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Effect of Supercritical Water Composition on the Corrosion of Engineering Materials

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Abstract

Canada is a major partner in the development of a next generation (GEN-IV) supercritical heavy water nuclear reactor (SCWR). The proposed SCWR uses supercritical water (SCW) as a working fluid in the primary heat transfer (PHT) system to take advantage of its single phase and high thermal efficiency. SCW has an extremely corrosive nature that must be considered in selecting engineering materials for the PHT system. This paper discusses the effect of the SCW composition on the corrosion of various candidate materials.

In order to understand the corrosive behaviour of SCW, its physical and chemical properties are discussed. The effects of density, dielectric constant, pH value, dissolved oxygen content, and presence of inorganic compounds and acids on corrosion are described. The impact of temperature and pressure on these properties is also considered, with discussions of how they can be used to "tune" the SCW to limit corrosion.

Introduction

In order to fill the void of depleting oil and gas reserves and a push for a safer, cleaner, economically feasible source of electricity, Canada is actively participating in the development of next generation nuclear reactors (called GEN IV reactors) [1]. Canada is collaborating in the development of Supercritical Water Reactors (SCWR) that would employ natural uranium oxide fuel [2].

One benefit of the proposed SCWR is simple reactor design due to the elimination of steam generators and steam separators [3]. The other advantage of a SCWR is the use of Supercritical Water (SCW) as the working fluid in the Primary Heat Transport (PHT) system [1]. SCW is a single phase fluid with high thermal efficiency [1]. A single phase working fluid is attractive because water does not boil or change phase after conducting heat at the core [1]. Due to its high thermal efficiency and excellent heat transport properties, SCW has previously been used in several fossil fuel power plants [4].

Current challenge facing engineers working on SCWRs is the extreme corrosive nature of SCW that can significantly damage reactor components and, in particular, PHT system components [4], [5]. A particular material that can withstand this corrosive environment has yet to be discovered or identified

[4]. Several studies have been conducted to understand corrosion mechanisms associated with SCW. In addition, significant amount of effort has been expended to characterize the behavior of different materials when exposed to SCW.

1. Physical and Chemical Properties of Supercritical Water

Supercritical water exhibits both liquid like and gas like characteristics [1]. The phase diagram of water (Pressure vs Temperature) is shown in Figure 1 where different phases of water are labeled. Water transitions to the supercritical phase beyond a Critical Point (CP), defined as a point where two or more coexisting fluid phases become indistinguishable [6]. There is no further phase transformation beyond CP and the substance is considered to be neither liquid nor gas, but rather a homogenous supercritical fluid [6]. The CP of water is at 374^{o}C temperature and 24 MPa pressure, as labeled in Figure 1 [6].

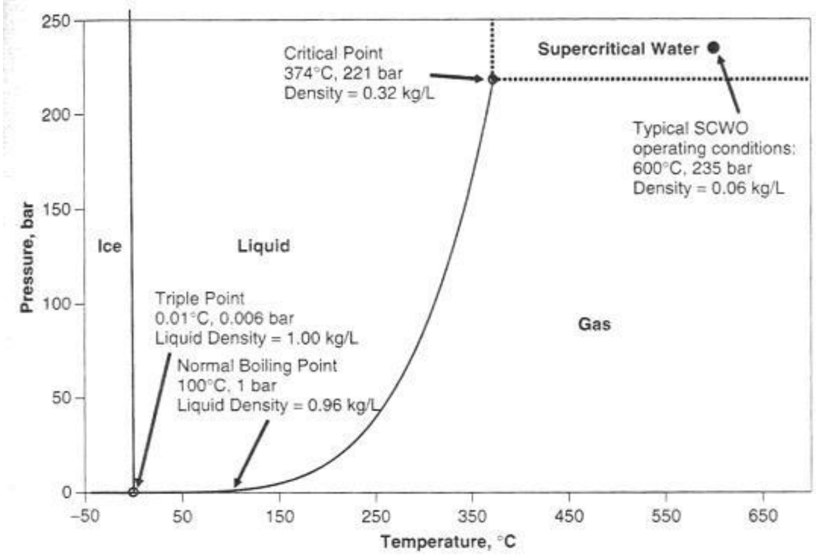


Figure 1: Phase diagram of Water (Pressure vs. Temperature) [6]

1.1 Density

As expected, the density of water at ambient temperatures decreases with increasing temperatures and liquid water turns into steam. However, the density of water decreases abruptly at the CP and the transition to supercritical phase occurs [6]. This phenomenon is illustrated in Figure 2 where there is sharp decrease in density at approximately 374^{o}C and at a pressure of 25 MPa [6], [7].

