THE EFFECTS OF WATER RADIOLYSIS ON THE CORROSION AND STRESS
CORROSION BEHAVIOR OF TYPE 316 STAINLESS STEEL IN PURE WATER

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ABSTRACT

The corrosion and stress corrosion behavior of Type 316 stainless steel (316 SS) was observed under irradiated and non-irradiated conditions. The pure water solution was 0.0005M (mole/liter) potassium sulfate (K_2SO_4), deaerated with hydrogen or argon, at temperatures of 50 and 90°C. Gamma irradiation in hydrogen-deaerated solution at 50°C showed approximately 100 mV potential shift in the active direction. The potential shift was attributed to polarization of the 316 SS by reducing radiolysis products. In addition, solution irradiation resulted in nearly an order of magnitude increase in the passive current density of 316 SS. The increase in current density was partially attributable to increased surface reaction rates involving radiolysis products as well as increased metal corrosion rates. The apparent increase in metal corrosion rate was not considered to be significant.

A computer code was used to simulate pure water radiolysis at 50, 90, and 130°C with gamma dose rates of 10^{18} - 10^{24} electron-volt/liter/second (eV/l/s). The concentrations of the molecular radiolysis products, H_2 , H_2O_2 , and O_2 varied directly with dose rate and inversely with temperature. In order to determine the effects of different environments, simulations of pure water radiolysis were performed with hydrogen, argon, and argon + 20% oxygen deaeration. Hydrogen peroxide yields were generally highest with argon + 20% oxygen, lower with argon, and lowest with hydrogen deaeration. Oxygen yields were lower in hydrogen-deaerated simulations than in argon-deaerated simulations.

Slow strain rate tests (SSRT) were conducted to investigate stress corrosion cracking (SCC) susceptibility. The results suggest that Type 316 stainless steel was not susceptible to SCC in hydrogen- or argon-deaerated 0.0005M K_2SO_4 at 50°C. This has been shown for both annealed and the sensitized stainless steel at open circuit potentials between -0.690 to -0.590 V and at -1.055 V vs Hg/HgSO₄. The slip dissolution model was applied to the analysis of these results.

Modeling of irradiated water chemistry was performed, taking radiolytic species concentrations from a radiolysis simulation in argon-deaerated pure water at 10^{24} eV/l/s and 50°C. The cumulative effect of additions of approximately 0.2 ppm H₂, 1 ppm O₂, and 1 - 1.2 ppm H₂O₂ to argon-deaerated, 0.0005M K_2SO_4 at 50°C was observed. The open circuit potential of both sensitized and annealed 316 SS showed a net shift of approximately 800 mV in the noble (positive) direction. Steady-state potentials of -0.180 V for the sensitized 316 SS wire and -0.096 V vs. Hg/HgSO₄ for the annealed 316 SS wire were achieved and were independent of the presence of oxygen. The resulting potential shift for sensitized 316 SS to -0.180 V vs. Hg/HgSO₄ is likely to promote SCC, based upon the predictions of the slip dissolution model.

1. INTRODUCTION

The Conceptual Design Activity (CDA) for the International Thermonuclear Experimental Reactor (ITER) identifies pure water as the coolant for the major reactor components and solution annealed Type 316 austenitic stainless steel as the structural alloy for these components. Extensive welding will be required in the reactor construction. [1]

The coolant and structure will be subject to intense, high energy radiation which will result in water radiolysis. Water radiolysis involves water decomposition by the action of ionizing radiation, into free radical components H and OH. The net result of water radiolysis is the formation of the molecular products hydrogen (H_2), hydrogen peroxide (H_2O_2), and oxygen (O_2). [2] The presence of these species in aqueous systems may effect the overall oxidizing or reducing nature of the solution. This will in turn cause a shift in the measured electrochemical potential (ECP) of 316 SS in the system.

A principle concern in the ITER design is that the formation of radiolysis products may increase the stress corrosion cracking (SCC) susceptibility of 316 SS.[3] SCC in austenitic stainless steels is known to occur in hot acidic chloride (Cl^-) environments, in concentrated caustic (NaOH) solutions and in many other environments.[4,5] SCC in chloride-bearing environments is transgranular in nature, however the majority of SCC cases involve intergranular cracking.[6] Of interest in this work is the history of intergranular stress corrosion cracking (IGSCC) susceptibility in pure water systems of boiling water reactors. [7,8] Susceptibility to

IGSCC in high purity water generally requires an applied stress greater than yielding, and some combination of dissolved oxygen and another contaminant must be present. [8] Austenitic stainless steel in the sensitized metallurgical condition, that is depleted to less than 12% chromium at grain boundaries, [9] is the most susceptible, although IGSCC was noted in non-sensitized Type 304 stainless steel. [7]

Austenitic stainless steels form a protective, passive film that imparts corrosion resistance. Nearly all metal/environment combinations that exhibit SCC susceptibility are known to form a surface film, such as a the passive layer or a tarnish film. However, formation of a surface film does not imply that SCC will occur, nor is a film required for SCC. [10]

A currently accepted theory for the initiation of stress corrosion cracking is the slip-dissolution model. [5] This model postulates that SCC will occur for a susceptible environment/alloy combination in electrochemical potential ranges where the passive film is unstable [8]. It is important to examine the possibility that 316 SS may be susceptible to IGSCC in an irradiated aqueous environment where radiolytic species exist.

The coolant temperature in the ITER CDA design is estimated at 60 - 100°C. [1] Due to the limited corrosion and stress corrosion data for 316 SS below 100°C, testing was performed in pure water at 50 and 90°C. Electrochemical tests were performed in laboratory and gamma-irradiated solutions in order to observe the effects of radiolysis products on the corrosion behavior of the stainless steel. The shift in electrochemical

potential with irradiation and the possible increase in passive corrosion rates were investigated.

