Effects of temperature and pressure on Henry's law constant for hydrogen in the primary water of a simulated pressurized-water reactor

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ABSTRACT

The measurement of dissolved hydrogen in the primary systems of pressurized water reactors (PWRs) is difficult; hence, hydrogen concentrations are predicted by model equations. An accurate value for the Henry's law constant for hydrogen is needed if the use of these equations is to be meaningful. The purpose of this study is to develop an empirical correlation for determining the Henry's law constant for application to nuclear reactors. The effects of temperature and pressure on the Henry's law constant are investigated using simulated PWR primary-water conditions. The Henry's law constant was calculated by an in-situ measurement of the partial pressure of hydrogen using a hydrogen sensor based on a Pd–Ag alloy tube. At 20 MPa, the Henry's law constant decreased by ∼40% as the temperature increased from 290 to 330 °C. The Henry's law constant increased by an average of 9% as the pressure increased from 13.8 to 20 MPa at each temperature. Thus, it depends more strongly on the temperature than on the pressure. Based on the experimental data, an empirical correlation for predicting the Henry's law constant was developed using a linear regression method, which was validated by comparing with results in the literature. The deviation between the Henry's law constant obtained using our model and that reported in the literature was in the range of 0.5%–10%. The hydrogen fugacity estimated using our model was within 10% of that found in the literature. Thus, the proposed empirical model appears to be more accurate than previously published models.

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1. Introduction

In pressurized-water reactors (PWRs), hydrogen is added to the reactor coolant system (RCS) to reduce the oxidation of water by radiolysis and to maintain reducing conditions. It is important to maintain the hydrogen concentration within a certain range. This is because this parameter can lead to primary water stress corrosion cracking (PWSCC), general corrosion of the primary structural materials, higher radiation fields, and deposit build-up on fuel rods of a PWR (Fruzetti, 2005). Several researchers have demonstrated that the hydrogen concentration influences the corrosion of structural materials in PWRs (Cassagne et al., 1997; Lee et al., 2002; Ahluwalia, 2007). However, the amount of dissolved hydrogen, which affects the material susceptibility, exhibits a wide scatter. Computational work has suggested that dissolved hydrogen concentrations lower than 15 cc/kg are sufficient to scavenge oxidizing species under normal PWR operating conditions (Fruzetti, 2005). During operation, the concentration of dissolved hydrogen is controlled by varying the hydrogen overpressure in a volume control

tank (VCT). Since the primary water flows from the VCT into the RCS, the temperature, system pressure, and solution chemistry in the RCS can affect the hydrogen concentration. In addition, hydrogen from the RCS diffuses through the steam generator tubes. To ensure an optimal operating margin, the Electric Power Research Institute (EPRI) PWR primary chemistry guide-lines require hydrogen levels of 25–50 cc/kg as an optimal margin. To mitigate PWSCC, the recent EPRI Hydrogen Management Program for fuel and material reliability focused on plant operations using hydrogen levels of up to 60 cc/kg (Hass et al., 2010). The optimization of the hydrogen concentration in the RCS is regarded as one approach to the management of material integrity and the reduction of radiation sources in the primary circuit.

The solubility of gases in water and aqueous solutions is of considerable industrial and theoretical importance. Solubility depends on many factors, including temperature, pressure, association, dissociation, and the type of solvent (Himmelblau, 1960). However, inert gases like the hydrogen that is used in the RCS of PWRs do not react with water or ionize in water, so only the effects of temperature and pressure on the solubility are considered. The amount of hydrogen dissolved in water is directly proportional to the hydrogen fugacity (hydrogen partial pressure) in the gaseous

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phase. Thus, the measured hydrogen fugacity can be used to calculate the Henry's law constant (Himmelblau, 1960). The Henry's law constant is important because it is necessary to predict the dissolved hydrogen concentration in a PWR. Using the Henry's law constant, the amount of dissolved hydrogen at a given temperature and pressure can be calculated. Alternatively, when the dissolved hydrogen concentration is known, the hydrogen fugacity can be determined using the Henry's law equation. The values obtained for the dissolved hydrogen concentration affect the Ni/NiO phase transition in nickel-based alloys, shifting the Ni/NiO phase boundary up or down. For PWRs, these data can yield erroneous results in the prediction of PWSCC, and hinder the development of a model to fit the hydrogen concentrations (Attanasio and Morton, 2003; Lee et al., 2002; Moss and Was, 2015). Thus, accurate means of measuring and monitoring the hydrogen fugacity in PWRs are needed.

In the present study, to measure the hydrogen partial pressure, we fabricated a sensor based on a Pd–Ag (75/25 wt.%) tube. Using this sensor, we measured the hydrogen partial pressure in situ as a function of temperature and pressure in a simulated PWR primary solution containing lithium hydroxide (LiOH) and boric acid (H_3BO_3). Based on the data collected in our experiments, an empirical correlation for predicting the Henry's law constant was developed using a linear regression method. It was validated by comparing the obtained results with the values reported in the literature.