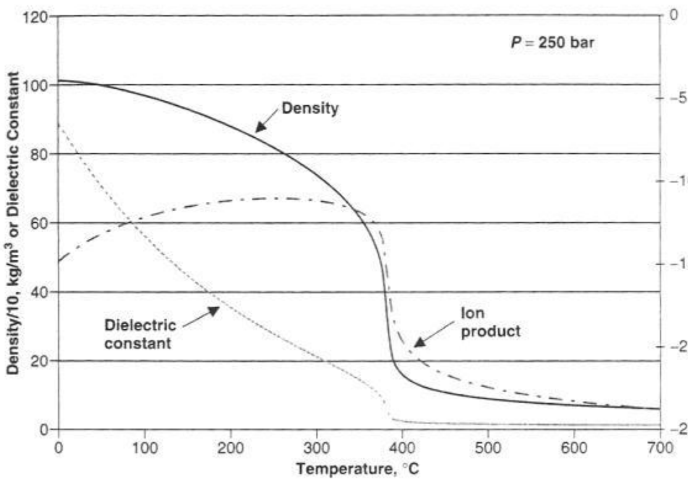


Figure 2: Physical Properties of water at subcritical and supercritical water [6]

Since supercritical fluids do not undergo any further phase changes, physical properties such as density, ionic product or dielectric constant can vary dramatically with changes in pressures [6]. The step size associated with the abrupt decrease in density at CP can be reduced with higher pressures, as shown in Figure 3 [7].

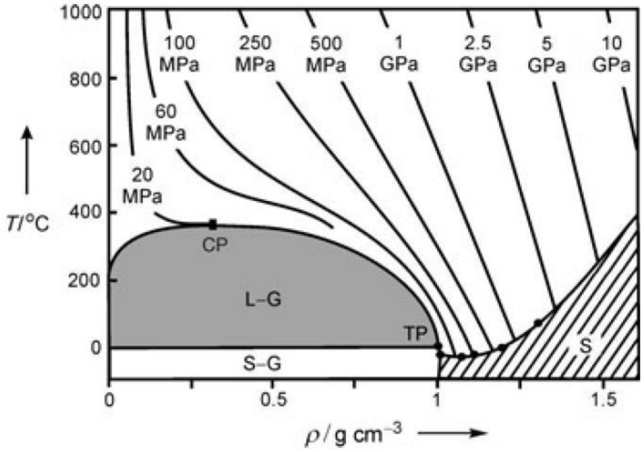


Figure 3: Density and Temperature of water at different pressures and phases [7]

1.2 Hydrogen Bonding and Dielectric Constant

Water at room temperature has a strong polarity due to a dipole caused by significant difference in the electronegativity of oxygen and hydrogen atoms [6]. The factor that quantifies this polarity is called the dielectric constant, and is typically denoted by ε [6].

As a result, water molecules form hydrogen bonds amongst themselves in ambient conditions [8]. The polarity of the water molecule is responsible for the solubility of different salts or inorganic compounds in water [9]. High polarity favors solubility and dissociation of ionic species (such as salts) as demonstrated in Figure 4 [9].

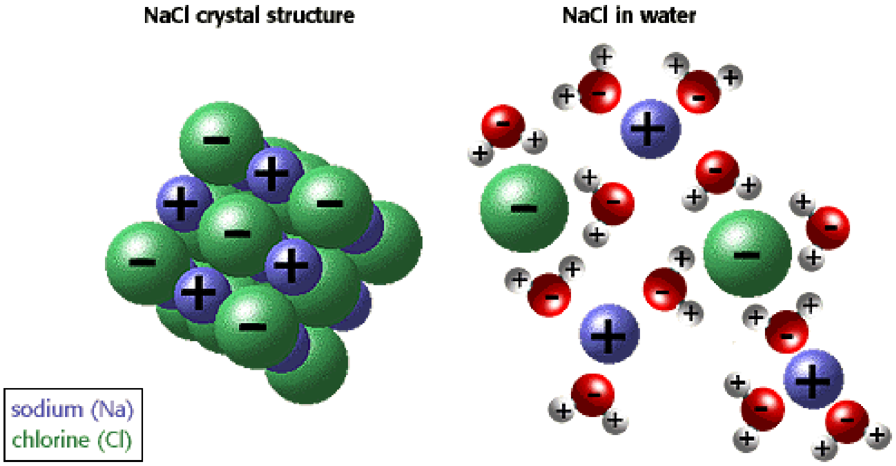


Figure 4: Solubility of ionic salts [9]

Above the CP, the density of water decreases and, despite liquid-like behavior, the hydrogen bonding among the molecules cannot be sustained [6]. A visual representation of this behavior is presented in Figure 5. Due to the decrease in hydrogen bonding and density the polarity of water diminishes significantly [6], [7]. This is evident in Figure 2 where the value of ε decreases abruptly.