To evaluate SCC susceptibility, the slow strain rate test (SSRT) was used. Aqueous SSRT experiments were designed to model the irradiated water chemistry rather than test directly in the radiation field. Water chemistry modeling was accomplished using a radiolysis code. Solution annealed 316 SS was tested, which is the specified alloy in the ITER CDA design. [1] As welding will be performed extensively in fabrication, sensitized material was also investigated in stress corrosion cracking experiments.

2. TECHNICAL BACKGROUND

2.1 International Thermonuclear Experimental Reactor (ITER)

The ITER CDA design incorporates an integrated first wall, blanket, and shield structure. The purpose of this structure is to define the fusion chamber, absorb and recover heat, produce tritium through a breeder system, and absorb neutron and gamma radiation. [11]

The option selected for the ITER CDA is the solid ceramic breeder, incorporating Li_2O or a ternary ceramic as the tritium breeder material. Beryllium (Be) is used as a multiplier of the fusion neutrons to boost tritium production in the breeder. Solution annealed Type 316 austenitic stainless steel is selected as the reference structural material due to the available data base and its ease of fabrication. The reference coolant is high purity water at 60 - 100°C and 1.5 MPa. [1] Water flows through a layered integral blanket with a general layering scheme of H_2O /316 SS /Be / Li_2O under consideration. [3]

Aqueous stress corrosion cracking (SCC) of the stainless steel in pure water is a design concern, with the additional problems arising from irradiation-assisted stress corrosion cracking (IASCC), high hydrogen generation at low operating temperatures, and radiolysis and/or electrolysis of the coolant. [3] It was proposed that aqueous SCC of austenitic stainless steels be controlled by adopting practices such as those used in light water fission reactors, [12] such as hydrogen water chemistry and the use of nuclear grade, low carbon stainless steels.

2.2 Effects of Irradiation

2.2.1 Water Radiolysis

On the basis of free radical theory [13], water decomposes into radicals (H and OH) upon irradiation:

The steps leading to this decomposition are as follows. [14] With high energy radiation, water molecules become ionized along the track of an energetic particle, creating a secondary electron,

The secondary electrons are themselves energetic enough to ionize other water molecules, resulting in groups of ions or 'spurs'. A secondary electron's energy is reduced through inelastic collisions, at which point the electron interacts along either of two paths.

In the Samuel-Magee [15] hypothesis, the secondary electron eventually loses its energy and recombines with the parent ion.

The excited water molecule (H_2O^*) in turn splits into radicals,

The Lea-Gray-Platzman theory [16,17,18] postulates that the radicals are formed in a different manner. When the secondary electron loses its energy, it becomes hydrated rather than reuniting with its parent ion.

The result is that a hydrogen radical and a hydroxyl ion are formed. The parent ion is then able to dissociate further into a hydroxyl radical and a hydrogen ion.

With low energy particles and secondary electrons, the water molecules may become excited to a level below which ionization occurs but high enough to overcome the H_2O molecular bonds. The excited molecule simply splits into H and OH radicals.

Dissimilar radicals can readily recombine into water after they lose energy in collisions with molecules. [14]

The radicals may also combine with other like radicals to form molecular products H_2 and H_2O_2 , especially when they are present in large concentrations in the spurs. [19]

The relative amount of molecular products or radicals formed depends on the density of radicals in the radiation track. Under heavy particle irradiation, the HO_2 intermediate can form independently, or by radical and molecule interaction: [2]

The primary yields from radiolysis are therefore e_{aq}^- , H, H_2 , OH, and H_2O_2 , and in some cases HO_2 .

Oxygen is produced indirectly by the interaction between radicals and H_2O_2 . [2]

Reactions involving the primary radiolysis products leads to additional species, such that the primary and secondary products are e^-_{aq} , H, H_2 , OH, H_2O_2 , HO_2 , HO_2^- , O_2 , O_2^- , H^+ , and OH^- . [2,14]

Two important variables must be introduced at this point. The yield of a radiolytic reaction, denoted as G, is the number of molecules or species produced for each 100 electron-volt (eV) of energy absorbed by the medium. [2] The linear energy transfer (LET) is the amount of energy absorbed by the medium per unit track length of the radiation. The LET varies for each type of radiation. Heavy particle radiation, such as alphas and neutrons, deposit their energy in a short distance with high LET. Conversely, light particles such as beta, gamma, and X-radiation have a low LET, penetrating farther while dissipating their energy.

Irradiation with high LET particles, such as alphas or neutrons, produces high track densities of radicals. In this case the probability of like radical collisions is greater than the probability of radicals escaping from the track, and the molecular products yield is high compared to the free radical yield. In contrast, irradiation by particles of low LET, such as X-ray or gamma, produces lower concentrations of radicals in the track. Here, free radicals can diffuse out of the track, like radical interaction is less probable and radical recombination to form water is more likely. [2]

The process of water radiolysis can be simulated with computer models. The secondary reactions involving free radicals and molecular species can be solved simultaneously using numerical solutions to a set of partial differential equations. A computer code was used in this work; details of this code and others are found in Appendix A.

2.2.2 Radiolysis Water Chemistry

In pure water, reducing radiolytic species (e^-_{aq} , H, H_2) are generally balanced by oxidizing species (OH, H_2O_2 , O_2 , and HO_2), however oxidizing or reducing radicals predominate when certain solutes are present. For instance, oxidizing solutes such as Fe^{3+} and ions can react preferentially with, or 'scavenge' reducing radiolysis products and affect the relative yield. Likewise, reducing solutes scavenge oxidizing products.[2] The cover gas used similarly alters the outcome of radiolysis. [20] With hydrogen gas, dissolved H_2 , is reducing and scavenges oxidizing species. This results in lower H_2O_2 and O_2 yields but higher reducing species yields. Conversely, with oxygen present in the cover gas, dissolved O_2 scavenges e^-_{aq} and H resulting in a decreased H_2 and increased H_2O_2 yields. [2,20,21] The overall result is that reducing radiolysis products are favored when reducing species exist in solution and oxidizing species will be favored where the environment is initially oxidizing.

