Stainless Steel 316 corrosion testing at sub- and supercritical water conditions: An insight into the pH effect

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Summary

Corrosion tests of stainless steel 316 are performed under conditions relevant to the operation at the PWR and SCWR. The experiments are performed in a flow-through tubular reactor at 350, 400, 500 and 650 °C and 25 MPa, and at pH_{25}=7 and 10, adjusted by LiOH addition. The corrosion rate is estimated from the concentrations of Fe, Ni and Cr in the effluent.

1. Introduction

The main purpose of this study is to estimate the corrosion rate of stainless steel at sub-critical and supercritical water conditions. In its supercritical region, water acts as a non-polar solvent, increasing solubility of gases like oxygen and hydrogen, and organic compounds[1, 2]. In nuclear power systems, the presence of reactive radicals (product of the radiation deposited in the water), provides a very harsh environment for reactor materials, leading to severe corrosion conditions[3, 4]. It has been hypothesized, that the pH of the solution is one of the factors, which may also have a serious influence on corrosion in high temperature water[5, 6]. High or low values of pH lead to chemical dissolution of the oxide layer formed on metal surfaces. To control the pH of the solution, suitable corrosion inhibitors are added to water in the nuclear systems. $LiOH_{(aq)}$ has been used as a corrosion inhibitor in Pressurized Water Reactors (PWR)[7-9]. Studies of LiOH behavior in supercritical water are however limited [10-12]. Plugatyr *et al.*[13] used molecular simulations of ion association constant to predict the pH of high temperature and supercritical LiOH solutions. This study showed that at water densities above 0.3 g/cm^3 pH control appears to be feasible. Below this density, LiOH seems to be completely associated and pH control will no longer be suitable. Figure 1 shows pH variation with temperature of LiOH solutions at supercritical water conditions, as found in this simulation study[13].

The lack of knowledge of supercritical water chemistry is one of the main obstacles in the development of the specification for water chemistry (e.g. pH, dissolved oxygen/hydrogen concentration, etc.) that would minimize corrosion and corrosion product transport. Water chemistry is crucial for the selection of fabrication materials to be used in the SCWR. Computer modeling and experimental tests are urgently needed to elucidate the behaviour of water coolant at supercritical conditions and to understand the materials resistance to corrosion at these conditions. For the present work, molecular dynamics simulations were used to elucidate the association of LiOH and to estimate pH value in aqueous solutions at supercritical water reactor conditions. Experimental corrosion tests with stainless steel 316 tubes in a flow-through reactor were then performed at 4 different temperatures and constant pressure of 25 MPa, and with or without LiOH additions. The results confirm that at very high temperatures (650°C) LiOH seems to be completely associated and pH control is not effective as seen by increase in concentration of metals in the effluent.

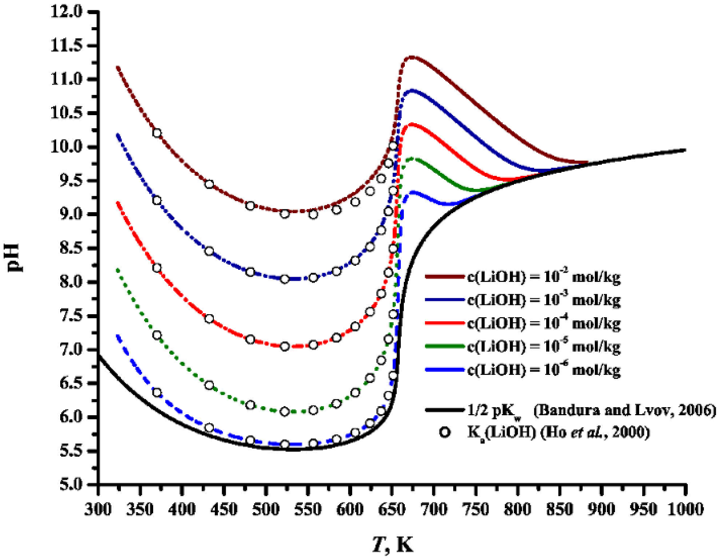

Figure 1. pH values for dilute $LiOH_{(aq)}$ solutions along the 25 MPa isobar. Lines represent the pH values calculated using ion association constants of LiOH obtained in this study. Open circles are the pH values calculated using experimental K_a(LiOH) data from Ho *et al.*[12]. See Plugatyr *et al.*[13]