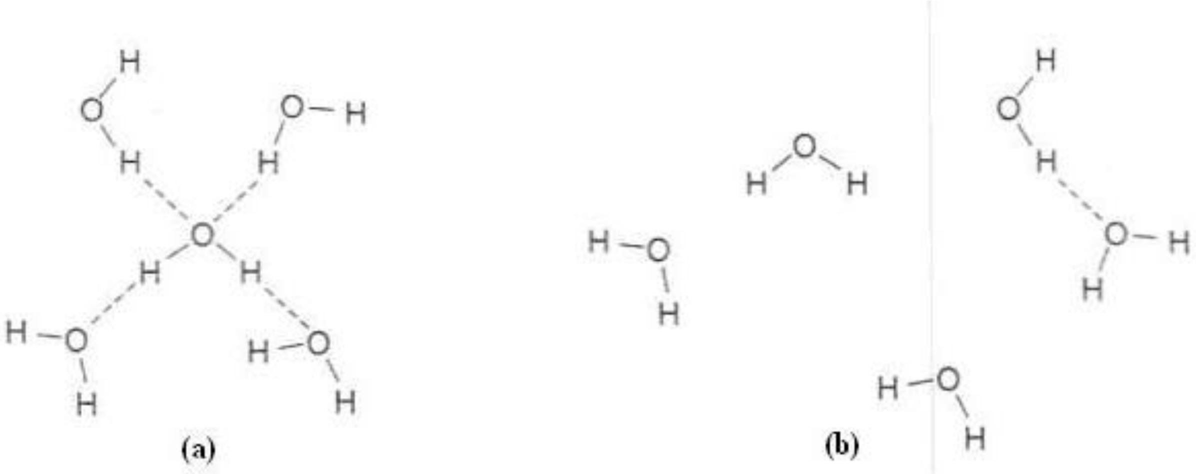


Figure 5: Hydrogen bonding of water molecules (a) under ambient conditions (b) under supercritical conditions [6]

Lack of hydrogen bonding among water molecules and decrease in ε inhibits the solubility of inorganic compounds, such as salts [6]. This has severe implications for corrosion of materials and will be discussed in the following sections. It is important to note that the dielectric constant varies for different pressures, and hence can be controlled just like the density [6], [8].

1.3 Ionic Product and the pH

The value of the ionic product, which is the measure of ions present in a particular solution decreases sharply at the CP, as shown in Figure 2. Liquid water under ambient conditions self-disassociates into H^+ and OH^- ions and the chemical reaction is in equilibrium as shown in Eq. (1) below [8].

$$H_2O \leftrightarrow H^+ + OH^- \tag{1}$$

The reaction above is an endothermic reaction and thus the production of ions is favored by increasing temperatures [10]. The overall pH value of water remains constant at 7 and is considered both acidic and alkaline. Like other physical properties of supercritical water (density or dielectric constant), the ionic product drops significantly as the temperature increases but the value of the ionic product is also influenced by the pressure [10]. Ionic product of high temperature water and supercritical water as a function of pressure is shown in Figure 6. At low pressures, steam or high pressure water behaves like a non-polar solvent with low self-dissociation [6]. In high density supercritical water (high pressure and high temperature), the ionic product increases [6], [8]. This increase in the ionic product may form mineral acids or bases due to the presence of ions and high dissociation rate of water [8] and can affect the pH value of the solvent and the corrosion properties (discussed below).

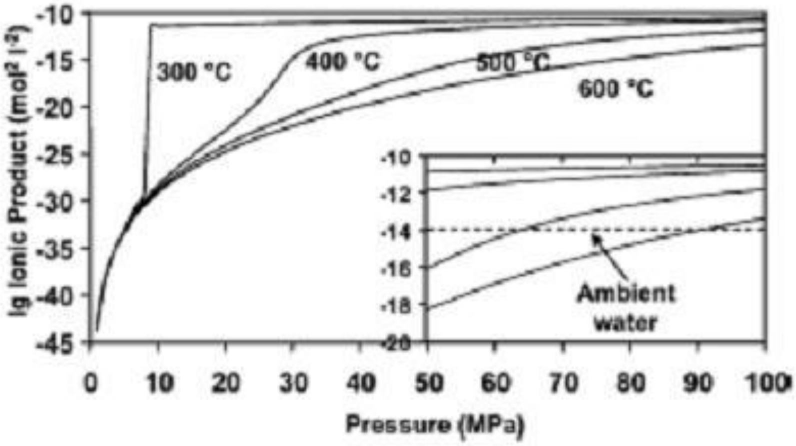


Figure 6: Ionic Product vs Pressure at different temperatures [8]

1.4 Oxygen Solubility

Most gases show high solubility in supercritical water. The concentration of dissolved oxygen in supercritical water is responsible for thickness and stability of the protective oxide layer in many metals and alloys [8]. It will later be shown that high solubility of oxygen increases the oxidizing power of supercritical water and has detrimental effects on the corrosion resistance of several materials.