2.2.3 Electrochemical Potential

The oxidizing power of the environment is reflected by the electrochemical potential. Research in high purity water at 275°C has shown that the potential becomes more positive (noble) as the dissolved oxygen content increases [22] and it becomes more negative (active) as the dissolved hydrogen/oxygen ratio increases [23].

2.3 Austenitic Stainless Steels

2.3.1 Passive Film And Sensitization

Stainless steels derive their corrosion resistance through the formation of a chromium-rich passive film. A minimum of 12% chromium was found to induce passivity in Fe-Cr alloys in solutions at pH 7. [4] Thus, 12% chromium is widely recognized as the critical level required for corrosion resistance in neutral aqueous environments. Heating austenitic stainless steels in the range of 425 to 815°C may result in the alloy becoming sensitized, that is, prone to intergranular attack in corrosive environments. This phenomenon is associated with the precipitation of chromium carbide (Cr_{23}C_6) and the time to precipitate is dependent on both temperature and carbon concentration. The most rapid sensitization occurs at approximately 650°C. [9] The degree of sensitization achieved for a given time and temperature is very dependent on the carbon content, with less sensitization resulting as the carbon content is decreased. [4] Sensitization in austenitic stainless steels is typically associated with the heat affected zones of welds, giving rise to the term 'weld decay'. [9]

Aborn and Bain [24] accurately described the sensitization process. They observed that chromium-rich carbide formation at grain boundaries was accompanied by increased susceptibility to corrosive attack in the grain boundary region. They believed that this occurred by carbon migration to regions of higher atomic mobility, such as grain boundaries, with concurrent chromium depletion in the neighboring matrix as the

chromium-rich phase precipitated. As a result of this depletion the chromium content dropped below 12%, causing a local loss of corrosion resistance at the boundaries. This theory has been widely accepted as the mechanism for sensitization in austenitic stainless steel.

2.4 Theories of Stress Corrosion Cracking

2.4.1 General Observations

Stress corrosion cracking generally requires that three conditions exist simultaneously: "a critical environment, a susceptible alloy, and some component of tensile stress. Environmental species are often specific to the alloy system and may not have an effect on other alloys of different type." [5] Engell noted that the formation of a surface film seemed to be inherent to nearly all alloy-environment systems where SCC was observed, but this was not a prerequisite for SCC. [10] The electrochemical potential is important to SCC; observations of accelerated stress corrosion cracking and the relationship to electrochemical potential is best explained by competing theories, the stress sorption model and the slip-dissolution model. However, the embrittling action of hydrogen in metals compelled many to implicate it in the mechanism of SCC. Therefore, the hydrogen theory is presented first.

2.4.2 Hydrogen Theory

One theory behind stress corrosion cracking (SCC) in austenitic steels is based upon hydrogen SCC (hydrogen embrittlement) in high strength steels. The FCC phase in austenitic stainless steels is metastable at room temperature and transforms to BCC ferrite with cold work. [4,24]

Phase transformation does not change the corrosion resistance substantially, but it does introduce hydrogen cracking susceptibility. [4] It is possible, under the influence of cathodically generated hydrogen, [8] that unstable austenite transforms to martensite in the strain field of the crack tip. Hydrogen would then embrittle this harder phase by lattice weakening and decohesion or through precipitation of a brittle hydride phase.

Of the several arguments against this theory, [8] two are readily observed. First, the tendency towards hydrogen cracking in high strength steels increases as strength increases, however SCC susceptibility in austenitic stainless steels decreases with increasing strength from cold work. Second, cathodic polarization accelerates the evolution of hydrogen, the embrittling agent. Cracking is promoted in high strength and ferritic stainless steels at cathodic potentials, yet austenitic stainless steels are protected against SCC at these low potentials. [25] These and other arguments [8] disallowed the hydrogen theory from application to SCC of austenitic stainless steels.

2.4.3 Stress-Sorption Model

Stress-sorption cracking is a theory of SCC based upon the adsorption of a certain species which consequently promotes cracking. This theory postulates that the surface energy in the Griffith relation [26,27] is lowered, that is γ_s is decreased such that the stress required for crack propagation is lowered.

$$\sigma_f = \sqrt{\frac{2E\gamma_s}{\pi c}}$$

σ_f = Stress for fracture

γ_s = Surface Energy

c = Length of a surface crack

E = Elastic Modulus

This theory had been accepted as the mechanism for the cracking of glass by water and for liquid metal embrittlement in metals. [4] Uhlig suggested [4,28] that the specificity of damaging ions in SCC was a result of the specific nature of chemisorption, and other ions could displace damaging ions and inhibit SCC. He also explained the electrochemical potential dependence of SCC on very potential-dependent adsorption. Observations that SCC was suppressed by cathodic protection seemed to support this argument.