2. Aqueous Chemistry of Metals under Supercritical Conditions

2.1 Experimental Procedure and Parameters

Four set of experiments at temperatures of 350, 400, 500 and 650°C were performed using a bench-top flow-through tubular supercritical water reactor, described by Plugatyr, *et. al* [14]. For each temperature value, two runs were carried out, one at neutral pH (pH_{25}=7±0.3) and the second one at alkaline pH (pH_{25}=10±0.3). The pH was controlled by adding stock 0.1M LiOH solution to the milli-Q water in the feedline. Water was introduced at a flow rate of 0.1 ml/min. The feed water was degassed by He for 48 hours.

The analysis of nickel, iron and chromium concentration in the effluent was analyzed using Adsorptive Striping voltammetry, via Hanging Mercury Drop, in a 797 VA Computrace (Metrohm) instrument. The methods used for nickel, iron and chromium trace detection were modified from the Metrohm VA Application Notes No. V-87[15], V-123[16] and V-82[17], respectively.

Surface analysis was made for stainless steel tubing materials used at 350 and 500°C. The Optical metallographic Cross-sections were made by the Metallographic Laboratory of AECL (Atomic Energy of Canada Limited).

2.2 Corrosion of Stainless Steel 316 at Supercritical Water Reactor Conditions

Figure 2 shows representative average concentration of nickel and iron in the effluent for temperatures of 350, 400 and 500°C. Loss of Ni is low and remains steady for most of the runs, which confirms the stability of nickel oxides in neutral and alkaline environments[18]. Chromium concentrations were found to be below the detection limit (<0.7 ppb), as O_2 is not present to form chromate ion $HCrO^{4-}$, soluble in water. On the other hand, iron is present at high concentrations.