The physical and chemical properties of supercritical water discussed above are highly sensitive to the pressure and temperature of the water [8], [10]. Slight modifications to temperature and pressure can be used to engineer these properties (to suit certain applications [8], [10]. There have been attempts to tune the solution properties such that a material can withstand harsh conditions when exposed to supercritical water. However, no such combination of properties has yet been discovered. Following sections will outline several mechanisms that affect the corrosion resistance of materials exposed to supercritical water.

2. Properties of Supercritical Water Influencing Corrosion Mechanisms

The key factor that affects the corrosion properties of metals or alloys is the integrity of the protective oxide layer. The phase, composition, and morphology of the protective oxide layer are strictly dependent on the exposure conditions. At ambient conditions, a protective layer might be thermodynamically stable; however, it might become thermodynamically unstable under supercritical conditions leading to dissolution of the layer [8]. The following sections discuss how exposure to supercritical water can deteriorate the oxide film leading to an accelerated corrosion of a metal or an alloy.

2.1 Effects of Temperature and Pressure

As discussed in the previous section, the density, ion product, and the hydrogen bonding of water decrease abruptly at the critical point. It is important to consider that the results presented in Figure 2 assume that other solution parameters (pressure, acidity, etc) remain constant and temperature is the only changing parameter. Exposure to supercritical water at 500^{o}C yielded a lower corrosion rate than exposure to subcritical water at 300^{o}C. This surprising result can be attributed to changes in the physical and chemical properties of water that do not promote deterioration of the protective oxide layer [8], [10].

However, exposure to such high temperatures can cause phase change of compounds present in the protective oxide layer [10]. At room temperature, stainless steel alloys are protected by an amorphous chromium oxide layer [10]. An increase in the temperature favors a decrease of the water content of the oxide layer, and a crystalline Cr(III) based oxide layer is favored. This phase change can lead to surface defects and can cause rapid dissolution of the protective layer at high temperatures [10].

Further studies have yielded a strong correlation between pressure and corrosion rates of metals or alloys under supercritical conditions. An increase in pressure always resulted in a higher corrosion rate and lead to rapid dissolution of the protective layer [8]. This is further discussed below.

2.2 Effect of pH Value

The pH value is an important solution parameter that influences the dissolution of the protective oxide film and can lead to corrosion [8]. The effect of pH value on the oxide layer is typically determined by a Pourbaix diagram that plots the pH value against the electrochemical potential (in Volts) [11]. These diagrams vary by temperature and are unique for each metal or alloy [11] [12]. An example of this is presented in Figure 7.

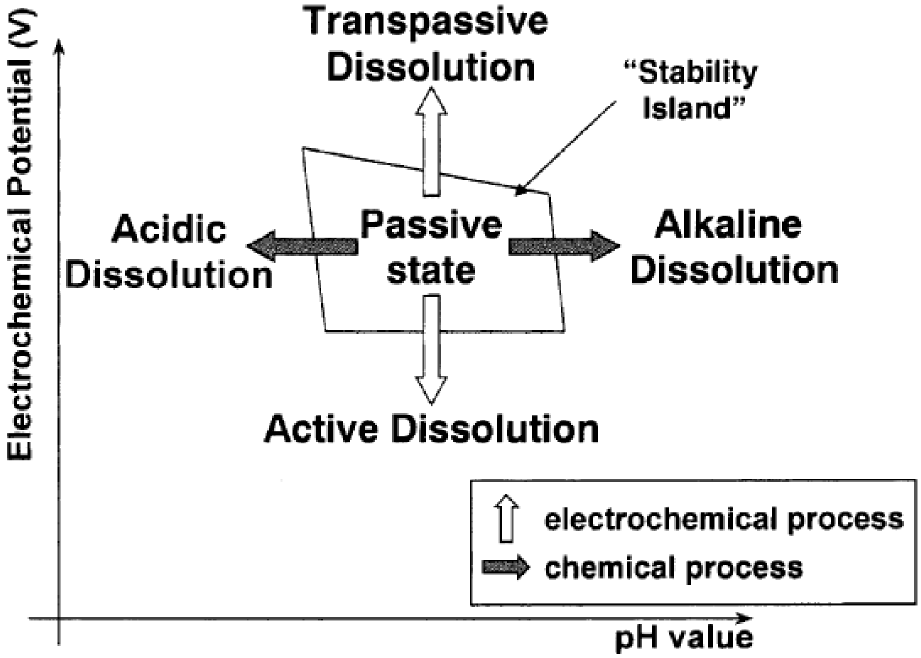


Figure 7: 'Stability island' of a protective oxide and the principle mechanisms for its dissolution [10].