Staehle [8] rejected the stress-sorption model in favor of the slip dissolution model on the basis of three issues. Cracking in ductile metals involved crack tip blunting, whereas the Griffith model is only valid for brittle materials with little or no plastic deformation. [27] Dissolution at the crack tip would make cleavage unlikely as a fracture mode. Finally, instances of SCC were found with less specific environment/metal combinations, leading to the author's conclusion that "The specific ion concept can now be disregarded." [8]

2.4.4 Slip Dissolution Model

Slip dissolution, also known as electrochemical dissolution, is the model for SCC which involves slip steps breaking the passive film,

localized anodic dissolution of the unprotected rupture, and concurrent crack advance. Engell [10] noted that the formation and propagation of a crack involved the establishment of active-passive galvanic cells, where the anodic current was concentrated at the crack tip and the cathodic current was supported on the surrounding passive surface. The metallurgical conditions favoring SCC are coarse or co-planar slip such that the slip step height is larger than the passive film thickness. [10]

At this point in the process the film repassivation kinetics play an important role. Staehle noted that there are two extremes for the repassivation of the bare metal at the slip step -- rapid repassivation, protecting the alloy, and very slow repassivation, which leads to "extensive or non-restricted lateral dissolution" [8] or shallow pitting. If the repassivation kinetics are somewhere between the two limits, passivity is not stable with respect to slip step emergence at the surface and SCC is favored. It was postulated that in a susceptible alloy-environment combination, there are electrochemical potential ranges where the repassivation kinetics lead to unstable passive films. [8] Figure 2.1 shows these cracking potential ranges. Zone 1 is the active-passive transition near the primary passivation potential and zone 2 is the range near the breakdown potential.

Figure 2.1. Schematic polarization diagram showing zones of stress corrosion cracking susceptibility. [8]

Slip dissolution is generally accepted as a necessary step to initiate SCC [5]. The model is applicable to both IGSCC and TGSCC. In a strained polycrystalline solid, slip leads to localized strain and high dislocation densities at the grain boundaries. [27] The strain energy associated with these dislocations leads to a strain energy concentration at the grain boundary which is prone to preferential corrosion. The corrosion at the grain boundary leads to a preferred intergranular crack path and IGSCC. [29] In alloys with low stacking fault energy where planar slip is favored, slip is localized within grains along slip bands. Here, the preferential corrosion at slip bands leads to transgranular crack path, [29] which can explain TGSCC of austenitic stainless steels in chloride-bearing solutions. [6]

However, the slip dissolution model does not adequately describe the growth of a crack. Anodic dissolution at the crack tip should obscure any characteristic features of fracture surfaces. The fracture surfaces from transgranular SCC show crystallographic cleavage features and those of intergranular SCC display distinct grain boundaries. [5] Although the slip dissolution model does not fully explain all stages of SCC, it is accepted for crack initiation and can be used in the present work.

With the slip dissolution model defined, predictions of SCC behavior can be made. [8] Conditions which elevate the potential into or above the cracking range, such as oxidizing agents (O_2 , Fe^{3+}) may promote SCC. Environmental factors that produce local film instabilities, such as chlorides and possibly other halides, will initiate SCC. Intergranular SCC (IGSCC) of sensitized stainless steel in oxygen-bearing pure water can be explained. The chromium depleted Fe-Ni grain boundaries apparently repassivate slower than the bulk grains at elevated potentials. As a result, dissolution is accelerated at the grain boundaries, promoting IGSCC.

2.5 Intergranular SCC of Stainless Steels In High Purity Water

IGSCC of austenitic stainless steels in pure water has been a notable problem for many years. IGSCC failures were noted in both sensitized and non-sensitized stainless steel in boiling water reactor (BWR) environments. This environment was typically high purity water at $300^\circ C$ with oxygen present. [7,8] Later work [22] showed that oxidizing potentials promoted IGSCC.

2.5.1 Electrochemical Potential And IGSCC

Cowan and Kaznoff [30] showed that, at 288°C with hydrogen over-pressure, sensitized Type 304 stainless steel (304 SS) was susceptible to IGSCC at highly oxidizing potentials, (+0.32 volts [V] vs. standard hydrogen electrode [SHE]), but was not at low potentials (-0.65 V vs. SHE). Annealed (non-sensitized) 304 SS did not exhibit SCC even at +0.80 V vs. SHE. These test were performed in 0.1M Na₂SO₄ which was considered an innocuous solute. However, the annealed alloy exhibited TGSCC in 0.1M sodium chloride (NaCl).

Indig and McIlree [22] related the electrochemical potential and the IGSCC of as-welded Type 304 in simulated boiling water reactor water at 274°C. They reported that the IGSCC in the sensitized material was eliminated if the potential was dropped below a threshold or value of -0.250 V vs. SHE. Further testing in an operating BWR [31] showed that the "protection potential" was -0.230 V vs. SHE. The reactor was run under hydrogen water chemistry (HWC) conditions and the protection potential was reached by injecting hydrogen to the point where the dissolved oxygen was less than 20 ppb. Note that hydrogen was observed to decrease the reversible potential on platinum at 275°C as the dissolved hydrogen/oxygen ratio increased. [23] It became clear that HWC in boiling water reactors could provide the electrochemical potential control that would eliminate stress corrosion cracking in sensitized 304 SS. [31]

2.5.2 IGSCC In Lower Temperature ($\leq 100^{\circ}\text{C}$) Pure Water

The IGSCC susceptibility of sensitized austenitic stainless steel at lower temperatures has been pursued by several workers. However, the results have not been in agreement in all cases. In general, for IGSCC susceptibility in sensitized 304 SS, the presence of oxidizing potentials or oxygen were required [32,33,34]. No IGSCC except in chloride-bearing solutions above the pitting potential was observed in sensitized 304 SS. [35] Cracking was seen in sensitized 304 SS in the active-passive transition potential. [36] Annealed 316 SS was only slightly susceptible in chloride solutions [37] and in oxidizing crevice conditions [38]. Crack growth in lightly sensitized 316 SS was slower under gamma irradiation in a limited test. [39]

In view of the limited data for 316 SS in lower temperature environments which are specific to the ITER CDA design, this work reports the SCC susceptibility of 316 SS under conditions expected in the ITER CDA design.

