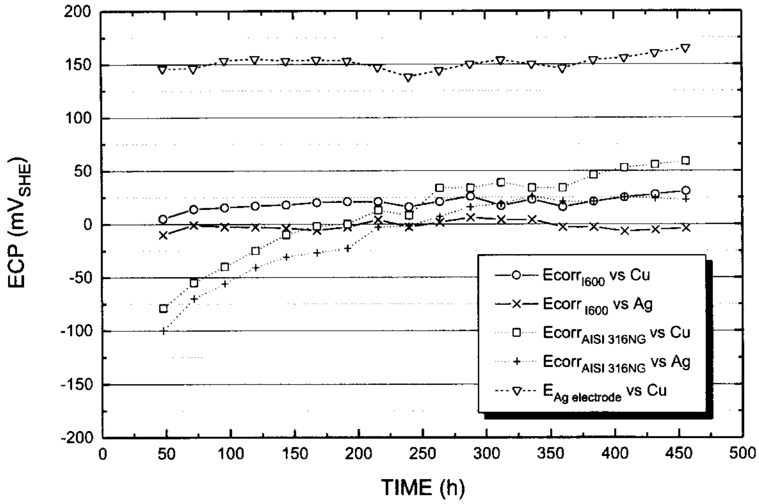

Fig. 6. Corrosion potentials of AISI 316NG SS, Inconel 600 and electrode potentials under NWC + 100 ppb SO_4^{2-}.

sion potential, probably owing to oxide film formation, was observed in the first days when the electrode surface was fresh (Fig. 7). Occasionally, the corrosion potential decreased in the first measurements until desired gas concentrations were achieved.

The results obtained in these measurements were consistent with those reported in the literature. The corrosion potential showed a clear dependence on the dissolved oxygen level. However, the changes observed on the corrosion potential owing to chemical additives, within the ppb range, were small in agreement with other authors (Lin et al., 1992), and in practice sometimes were negligible because of the small conductivity variations.

4. Summary

The corrosion potential of a metal or alloy exposed to aqueous solution is a key parameter

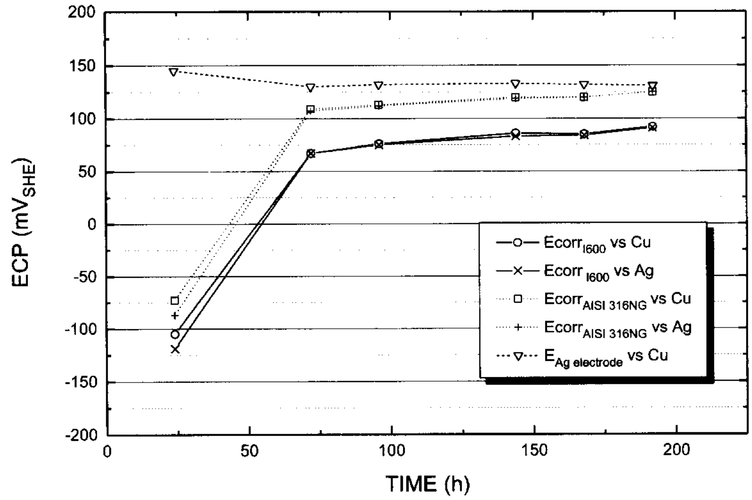

Fig. 7. Corrosion potentials of AISI 316NG SS, Inconel 600 and electrode potentials under NWC + 20 ppb Cu^{2+}.

for determining the corrosion behaviour of materials. However, ECP measurements are difficult because it is necessary to develop a high temperature reference electrode and great care is required to assure that valid and useful data are being obtained.

In this work, particular emphasis has been placed on the improvements of system integrity, reliability and materials stability of the reference electrodes. The accuracy and reliability of these sensors have been studied in a variety of chemical conditions by means of electrode potential and corrosion potential measurements. Most of the electrochemical potentials, measured with the different electrodes, were equal and reproducible. Therefore, this indicated that the reference electrodes were reliable and had chemical stability. In addition, the designs yielded reproducible results and were free from seal failure.

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