The diagram highlights an envelope of pH values within which the protective oxide layer remains stable [10], [14]. Horizontal direction means 'chemical dissolution' (variation of the pH without changing the potential), while vertical direction means 'electrochemical dissolution (variation of the electrochemical potential without changing the pH). The stability island correlates with the 'passivity region' of the metal [10]. This envelope is labeled as 'Passive state' in Figure 7 and can shift or in some cases shrink based on the temperature [10].

pH values that are higher (alkaline solution) or lower (acidic solution) than the stability envelope can lead to chemical dissolution of the protecting oxide layer. There have been several experimental studies that have focused on the chemical dissolution of iron, chromium and nickel oxide layers due to exposure to supercritical water with different pH values [12]. Generally, chromium oxide layers showed a minimum dissolution while Ni oxide layers showed the highest dissolution [10].

2.3 Electrochemical Potential

Corrosion reactions are oxidation reactions and heavily dependent on the solution's electrochemical potential. As demonstrated in the Pourbaix diagram, the metal or alloy undergoes active or and transpassive dissolution depending on the electrochemical potential value [8].

The stable Cr(III) oxide layers (in the passive state) formed on most stainless steels and Ni alloys transform to Cr(II) compounds below a certain potential. Cr(II) compounds do not form a protective layer and lead to rapid corrosion of the metal or the alloy [10]. This is also known as active dissolution. Electrochemical potential above the passive region leads to transpassive dissolution of the protective layer due to the formation of chromates, hydrogen chromates or chromic acid [8]. It has been reported that Titanium and Tantalum do not do not undergo transpassive dissolution at room temperature up to potentials of approximately 100 V and hence possess excellent corrosion properties in highly oxidative environments [8].

The changing properties of oxide film at high temperatures can also accelerate corrosion [10]. Therefore, the passive state region may shrink at high temperatures and metals with high corrosion resistance at room temperature may corrode faster in supercritical conditions [8].

At supercritical conditions, oxygen is completely miscible in water. This, coupled with high temperatures, increases the oxidizing power of the solution and as a result the electrochemical processes become significant, as shown in Figure 8 [10]. In a chromium oxide layer, low concentrations of oxygen lead to the formation of chromates [10]. These can either lead to further deterioration of the oxide layer or can precipitate out of the solution as corrosion products [10]. In addition, the Cr(III) oxide layers changes phase to Cr(VI) compounds that are soluble in water [10]. Degradation of the protective chromium oxide layer may be furthered by high pH values (due to active dissolution) that encourage transformation to Cr(VI) [10].

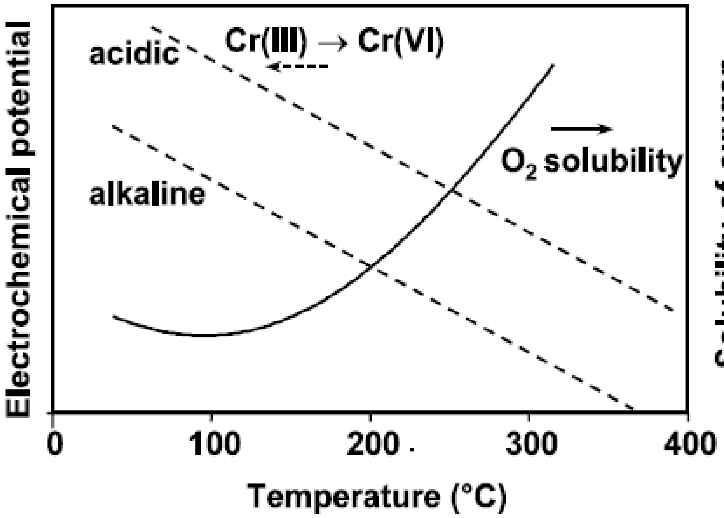


Figure 8: Schematical course of the electrochemical potential for the formation of soluble chromate in acidic and alkaline solution [10]

All of these factors can accelerate the dissolution of the protective chromium oxide layer and promote corrosion, unless another alloy component forms a protective oxide layer [8].

2.4 Passive State at Different pH and Electrochemical Potentials

The Pourbaix diagram can be used to ensure the protective oxide layer remains intact against corrosion. Figure 9 shows the passive state of chromium and nickel oxide layers at a specified operating temperature.

