Application of Corrosion Test for Austenitic SS 304 in PWR with Electrochemical Quartz Crystal Microbalance (EQCM)

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1. Introduction

The secondary system of a pressurized water reactor (PWR) is a loop composed of: a) steam generator, b) steam transport piping, c) steam turbine and d) condenser and some optional component. The materials of these components are mainly carbon steel, different grades of stainless steel, high nickel alloys (Inconel-600 and Incoloy-800), Copper alloys. Among these materials, austenitic stainless steel 304 is widely used in tubing for large-surface condenser exposed to seawater as coolant of steam condenser [1].
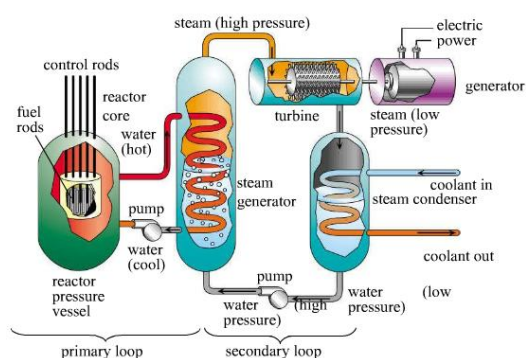

Fig. 1 Schematic view of PWR power plant

Stainless steels show much greater resistance to erosion-corrosion than copper alloys used in steam condenser tubing and are also immune to ammonia attack, ammonia induced stress corrosion cracking. Also, the chloride induced stress corrosion cracking has not been reported in stainless steel tubing in power plant condenser. Nevertheless, it is well known that stainless steels are susceptible to pitting and crevice corrosion in the seawater environment including chloride ions [2, 3].

Metallic materials exposed to untreated seawater suffer the well-known phenomenon of fouling consisting of the formation of an unwanted deposit that covers the surfaces in contact with the water. Five types of fouling are usually considered as biological, corrosion, particulate, chemical and precipitation fouling. Pitting corrosion is aggravated by stagnant or low flow conditions in which sludge such as corrosion of copper alloys in the secondary system can form in the tube surface. From the operational maintenance viewpoint, pitting attack has destructive effect of structural materials on operation of NPP. Countermeasures such as copper alloys replacement, water chemistry control and chemical cleaning were implemented to mitigate the pitting [4, 5].

Although the many studies are performed macroscopically to reduce pitting corrosion in the secondary system, little work has been done to understand mechanism of fouling formation and to confirm the quantitative analysis of the fouling between the metal and coolant water.

Electrochemical Quartz Crystal Microbalance is a new electrochemical technique developed in recent years able to be applied to study the filming kinetics of corrosion phenomena using piezoelectric effect. The high sensitivity of EQCM is the basis for its applications in thin film studies. In addition, interfacial process can be measured with the exact time scale depending on the frequency counter used [6].

The purpose of this study is to understand the corrosion inhibition mechanisms of pitting corrosion for stainless steel 304 using inhibitor based on phosphoric acid and to contribute the application of corrosion test by EQCM techniques for corrosion research of steam condenser tube exposed of seawater coolant in the secondary system of NPP.

2. Experimental and Results

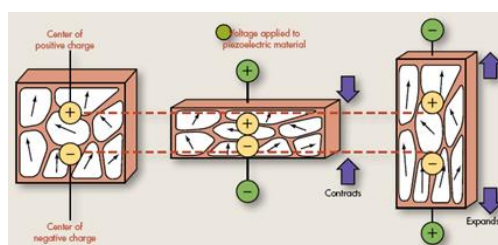### 2.1 Basic theory of EQCM

Fig. 2 Schematic diagram of piezoelectric effect

The EQCM method for mass change monitoring is based on the inverse piezoelectric effect in which a voltage applied to an SS 304 coated with quartz oscillator producing physical distortion. This means

that the addition of mass to an oscillator would change its frequency. An equation developed in 1959 by Sauerbrey shows that a linear relation can be obtained between the shift in resonant frequency and deposited mass [6]. For AT cut quartz crystals vibrating in a thickness shear mode the equation is followed as:

$$\Delta f = -f_0^2 \Delta m / A(\mu_q \rho_q)^{1/2} \qquad (1)$$

Where f_0 is base resonance frequency of the crystal, A is Area, μ is shear modulus of quartz and ρ is density of quartz.

2.2 Experimental setup

In this study, AT cut quartz crystal coated with SS 304 was employed to three electrode corrosion cell. Counter electrode was a graphite rods, the saturated calomel electrode was used to as the reference electrode. Electrolyte was 3.5% NaCl solution purged using N_2 gas with or without corrosion inhibitor. Corrosion inhibitor used in this study was phosphoric acid due to the ability of scale removal effect [7]. Open circuit potential (OCP) was measured by using the 273A Princeton potentiostat coupled with SEIKO EG & G QCM922 for frequency acquisition.

3. Results and Future Work

In order to confirm the effect of corrosion inhibitor and to understand the corrosion behavior of SS 304, potentiodynamic polarization measurement were perform potentiondynamically at OCP with a sweep rate of 1mV/sec. Fig. 3 shows the polarization curve with or without corrosion inhibitor
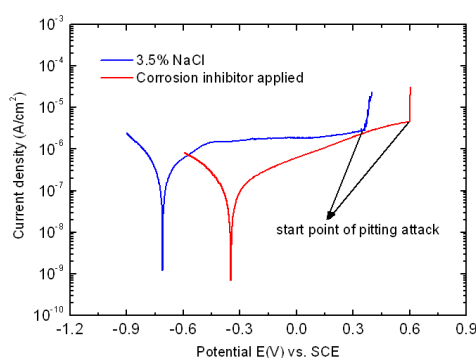
Fig. 3 Potentiodynamic polarization curves in 3.5% sodium chloride solution with or without corrosion inhibitor

Our future work is to measure the mass change of the surface on SS 304 at OCP with or without corrosion inhibitor. The predictable results about OCP measurement and mass change of SS 304 quartz crystal are likely to the reference data as shown Fig. 4 [8].
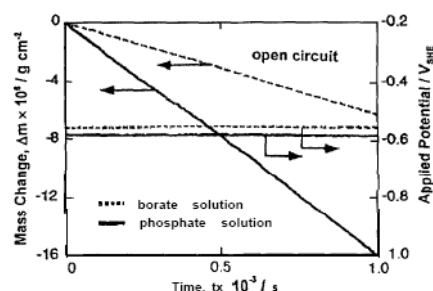
Fig.4 Predictable results about OCP and mass change measurement as a function of exposure time

4. Summary

The predictable results of OCP and mass change measurement can be assumed that in corrosion inhibitor applied solution corrosion rate of SS 304 quartz crystal will be greater than that in 3.5% NaCl solution.

The EQCM technique combined with DC polarization measurement is powerful tool to quantitative surface analysis of SS 304. This method can be used to pitting corrosion studies of metallic materials for secondary system of NPP and can provide valuable information in aqueous corrosion kinetics. In addition, when combined with other techniques, it can provide complementary information such as thin film chemical composition or environmental analysis data.

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