



SENSORS FOR ON-LINE MONITORING OF WATER CHEMISTRY PARAMETERS FOR NPP's

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Abstract

The on-line monitoring of the water chemistry parameters of aqueous solutions in nuclear power plants is considered essential to control corrosion phenomena. New sensors and electrodes that can be used under plant operating conditions are key components to the application of this technology. The research and development programs are running to develop practical instruments. The experimental capabilities available to research high temperature and pressure phenomena is growing rapidly. It is now possible to experimentally measure all information needed to make estimations and predictions concerning reactions taking place in the coolant of an operating reactor. However, further development of devices and practical experiences are needed to meet the requirement of power stations.

1. INTRODUCTION

Corrosion phenomena, particularly stress corrosion cracking and corrosion fatigue, are caused by the interaction of environment, materials and stresses. Also general corrosion and erosion corrosion are controlled by the material selection and the chemical environment. Material selection is decided during plant design and thus it is not easily changed in an operating power plant. However, water chemistry can be modified even in operating plants or it can be adjusted to improve the reliability. Successful water chemistry control requires regular and continuous monitoring of such water chemistry parameters as dissolved oxygen content, pH, conductivity and impurity contents. Conventionally the monitoring is carried out at low pressures and temperatures, which, however, has some shortcomings because parameters such as pH, conductivity and redox potential are changing as a function of the temperature.

Electrodes designed for the on-line monitoring of water chemistry parameters at high temperatures and pressures can improve the knowledge of chemical

environment in power plants. This kind of electrodes have existed already several years, but the application in real power plants has not become popular. The plants need commercially available electrodes which are reliable for months and have zero or minimal maintenance.

The present status of electrodes design has improved reliability but at the same time new needs and applications has appeared for on-line monitoring. This paper describes the development and some of the latest applications of the on-line water chemistry monitoring electrodes.

2. WATER CHEMISTRY AT ELEVATED TEMPERATURE

In power plants extensive instrumentation and laboratory analysis programs are applied to provide rapid and reliable diagnosis of water chemistry. However, at present chemical monitoring is applied mainly in low temperature, low pressure conditions or by using grab samples. More relevant information concerning the chemical environment could be obtained by using high temperature, high pressure measurements at least for pH, conductivity and electrochemical potentials.

2.1 pH at high temperature

Temperature has a great influence on pH, i.e on the activity of hydrogen ions. Owing to the nature of pure water, pH usually shifts towards neutral values at higher temperatures. In general the pH of base solutions is lower and the pH of acidic solutions higher when temperature increases, Fig. 1. This neutralizing effect is caused by the interaction between the water and the dissolved species. The resulting pH of the solution is highly dependent on the buffering capacity of these dissolved species.

2.2 Conductivity at high temperature

The conductivity of pure water increases with temperature, Fig. 2. This is due partly to the dissociation of pure water itself and partly to the increase in dissolved impurities at higher temperatures. Additionally the deposition of

dissolved ions changes the conductivity of the solutions in sampling lines if the temperature decreases.

2.3 Redox potential and corrosion potentials at high temperature

The electrochemical i.e. corrosion potential of a metal is a measure of the equilibrium reaction obtained between the surface and the environment. Because most metals form some kind of oxide layer on their surface in water-containing solutions, the electrochemical potentials are mainly controlled by the oxygen content and the temperature of the environment, Fig. 3.

Redox potential of the water is a function of the oxidizing and reducing species in the environment and can be measured as a corrosion potential of noble metals which do not have corrosion reactions of their own.

3. REFERENCE ELECTRODES

The most important parameters that should be monitored in power plant heat transport circuits are the corrosion potential and pH. This is also because these