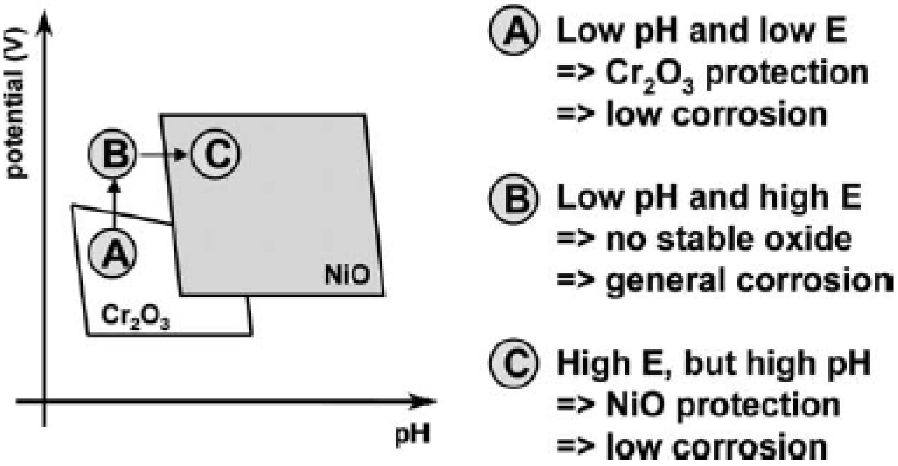


Figure 9: Stability islands of chromium and nickel. *E* = electrochemical potential [8]

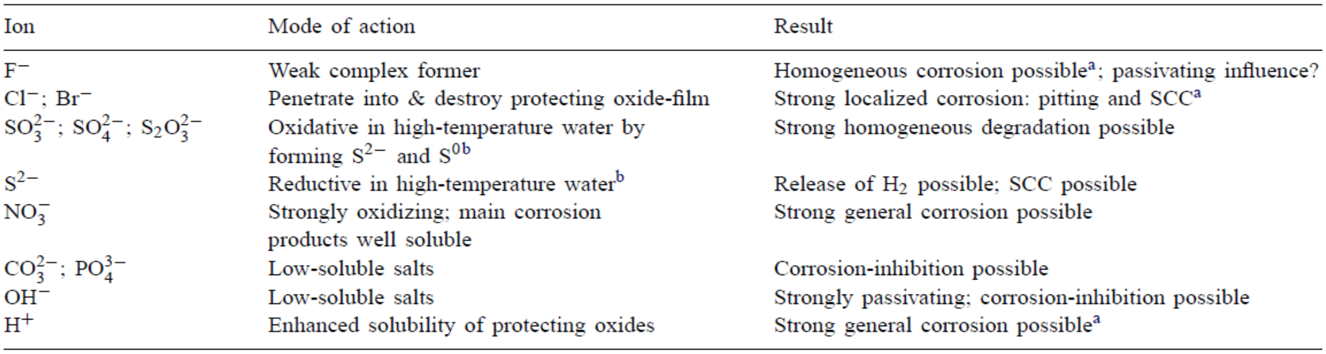
Chromium is more stable against acidic solution, while nickel better tolerates oxidizing conditions. The chromium oxide layer protects the metal at low pH and low potential values as labeled A on the figure [8]. The chromium oxide layer goes through transpassive dissolution due to an increase in the potential beyond the passive state (B), and the nickel would go through a chemical dissolution [8]. However, if the alloy needs to operate at such high potentials, the pH value can be increased to allow the formation of a nickel oxide layer to protect the metal (C) [8].

2.5 Presence of Inorganic Anions

Anions present in the solutions can corrode the alloy in conjunction with other corrosion mechanisms. The dissolution of protective oxide layer can be promoted by the presence of the halides chloride, bromide, and iodide [8]. Inorganic anions, such as nitrates can act as oxidizing agents in the absence of oxygen [8]. Some anions that are not considered strong oxidizers at room temperature become strong oxidizers under supercritical conditions [8] such as sulfates that form the thermodynamically favored sulfides, sulfites or elemental sulfur under supercritical conditions [10]. These compounds dissolve in the solution leading to fast active dissolution of the metal or alloy [10].

In contrast to the dissolution of the oxide film or the metal, the presence of some anions in the solution can enhance the stability of the oxide film [8]. Several studies have demonstrated that carbonate, phosphate, fluoride, and hydroxide are incorporated into the oxide layer and lead to the enhanced stability of nickel alloys in high temperature water [8]. Table 1**Error! Reference source not found.** summarizes the effects of several anions on nickel-base alloys and stainless steels in high temperature water.

Table 1: Influence of inorganic ions on the corrosion of nickel-base alloys and stainless steels in high-temperature water [10]



Ion	Mode of action	Result
F^-	Weak complex former	Homogeneous corrosion possible[a]; passivating influence?
Cl^-; Br^-	Penetrate into & destroy protecting oxide-film	Strong localized corrosion: pitting and SCC[a]
SO_3^{2-}; SO_4^{2-}; $S_2O_3^{2-}$	Oxidative in high-temperature water by forming S^{2-} and S^0[b]	Strong homogeneous degradation possible
S^{2-}	Reductive in high-temperature water[b]	Release of H_2 possible; SCC possible
NO_3^-	Strongly oxidizing; main corrosion products well soluble	Strong general corrosion possible
CO_3^{2-}; PO_4^{3-}	Low-soluble salts	Corrosion-inhibition possible
OH^-	Low-soluble salts	Strongly passivating; corrosion-inhibition possible
H^+	Enhanced solubility of protecting oxides	Strong general corrosion possible[a]