3. EXPERIMENTAL PROCEDURE

3.1 Irradiation Facility

Conventional electrochemical polarization experiments were conducted in the test solutions, and compared with experiments conducted in irradiated solutions. Irradiation was performed in a Linear Electron Accelerator (LINAC). A high voltage (≈ 200 kV) electron gun produced a beam of electrons at a current of 55 - 70 micro amperes (μA). This electron beam was accelerated to 60 million electron-volts (MeV) in an evacuated conduit. The high energy electron beam was used with a tantalum target to produce a photon radiation field via Bremsstrahlung (decelerating radiation). A plan view of the LINAC facility is shown in Figure 3.1. The electrochemical cell was placed approximately 4 meters away from the target. The electrochemical cell was subject to photon energies of 60 MeV maximum and 20 MeV average. The average dose rate to the solution was 340 krad/hour (3×10^{18} eV/liter/second). Electrochemical measurements were made during solution irradiation using a shielded potentiostat/galvanostat and remote data acquisition.

Figure 3.1. Floor plan view of the Linear Electron Accelerator (LINAC) facility used for irradiated solution testing.

3.2 Aqueous Test Environment

3.2.1 Solution

The test solution was high purity water at 50 and 90°C, deaerated with hydrogen or argon gas. In order to obtain sufficient solution conductivity for potentiodynamic measurements, 0.0005 mole/liter (M) potassium sulfate (K_2SO_4) was added to the high purity water. The conductivity of this reference solution was approximately $180 \mu S cm^{-1}$. Laboratory results obtained in this program have shown that this concentration of K_2SO_4 does not affect the corrosion behavior of 316 SS in non-irradiated, deaerated solutions. [40] The dissolved hydrogen concentration $[H_2]$ was approximately 1450 ppb at 50°C, the solubility limit for the gas at 1 atmosphere (atm) hydrogen pressure. [41].

3.2.2 Gases

The solution was stirred, and the cell was deaerated using a gas diffuser tube. High purity grade hydrogen (99.999%) and argon (99.995%) gases were used in all experiments. Solutions that modeled the irradiated solution chemistry utilized certified standard gas mixtures of Ar/O₂ ($9.17 \pm 0.18\%$ O₂) and Ar/H₂ ($38.4 \pm 0.77\%$ H₂).

3.3 Material

3.3.1 Electrochemical Test Material

The 316 SS samples were cut into 1 cm² coupons from 0.19 cm thick plate, solution annealed at 1300°C for 0.5 hour and water quenched. The

chemical compositions obtained from chemical analysis of the sample materials are provided in Table I.

Table I. Composition of Type 316 stainless steel sample material based on chemical analysis.

Element	Fe	Cr	Ni	Mo	Mn	Si	C	S	P
Plate, wt. %	Bal.	16.6	11.8	2.4	1.7	0.7	0.06	0.02	--
Wire, wt. %	Bal	19.28	11.12	2.05	1.76	0.40	0.05	0.011	0.013

The samples were ground to 600 grit, polished using 15 μ and 9 μ diamond, with a final polish using 0.3 μ aluminum oxide in 10% oxalic acid. The samples were ultrasonically cleaned in ethanol, rinsed in high purity water and air dried. The samples were suspended in the test solution using stainless steel wire holders.

Figure 3.2 shows the microstructure of the solution annealed plate, etched with 50% nitric/50% hydrochloric acid. Annealing twins and spherical inclusions are revealed, however the grain boundaries are not clearly visible.

Platinum counter electrodes consisted of platinum mesh spot welded to platinum wire. Platinum electrodes for surface reaction tests were made by spot welding a 1 cm² bright platinum foil to platinum wire.

Figure 3.2. Solution annealed Type 316 stainless steel plate. Etched in 50% nitric/50% hydrochloric acid. Annealing twins and inclusions are visible. 400X.

3.3.2 SCC Test Material

Slow strain rate test (SSRT) specimens were 0.1588 cm diameter 316 SS wires, approximately 40 cm long. The metallurgical conditions of the alloy were solution annealed (SA) and solution annealed and sensitized (Sen.). Solution annealing was done in an argon atmosphere at 1060°C for 0.5 hours, followed by water quenching. The microstructure of solution annealed 316 SS wire is shown in Figure 3.3. This sample was electrolytically etched in 60% nitric acid in order to reveal grain boundaries and inclusions.

Sensitization was accomplished in an argon atmosphere at 650°C for 2 hours and air cooled, followed by an additional 24 hours at 650°C.

Testing for sensitization was performed on a sample wire using an oxalic acid electrolytic etch in accordance with ASTM A262-86 Practice A. [42]

The microstructure of sensitized 316 SS is shown in Figure 3.4. Heavy intergranular attack at sensitized grain boundaries is evident, extending from the wire surface into the microstructure. On the basis of the microstructure of etched samples after the initial 2 hour heat treatment, an additional 24 hours was necessary to ensure precipitation of chromium-rich carbides ($M_{23}C_6$). The 24 hour treatment is in agreement with the published time-temperature-precipitation (TTP) diagrams for 316 SS. [43]

Figure 3.3. Solution annealed Type 316 stainless steel wire. Electrolytically etched in 60% nitric acid. Grain boundaries and inclusions are visible. 400X.

The wires were mechanically polished to a 600 grit finish, cleaned with ethanol and rinsed with high purity water. Some annealed wire SSRT tests were performed on unpolished samples, with an air-formed film. Wire specimens used in electrochemical measurements were 12 cm long sections of the wire, taken from the same heat treatment batches used in SSRT experiments.

Figure 3.4. Sensitized Type 316 stainless steel wire. Electrolytically etched in 10% oxalic acid. Grain boundary attack is seen near the surface and light, round features are chromium-rich carbides. Smaller dark spots are etch pits and inclusions. 400X

3.4 Electrochemical Test Procedures

3.4.1 Apparatus

The test environment consisted of a conventional, two liter electrochemical cell. A schematic drawing is shown in Figure 3.5(a). The data were collected with a potentiostat/galvanostat using either a computer driven analog/digital interface or an analog DC output to a x-x'-t chart recorder. The reference electrodes used were mercury/mercurous sulfate (Hg/HgSO_4) in saturated K_2SO_4 with an reference potential of +0.640 volts (V) versus the standard hydrogen electrode (SHE).