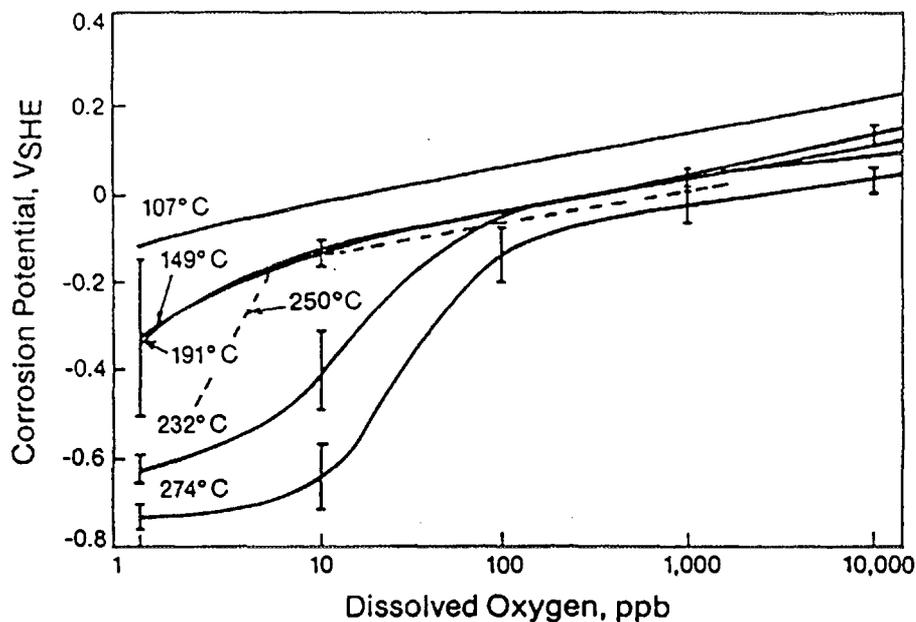


Figure 3. Corrosion potential as a function of oxygen concentrations at high temperatures [8].

two parameters define what corrosion processes are possible and hence provide a basis for interpreting the electrochemical reactions. The reference electrode must provide a potential that is independent of the composition of the environment and which can be placed on a viable thermodynamic scale. The electrode has to withstand the high temperatures and pressures, associated with heat-up and cool-down of the system. The most important characteristics of a reference electrode is that its potential must be related to a rational thermodynamic scale (e.g., the standard hydrogen electrode (SHE) scale), either by calculation or by direct calibration [4]. The reference electrodes that have been used in high temperature aqueous systems are external reference electrodes, or internal reference electrodes.

3.1 External Reference Electrodes

Macdonald, Scott and Wentrcek introduced in 1981 [5] a pressure balanced reference electrode in an attempt to produce a highly stable reference electrode for high temperature aqueous systems. A typical design is shown in Fig. 4. In this type of electrodes some parts fabricated from PTFE (polytetrafluoroethylene) are exposed to the high temperature aqueous environment which limits the maximum operation temperature. However, by employing alternate materials, reference electrodes have been developed that can operate under supercritical conditions ($T > 374\text{ }^{\circ}\text{C}$).

3.2 Internal Reference Electrodes

For highly accurate measurements, internal reference electrodes are preferred. Compared with external reference electrodes the internal reference electrodes are more accurate due to the lack of thermal liquid junction potentials. However, external reference electrodes offer considerable advantages in terms of long term stability and are ideally suited for measuring potentials in the systems where moderate accuracy is acceptable. The drawback of internal electrodes based on the Ag/AgCl electroactive element is thermal hydrolysis of AgCl, which generates a mixed potential rather than an equilibrium potentials as well as changing the chloride activity.