2.6 Interdependence and Inner Workings of Corrosion Parameters

It is evident from the discussion in the previous sections that density helps determine the corrosion rate of an alloy or metal. A model to predict the effect of solution density on the corrosion rate of stainless steels and nickel based alloys is presented in Figure 10, where the concentrations of oxygen and HCL in the solution are 0.05 mol/kg. Note that the lower temperature limit of general corrosion is independent of pressure, while the upper temperature limit strongly increases with pressure (and correlates with the density drop).

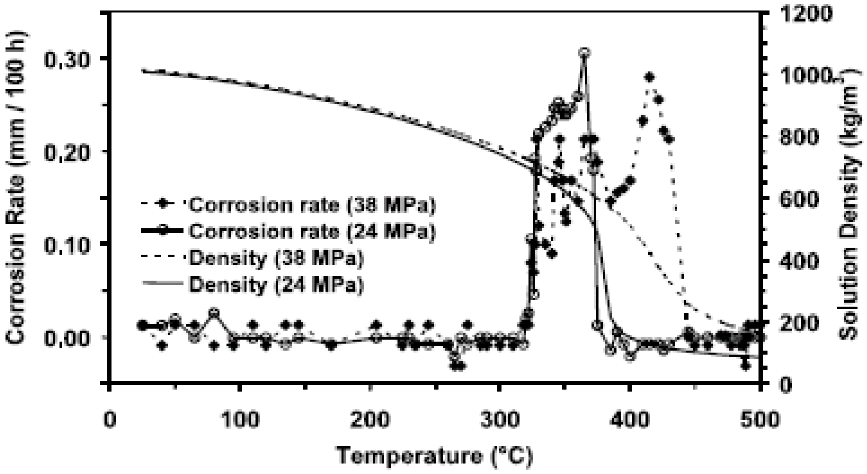


Figure 10: Experimentally found corrosion rates of general corrosion caused by HCl solutions at different pressures (T_{max} = 500 °C; p = 24/38 MPa; $[O_2]$ = 0.5 mol/kg; [HCl] 0.05 mol/kg) [10]

As mentioned above, the drop in the density at the critical point is regulated by the pressure and therefore high temperature high density water has high solvency of ionic species. The density of the oxidizing solution is therefore directly related to the solubility and dissociation of salts, acids and bases. The dissolution of the protective oxide layers (salts) formed on metals or alloys is attributed to the solution density which directly affects the corrosion rate [8].

It is the solution density, controlled by the pressure, which caused lower corrosion of metal when exposed to supercritical water at 500°C than subcritical water at 300°C. Figure 11 shows a density threshold below which general corrosion is low, with higher temperature solutions falling below it. However, increase in the pressure leads to high corrosion rate.

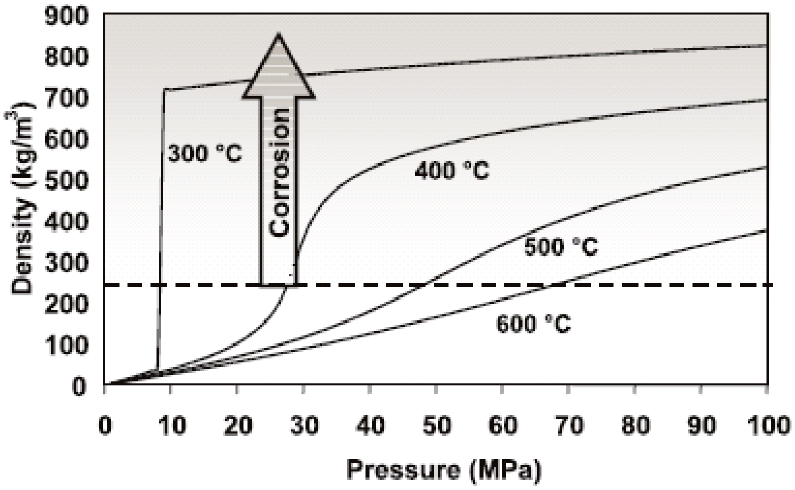


Figure 11: Density range of high corrosion at different temperatures [8]

This shows general corrosion is low at densities below about 200–300 kg/m3. At 300°C, a pressure of already 10 MPa leads to high corrosion rates, while at 500°C, pressures above around 50 MPa are necessary for high corrosion. Increasing the pressure at constant temperature increases the rate of electrochemical corrosion [8].