3.4.2 Potentiodynamic Polarization

Polarization curves were generated using potentiodynamic scanning techniques at a scan rate of 0.167 mV/sec, in accordance with ASTM Standard G5-87 [44]. Polarization curves were measured for 316 SS samples and platinum foil electrodes in both non-irradiated and irradiated solutions. In all cases, the sample (working electrode) was pre-conditioned cathodically at -1.5 V vs. Hg/HgSO_4 for 30 minutes, allowed to drift for at least 2 hours to a stable open circuit potential, then scanned through the potential range. In irradiated solution tests, the radiation beam was energized just prior to beginning the potential scan.

3.4.3 Open Circuit Potential

Open circuit potential versus time measurements also were made using the potentiostat as a potentiometer. The 316 SS sample was pre-conditioned as described previously, and allowed to drift back to a stable potential. Upon reaching a stable potential, the radiation beam was

energized and the resulting potential shift was recorded as a function of time.

Figure 3.5. Schematic drawings of test cells. a) Electrochemical cell. b) SSRT environment cell.

3.4.4 Passive Current Density

Passive current density experiments were performed on solution annealed 316 SS in irradiated and non-irradiated solutions. The electrochemical apparatus was used to set the ECP in the passive potential range at -0.270 V vs. Hg/HgSO_4 , and the current response was recorded as a function of time. The sample was cathodically conditioned at -1.5 V vs. Hg/HgSO_4 , followed by immediate potentiostatic polarization to the fixed potential. The test was conducted initially under irradiation and then repeated on a fresh sample in the laboratory.

3.4.5 Radiolysis Water Chemistry Modeling

Laboratory tests modeling the irradiated water chemistry were conducted in a similar manner. The open circuit potential was measured as a function of time on polished wire samples in argon-deaerated solution, however cathodic pre-conditioning was omitted as this step was not performed for the SSRT wire samples.

Radiolytic species concentrations of 0.2 ppm H_2 , 1 - 1.2 ppm H_2O_2 , and 1 ppm O_2 were targeted. Ar/H_2 and Ar/O_2 gas mixtures were procured which would yield partial pressures of 0.17 ± 0.033 atm H_2 and 0.038 ± 0.007 atm O_2 when bubbled together through the solution at 50°C . These partial pressures yielded 0.2 ± 0.04 ppm H_2 and 0.9 ± 0.2 ppm O_2 based on partial pressure and solubility data. [41] A schematic diagram of the gas mixing system is shown in Figure 3.6. Ten μl of laboratory grade, 30% hydrogen peroxide was added to two liters of solution, in order to yield 1.2 ± 0.3 ppm H_2O_2 by dilution. Concentrations of H_2 , H_2O_2 , and O_2 were not measured

during these tests to avoid disturbing of the water chemistry and the measured potential. Rather, the reported values are estimates based on handbook data [41].

The room temperature pH of the solution was 7.5. The solution was initially deaerated with argon for 3 or more hours. Ar/H₂ was admitted first, with the flow rate balanced 50:50 with argon. Ar/O₂ was then admitted and the flow rate was balanced 50:50 with Ar/H₂. H₂O₂ was added to the electrochemical cell after H₂ and O₂ were introduced.

Figure 3.6. Schematic diagram of the gas delivery system used to mix the gases to achieve the appropriate gas partial pressures.

3.5 Stress Corrosion Cracking

3.5.1 Slow Strain Rate Test Apparatus

The slow strain rate test (SSRT) technique [45] was used in the SCC evaluation. The system consisted of a tensile test platform equipped with a stepping motor and gear reducers. The specimens were elongated at a constant rate of 2.5×10^{-5} cm/sec. This rate corresponded to initial strain rates of 1.6×10^{-6} sec⁻¹ and 1.8×10^{-6} sec⁻¹ for aqueous tests and air tests, respectively. The difference in initial strain rates was due to a shorter gauge length used in the air tests. The specimens were mounted on fiberglass-reinforced epoxy resin snubbers which were designed for tensile testing wire specimens. [46] The snubber material is non-conducting in order to prevent stray electrical problems during electrochemically-controlled tests. The load was recorded on an x-x'-t chart recorder; during aqueous testing the open circuit potential was measured on the same scale. A potentiostat/galvanostat was used to monitor open circuit potentials.

The wire samples were not pre-conditioned but were allowed to come to a stable open circuit potential prior to the start of straining. During the deaeration period, the wires were loaded to 25% of the yield stress and the initial length measured using 35 cm stainless steel dividers.

Air tests at 50, 90 and 130°C were conducted using a thermocouple controlled, infrared heat lamp with an aluminum foil housing to provide a heated zone.

3.5.2 Environment Cell and Test Loop

The aqueous test environment cell was fabricated from clear acrylic plastic, with a volume of 0.5 liters. A schematic drawing of the SSRT cell is shown in Figure 3.5(b). The body was cylindrical, with a plate bottom and a flanged top ring. The sections were bonded together using 1,2 dichloroethane. The top plate was fastened to the flanged top ring over a 10 cm diameter O-ring. The wire specimens passed through the cell using small diameter vacuum fittings and Teflon™ sleeves. Vacuum fitting penetrations were also provided for the thermocouple, counter electrode, and salt bridge. The cell was part of a 6 liter volume recirculating system employing a peristaltic pump. Stainless steel, norprene and tygon tubing sections were used to connect the cell to a continuously deaerated and heated 6 liter glass vessel. The test loop and SSRT apparatus are shown schematically in Figure 3.7. In all aqueous tests, the test loop was deaerated for at least 3 hours prior to straining with hydrogen or argon gas at approximately 70 cm³/min.