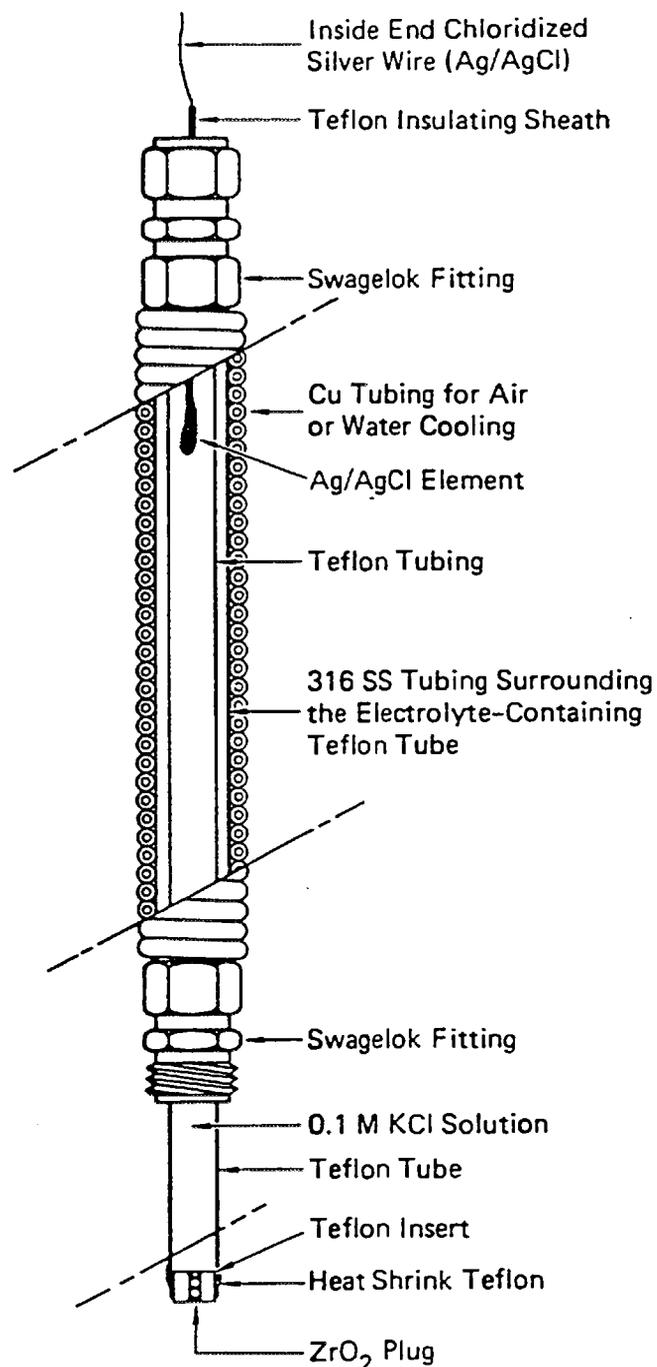


Figure 4. External pressure balanced reference electrode assembly [4].

3.3 Cathodically charged Pd electrode

One version of palladium hydrogen electrode is palladium-hydride electrode. The work of Macdonald and co-workers on palladium-hydride electrodes indicated that this system exhibits Nernstian responses up to 275 °C in various boric acid/lithium hydroxide buffer solutions [6]. However, the lifetime of the potential plateau

for palladium-hydride electrode was found to decrease with increasing temperature and therefore the electrode system could not be used for long term measurements. Research conducted at the Technical Research Centre of Finland (VTT) has shown that continuously cathodically charged palladium can operate as a reliable reference electrode for long periods at temperatures up to 360 °C, Fig. 5. The design consisted of a Pd rod which was placed inside of a sintered high purity platinum tube to minimize the effects of flow rate variations. Pd was chosen for hydrogen electrode because Pd potential is less sensitive to oxygen. Porous platinum tube around the Pd was also used to create large surface area for trace oxygen in the solution to react on. The test showed that the electrode was stable and that there was no junction potential at the electrode/water interfaces.

3.4 Pd membrane electrodes based on hydrogen diffusion

An other way to overcome the problem of unstable potential plateau is to use a palladium membrane as an electrode with suitable hydrogen partial pressure on the dry side to maintain the Pd/H ratio at the wet surface. In a membrane electrode based on a 75% palladium-25% silver alloy the electrode potential is controlled by the activity of the hydrogen ions and of the dissolved hydrogen in the vicinity of the electrode surface. The dissolved hydrogen activity is a function

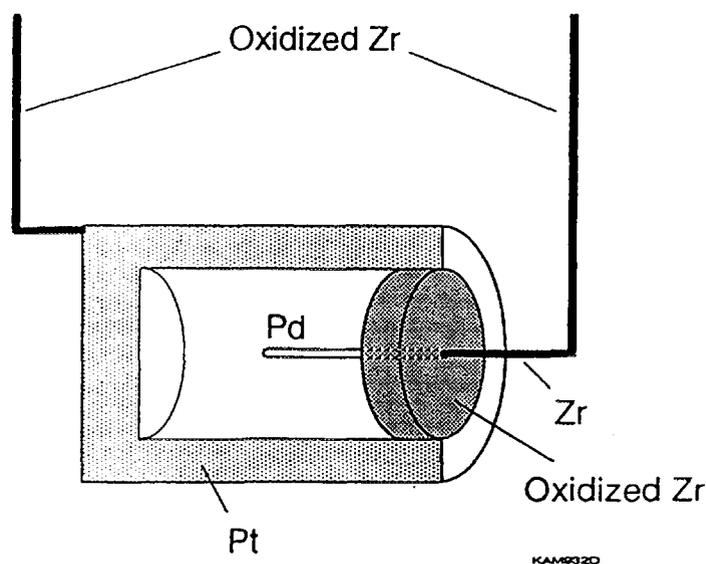


Figure 5. VTT Pd electrode.

of the hydrogen activity in the gas phase on the dry side of the membrane and the diffusion rate of the hydrogen through the membrane and into the solution [7]. For the ideal operation of the electrode, it is required that the diffusion rate through the membrane be much faster than that in the solution. The electrode design is shown in Fig. 6. This type of sensor results in a complex electrode and system design but the electrode is a suitable reference electrode for fast transient measurements.