In most cases, ionic products arise from the dislocation of acids at high temperature and can promote corrosion [8]. In addition, high solubility of oxygen in low density supercritical water promotes cathodic corrosion reactions at the metal surface as follows [8]:

$$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^- \quad (2)$$

This reaction results in the production of hydroxide ions that cannot be dissolved in supercritical water and thus further cathodic reactions are inhibited [8].

In contrast to the density and ionic product, the corrosion rate is not dependent on the dielectric constant since dielectric constant does not affect the solubility of salts in high temperature water [8].

Figure 12 illustrates all the solution parameters effecting the corrosion of metals or alloys under supercritical conditions. The influence of each factor can be determined by the thickness of the pathway.

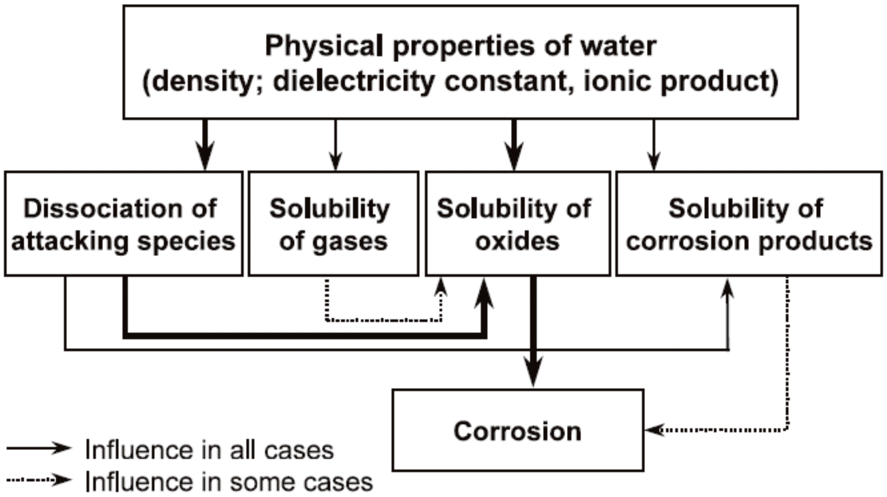


Figure 12: Connection between solution parameters and corrosion [10]

As discussed above, physical properties such as density have strong influences on the solubility of the protective oxide layer [8]. The dissociation of attacking species, such as acids, under supercritical conditions leads to an increase in the concentration of ions [10]. This may lead to the dissolution of the oxide layer. Other factors that may contribute to further corrosion are the solubility of gases and corrosion products that may be present in the solution. [10].

3. Effects of Dissolved Oxygen

The concentration of dissolved oxygen has a significant effect on the oxidizing power of the solution. Ideally, the weight gain reflecting oxidation rate should follow an Arrhenius distribution. This yields initial development of a stable outer oxide layer that inhibits further oxidation of the base metal [13]. The weight gain curve should plateau after the formation of a stable oxide layer. This pattern has been observed for several metals or alloys, where temperature or the exposure time was presented as the controlling factor for a stable oxide growth [13]. Concentration of dissolved oxygen in the oxidizing solution (SCW) also influences the development and integrity of the oxide layer.

T91 steel samples exposed to higher oxygen concentration had finer oxide grains with more interconnected porosity [13]. Increased porosity promotes oxygen ion diffusion that leads to further oxidation of the base metal and production of thick unstable oxide layer [13]. HCM12A FM steels demonstrate an initial decrease in the weight gain with increasing oxygen concentration, which then increases abruptly at oxygen concentrations of 2000 ppb [14]. Most FM steels behave similarly and therefore results of the effects of dissolved oxygen can be generalized for all FM steels [14]. Constant extension rate tests (CERT) conducted under SCW conditions determined that higher dissolved oxygen reduces the yield strength, UTS, and the ductility of FM steels [15]. In the case of HT-9 where there was evidence of IGSCC, crack density surged when the dissolved oxygen concentration increased from <10ppb to 300ppb [15]. Therefore dissolved oxygen plays a critical role in the SCC performance of the FM steels under SCW.

Dissolved oxygen has complex effects on austenitic steels. At short exposure times the weight gain in a highly oxygenated solution is lower than a less oxygenated solution [14]. However, the weight gain increases rapidly as exposure duration increases. For low oxygen concentrated solutions, the weight gain remains constant at high exposure time. This is due to equilibrium between weight loss due to spallation and weight gain due to oxidation [14]. Results of CERT on several austenitic steels show that higher dissolved oxygen in SCW increases the UTS, and decreases the ductility [14].

4. Conclusions

It is clear that the corrosion mechanisms of supercritical water are complex and influenced and a great number of factors, including temperature, pressure, density, pH value, electrochemical potential, inorganic ions, and dissolved oxygen. In designing a reactor a clear understanding of the composition of the supercritical water used is required to allow a passive state to be reached and limit the corrosion of the materials.

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