2. Theoretical background

2.1. Solubility of hydrogen in water

The solubility of hydrogen in water can be determined using the findings of Henry, given by Eq. (1) and known as Henry's Law (Himmelblau, 1960).

$$f = H \cdot x \cdot \phi \tag{1}$$

where f = fugacity of the solute gas in the vapor phase, H = Henry's law constant, x = mole fraction of the solute gas in the liquid phase, and Φ = activity coefficient of the solute gas in the liquid phase. For inert gases such as hydrogen, oxygen, and nitrogen, which obey the ideal gas law in the vapor phase above the solution, Eq. (1) can be rewritten to give Eq. (2).

$$p = H \cdot x \tag{2}$$

where p = partial pressure of hydrogen in the vapor phase and Φ = 1 for ideal solutions. Himmelblau developed theoretical equations to determine the Henry's law constant of inert gases at different temperatures using the data reported in the literature. In developing the modified Henry's law equations, Himmelblau used high-pressure data extrapolated to low pressures, and thus considered only the effect of temperature. He then correlated the solubility data with various data plots. The plotted data in the graph are correlated by Eqs. (3)–(5) (Himmelblau, 1960).

$$logH^* = 1.142 - 2.846(1/T)^* + 2.486(1/T)^{*2} - 0.9761(1/T)^{*3}$$
$$+ 0.2001(1/T)^{*4} \tag{3}$$

$$H^* = H/H_{max} \tag{4}$$

$$(1/T)^* = \frac{(1/T) - (1/T_c)}{(1/T_{max}) - (1/T_c)} \tag{5}$$

where $H_{max} \times 10^{-4} = 7.54$, $(1/T_{max}) \times 10^3 = 3.09$, and T_c = critical temperature of water (647 K).

However, Himmelblau's study was limited to the effect of temperature on solubility. In addition, the calculated Henry's constants are for ideal gases and solutions, and are applicable to low pressures only. For hydrogen, the low pressures appear to be 10.3 MPa (1500 psia) at 100 °C and about 13.8 MPa (2000 psia) at 300 °C (Himmelblau, 1960). Many researchers have used the Henry's law constants determined by Himmelblau's equations to calculate the hydrogen partial pressures or hydrogen concentrations at different temperatures. However, experimentally measured Henry's law constants have proven to be quite different from those calculated from Himmelblau's equations (Lee et al., 2002). This difference arises because his equations assume the concentration of dissolved hydrogen in water to be independent of pressure. This assumption gives rise to the difference between the theoretical and experimental data.

2.2. Sensor for measuring hydrogen partial pressure

The accuracy of the hydrogen-fugacity measurement was also affected by the hydrogen-sensing materials used. Considerable research has been directed toward developing high-performance hydrogen sensors with high permeability, high selectivity, a fast response time, cost-effective fabrication, and which are easy to use. Among the various hydrogen-sensing materials tested, metallic palladium (Pd) exhibits high permeability and selectivity with hydrogen (Ackerman and Koskinas, 1972; Yang et al., 1998). However, pure Pd undergoes phase transition and hydrogen embrittlement at high temperatures and pressures, leading to fragility after extended use. To avoid these problems, alloying of Pd with group IB metals such as Ag was attempted and an optimal value of hydrogen permeation was attained at an Ag content of ~25 wt.% (Knapton, 1977; Foletto et al., 2008). The advantage of using a Pd alloy is that the mechanical strength of the sensor is greater than that of one made from pure Pd. Several researchers have studied the effects of various parameters on the permeation of hydrogen through hydrogen sensors constructed using a Pd–Ag tube, film, and wire (Economy et al., 1987; Wang and Feng, 2007; Foletto et al., 2008).

3. Methods

3.1. Test loop

Fig. 1 shows a schematic of the test loop that we used. The hydrogen sensor was mounted in an autoclave with a temperature control precision of ±0.5 °C. Then, 100 l of the test solution was prepared by adding 2 ppm of nuclear-grade lithium (as LiOH) and 1200 ppm of boron (as H_3BO_3) to purified water produced using an ultrapure water system (18 MΩ·cm). This setup was used to simulate the representative PWR primary water chemistry. The amount of dissolved hydrogen was controlled by fixing the hydrogen overpressure in the feed tank at a temperature of 21 ± 1 °C. The amount of dissolved hydrogen was calculated using the Henry's law constant for 5.7 kPa (0.826 psia)/(cc/kg) (Himmelblau, 1960). The solution from the feed tank was fed into the autoclave using a high-pressure pump and a double-tube heat exchanger. The outlet solution from the autoclave was cooled to ambient temperature by passing it through a heat-exchanger and a cooler, after which it passed through the sensors for measuring the conductivity and dissolved oxygen content. Finally, the solution was returned to the feed tank. The dissolved oxygen concentration was measured using a DO-32A (TOADKK Co.) and recorded manually. Throughout the experiments, the measured oxygen concentration was less than 1 ppb.