4. CONDUCTIVITY ELECTRODES

Conductivity can be easily measured at high temperatures by the conventional electrode design based on the impedance measurements. The advantage obtained by measuring conductivity at high temperature is the increased sensitivity. Additionally, the specific conductances of ions are temperature dependent, thus the conductivity is also changing with temperature, Fig. 7. The high temperature conductivities can be estimated by using different mathematical models, but accuracy of these model is a problem. Therefore to have a clear picture of the monitored environment high temperature conductivity sensors should be used.

5. pH ELECTRODES

Over the past decade, considerable interest has arisen in using oxide ion-conducting ceramic membrane electrodes based on yttria stabilized zirconia to

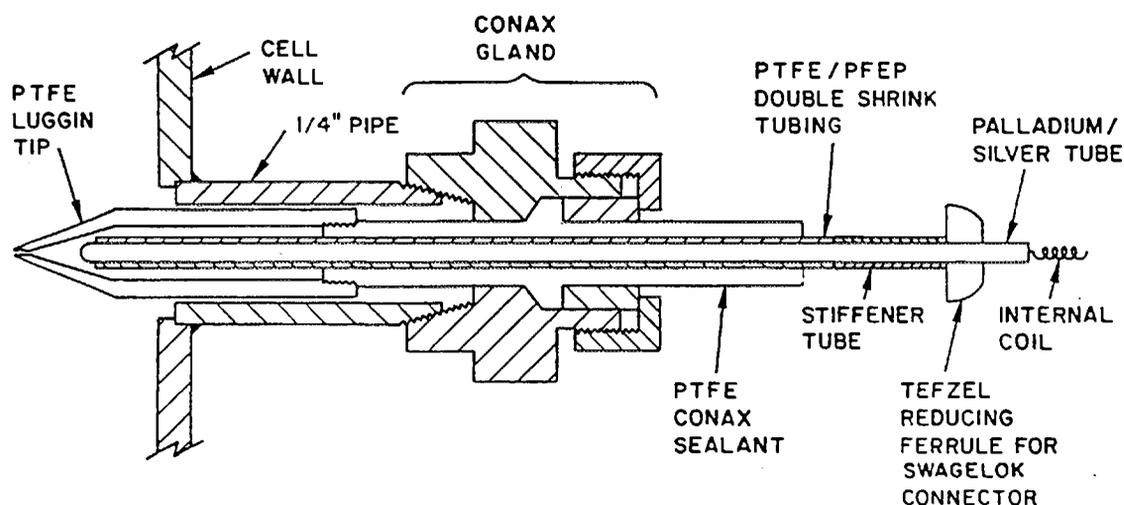


Figure 6. Palladium/Silver membrane electrode [7].

Limiting ionic conductances ($S\text{ cm}^2\text{ eq}^{-1}$)