Figure 3.7. Schematic drawing of the SSRT tensile apparatus, recirculating loop, and test cell.

4. RESULTS AND DISCUSSION

4.1 Electrochemistry

4.1.1 Electrochemical Potential Shift with Gamma Irradiation

Upon irradiating the solution at 50°C, the electrochemical potential of 316 SS was shifted by approximately 100 mV in the active direction. This shift was observed in open circuit potential versus time tests and in potentiodynamic polarization experiments. Figure 4.1 shows the potential shift with time for four different tests. The scatter in the non-irradiated potential at time = 0 is assumed to be due to slight variations in the pH or slight oxygen contamination of the test solutions. This scatter in open circuit potential was typical for all electrochemical tests at 50 and 90°C.

The ECP shift may also be seen by comparing the zero-current potentials of the polarization curves shown in Figure 4.2. Reduction/oxidation polarization curves on platinum with hydrogen deaeration, Figure 4.3, and argon deaeration, Figure 4.4, exhibit similar ECP shifts with solution irradiation. Two independent tests in non-irradiated solution are plotted in Figure 4.3 in order to show the scatter in the experiments. The current density on a platinum electrode reflects the oxidation and reduction reactions of species at the surface. These data indicate that the ECP shift is determined by radiolysis products forming in the solution.

Figure 4.1. Open-circuit ECP as a function of time for annealed 316 SS in hydrogen deaerated, 0.0005M K₂SO₄ at 50°C. Solution irradiation began at time = 0. Results are from 4 different tests. Note that the shift (ΔE) is virtually independent of the initial potential.

Figure 4.2. Potentiodynamic polarization curves for annealed 316 SS in hydrogen deaerated, 0.0005M K₂SO₄ at 50°C, irradiated and non-irradiated solution. The active zero-current potential shift and passive current density increase are noted with arrows.

Figure 4.3. Potentiodynamic polarization scans for platinum, in irradiated solution and in two different non-irradiated solution tests. Hydrogen deaeration, 0.0005M K_2SO_4 at 50°C. Active zero-current potential shift is noted with arrows.

Figure 4.4. Potentiodynamic polarization curves for platinum in irradiated and non-irradiated solution, argon-deaerated 0.0005M K_2SO_4 at 50°C. Active zero-current potential shift and current density increase are noted with arrows.

As mentioned in section 2, the oxidizing power of an environment is reflected in the electrochemical potential. The ECP of Type 304 stainless steel and the oxidation potential of platinum have been determined in 275°C water, showing positive (noble) changes in potential with increasing dissolved oxygen [22,23] and negative changes were seen with increasing dissolved hydrogen to oxygen ratio. [23] Several observations of shifts in the ECP of austenitic stainless steel have been made in aqueous solutions with gamma irradiation. [20,21,47,48,49] Generally, if oxygen was

present, the solution was initially oxidizing and a positive (noble) potential shift was noted. Conversely, if oxygen was maintained at low concentrations through hydrogen overpressure or with HWC, the solution was reducing and a negative (active) potential shift was seen.

The effect of gamma irradiation on corrosion behavior of 304 SS was carried out by others at 40°C in argon deaerated, 300 ppm Cl^- . [20] The potential increased with irradiation by 200-300 mV. H_2O_2 was detected after the test in concentrations of 0.1 to 1.1 ppm. H_2O_2 produced positive potential shifts in non-irradiated laboratory experiments, but not of the magnitude seen in the irradiated case. It was concluded that H_2O_2 alone could not have caused the irradiated potential shifts. It was postulated that, in addition to H_2O_2 , the oxidizing radicals, O_2^- and $\text{OH}^\cdot$, contributed by polarizing the stainless steel and inducing the noble potential shift.

This combined action of molecular and radical radiolysis products can occur in the reducing situation as well. The negative electrochemical potential shifts observed in hydrogen deaerated solution were due to the formation of reducing molecular (H_2) and radical (e^-_{aq} , $\text{H}^\cdot$) radiolysis products. The reducing radicals interacted on the stainless steel to polarize it in the active direction. The solutions were maintained at the solubility limit of hydrogen at atmospheric pressure. If molecular hydrogen alone was responsible for the negative potential shift, the hydrogen partial pressure would have to exceed unity according to the Nernst equation for the hydrogen reduction reaction: [4]

$$E_{\text{H}_2/\text{H}^+}(\text{SHE}) = E^{\circ}_{\text{H}_2/\text{H}^+} - \frac{RT}{2F} \ln \frac{p_{\text{H}_2}}{[\text{H}^+]^2}$$

$E_{\text{H}_2/\text{H}^+}$ = reversible hydrogen potential, V

$E^{\circ}_{\text{H}_2/\text{H}^+} = 0$, standard hydrogen electrode potential(SHE)

R = Gas constant, joule/K · mole

T = Temperature, K

F = Faraday (96,500 coulomb/equivalent)

p_{H_2} = Hydrogen activity or partial pressure

$[\text{H}^+]$ = Hydrogen ion concentration, mole/liter

The active potential shift observed on platinum with argon deaeration was larger in magnitude than the shift seen in hydrogen-deaerated solution. It could be construed that the potential-lowering effects of H_2 , H , and e^-_{aq} were greater without the initial dissolved hydrogen. However, a more plausible argument is that reducing radiolysis products scavenged dissolved oxygen persistent in the argon-deaerated solution prior to irradiation. Laboratory records showed that lower argon flow rates were used in these tests. As seen in Figure 4.4, the non-irradiated potential was approximately -0.380 V vs. Hg/HgSO_4 , a noble potential which indicated the presence of dissolved oxygen. Irradiation resulted in a shift to about -0.840 V. The reversible potential on platinum in non-irradiated, argon-deaerated solution was measured at -0.8 to -0.9 V vs. Hg/HgSO_4 in subsequent tests with more effective deaeration. The effect of water radiolysis in the irradiated, argon-deaerated solution was to promote scavenging of dissolved oxygen, shifting the potential to the 'true' platinum potential in argon-deaerated solution.