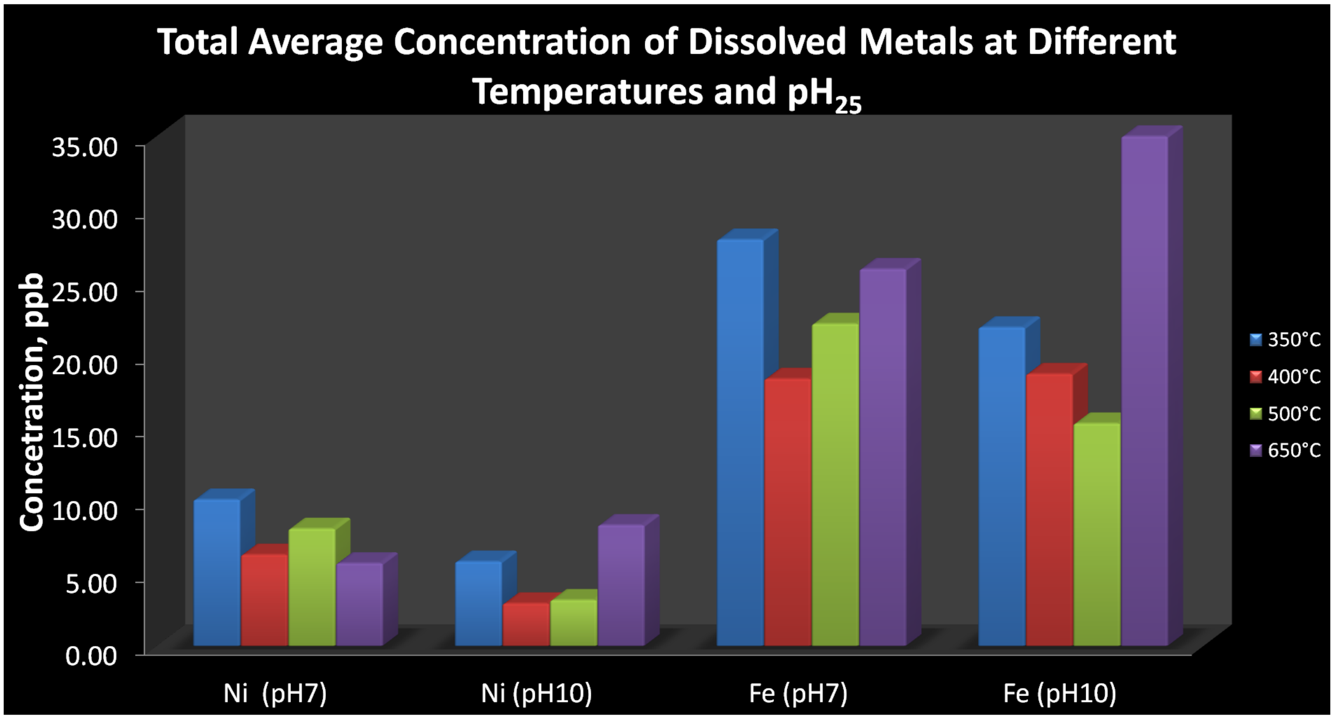

Figure 2. Total Average Concentration of Nickel and Iron at 25 MPa and 350, 400 and 500°C. The pH was set at 25 °C.

Corrosion rates of stainless steel at the four temperatures examined are shown in table 1. The rates are given in mils per year. We found that at 650°C complete association of LiOH and H_2 production reaction lead to more acidic medium, which in turn leads to higher dissolution of the metals. Overall, increasing the pH (which can be accomplished below 650°C) seems to stabilize the surface oxide layer and reduce metal dissolutions into the effluent.

Figure 3 shows metallographic cross-sections of the samples at 350°C and 500°C. The formation of a protective layer at 500°C in both neutral and alkaline conditions is detected, though a thicker layer is formed in alkaline environments.

Table 1. Corrosion Rates for SS 316 in supercritical water reactor conditions.

Corrosion Rate [mm/year]							
350 °C		**400 °C**		**500 °C**		**650 °C**	
pH$_{25}$ 7	**pH$_{25}$ 10**	**pH$_{25}$ 7**	**pH$_{25}$ 10**	**pH$_{25}$ 7**	**pH$_{25}$ 10**	**pH$_{25}$ 7**	**pH$_{25}$ 10**
3.05×10^{-5}	1.78×10^{-5}	2.79×10^{-5}	1.96×10^{-5}	3.56×10^{-5}	6.35×10^{-6}	1.78×10^{-5}	6.1×10^{-4}

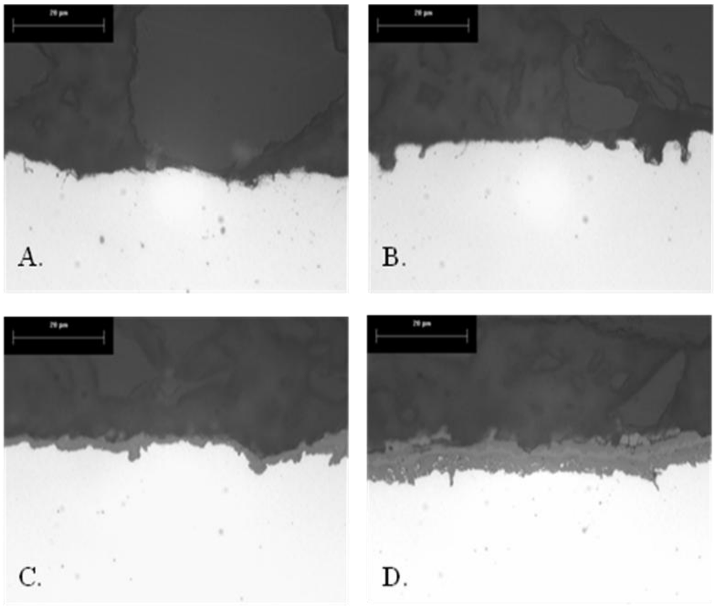

Figure 3. Optical metallographic cross-sections of inner surface of SS 316 reactor. **A**. 350°C and pH 7; **B.** 350°C and pH$_{25}$ 10; **C**. 500°C and pH$_{25}$ 7; **D.** 500 °C and pH$_{25}$ 10.

3. Conclusion

The pH control via addition of LiOH to supercritical water was confirmed to be effective for temperatures in the range of 350 to 500°C. At higher temperature of 650°C LiOH is assumed to be completely associated, which does not allow reducing corrosion by pH adjustment. Hydrogen production reaction was detected in the solution of pH 10 and 650°C. Formation of thicker oxide later on SS 316 surface was confirmed at 500°C and alkaline conditions.

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