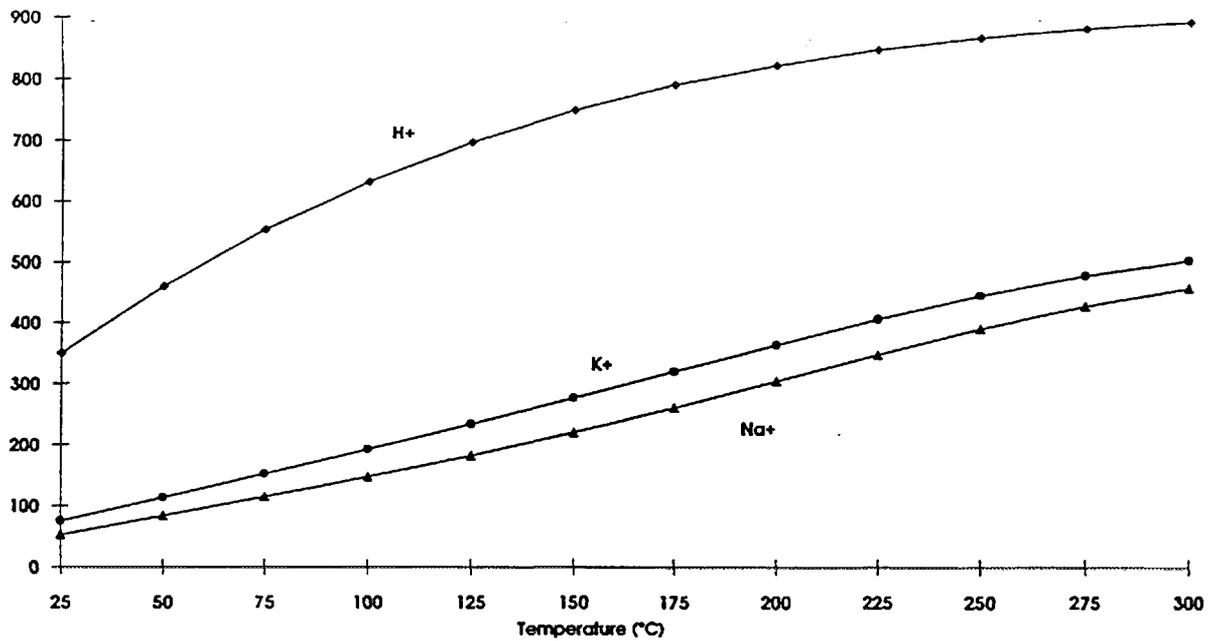


Figure 7. Limiting ionic conductances of the H^+ , Na^+ and K^+ as a function of temperature [8].

measure pH in high temperature aqueous systems. The most popular of these devices employs a metal/metal oxide internal reference element to fix the activity of oxygen vacancies on the inside surface of the ceramic membrane. The design of the $Ni/NiO/ZrO_2(Y_2O_3)$ sensor currently being used at VTT is shown in Fig. 8. However, the liquid junction potential of the reference electrode can be significant under certain conditions causing as large as 1 unit of pH error.

6. OXYGEN MONITORING

No commercial instrument exists capable of measuring oxygen directly in high temperature water. However, experimental sensors has been used to determine the oxygen concentration in both steam and liquid phases [4]. Also the differences in the kinetics of electrochemical reactions on noble metal electrodes has been used to study the oxidizing power and decomposition of H_2O_2 at high temperatures at VTT.

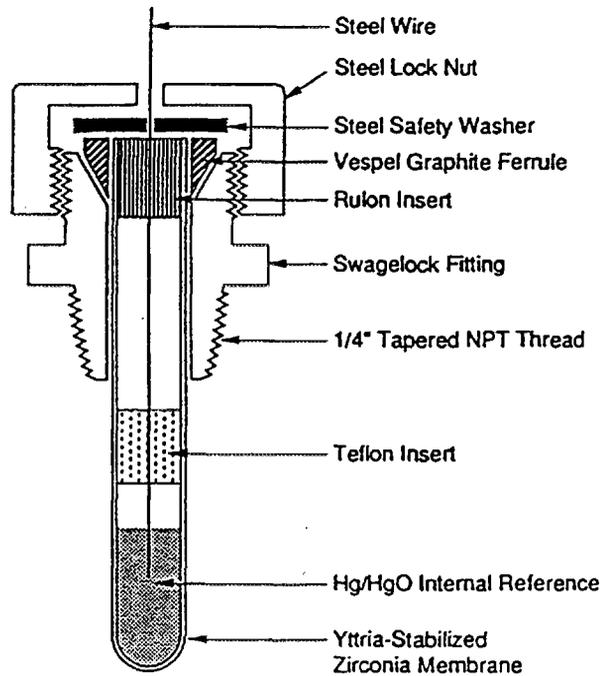


Figure 8. pH electrode design [1].

7. SUMMARY AND CONCLUSIONS

This paper described the use and status of reference electrodes, the pH sensor, the conductivity electrodes and an oxygen monitor for the on-line monitoring of water chemistry parameters in high temperature aqueous systems.

- External reference electrodes in present state can be used for monitoring electrochemical potentials over a wide range of temperature and pressure.
- Internal reference electrodes need further testing to provide needed stability for long term in core potential measurements.
- The pH sensors is a convenient and reliable device for measuring pH in both subcritical and supercritical aqueous systems. However, pH measurements requires a stable reference electrode.
- Conductivity electrodes already now fulfill the requirements for plant conductivity measurement.
- The oxygen sensors can be used to measure oxygen concentration, but further development is needed.

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