4.2 Radiolysis Simulations

4.2.1 Radiolysis Code

A radiolysis computer code was employed in this work in order to model irradiated water chemistry for laboratory corrosion and stress corrosion tests. Details of the code, known as WR87, can be found in Appendix A. Pure water radiolysis simulations were performed for temperatures of 50, 90, and 130°C at varying dose rates. Radiolysis product concentration data are reported in parts per billion (ppb). In some cases, the parts per million (ppm) unit is used. Dose rate is reported in electron-volt/liter/second (eV/l/s). Other units are watt/gram or watt/cm³ (w/g, w/cm³) and rad/hour, which can be converted to eV/l/s using water as the medium. The solution chemistries of interest in this program are pure water deaerated with hydrogen and argon. In order to simulate upset conditions with dissolved oxygen present, simulations with argon + 20% O₂ were also performed. The results of the radiolysis code simulations are shown in Figures 4.5 through 4.18.

4.2.2 Results of Pure Water Radiolysis Simulations

Figures 4.5 through 4.7 show the concentrations of radiolysis products with time at 10²⁰ eV/l/s for three temperatures in the argon-deaerated condition. Note that the concentrations of HO₂ and HO₂⁻ are not included, as these were consistently low (< 10⁻² ppb) for all argon simulations. The aqueous electron, e_{aq}⁻, exhibits a net zero concentration as it reacts with everything else as soon as it is formed. These data are representative of the trends seen in most radiolysis simulations, with the

exception of the argon/20% O₂ simulations which showed higher HO₂ yields, such as 0.37 ppb at 90°C and 10²¹ eV/l/s. The pH used in all simulations was 6.6, corresponding to 0.255 and 0.688 ppb of H⁺ and OH⁻, respectively.

Figure 4.5. Concentrations of radiolytic species as a function of time, 50°C, dose rate of 1x10²⁰ eV/l/s, argon-purged simulation.

Figure 4.6. Concentrations of radiolytic species as a function of time, 90°C, dose rate of 1×10^{20} eV/l/s, argon-purged simulation.

Figure 4.7. Concentrations of radiolytic species as a function of time, 130°C, dose rate of 1×10^{20} eV/l/s, argon-purged simulation.

The concentration values listed for the different simulation conditions were steady state values, reached within 60 seconds after initiation. The concentration of radiolysis products leveled out rather than increasing steadily with accumulated dose over time, indicating that equilibrium was reached between the production rate of primary species and the secondary reactions that follow. In a closed pure water system under low LET irradiation, low steady state concentrations of molecular products (H_2 , H_2O_2 , O_2) are expected. The low concentrations are the result of reactions with radicals: [50]

In all radiolysis simulations in this work, the concentrations of all species increased linearly with dose rate. This is attributed to higher instantaneous radical concentrations and subsequently a greater number of inter-radical reactions which form the molecular products H_2 , H_2O_2 , and O_2 . [50]

In all radiolysis simulations the molecular product concentration is inversely proportional to the water temperature. Energy deposition in water by gamma radiation results in the formation of spurs or small clusters of excited species. [50] The decreased molecular product yields at higher temperatures are ascribed to greater diffusion of the radical species out of the spurs with greater thermal activation. [50] Outside the spurs, radicals are less likely to react and form molecular products. As a

consequence, free radical concentrations should increase with temperature, as seen in Figures 4.5 through 4.7.

4.2.3 Molecular Product Yields in Different Environments

Figures 4.8, 4.9, and 4.10 compare the concentrations of H_2O_2 , O_2 , and H_2 for the three simulation conditions at 90°C . Observing the trend at 10^{21} eV/l/s and above, H_2O_2 and O_2 were highest in argon + 20% oxygen-deaerated pure water simulation, followed by the argon-deaerated condition. The pure water simulation deaerated with hydrogen exhibited the lowest H_2O_2 and O_2 levels. Qualitatively, as Ar-20% O_2 deaerated simulation is the most oxidizing simulation, it should yield the highest H_2O_2 concentration. The argon deaerated simulation is 'neutral' and yields intermediate levels of all three species. The hydrogen deaerated simulation is the most reducing and should yield the lowest H_2O_2 and O_2 concentrations.

Figure 4.8. Hydrogen peroxide concentration as a function of dose rate for three different solution types used in radiolysis simulation, 90°C

Figure 4.9. Dissolved oxygen concentration as a function of dose rate for three different solution types used in radiolysis simulation, 90°C

Figure 4.10. Dissolved hydrogen concentration as a function of dose rate for three different solution types used in radiolysis simulation, 90°C

This trend may also be explained with secondary reactions involving radiolysis products [2,50]. The Ar-20%O₂ simulation has excess oxygen present, scavenging e⁻_{aq}, and H and resulting in higher H₂O₂ yields:

In argon deaerated pure water with very low oxygen content, O₂ is produced by radical interaction with H₂O₂, and H₂O₂ levels are maintained as well.

In the hydrogen deaerated simulation, O₂ and H₂O₂ yields are the lowest. Excess molecular hydrogen reacts with OH, blocking the O₂ reaction chain:

This reaction adds to the H radical population, which can scavenge H₂O₂

There does not appear to be a reason why the H₂ levels are higher in the Ar-20%O₂ deaerated case than in the argon deaerated case. Dissolved oxygen scavenges e⁻_{aq} and H and should minimize H₂ production by impeding the reaction H + H → H₂.

Figures 4.11 through 4.18 summarize the radiolysis simulation molecular yields (H_2 , H_2O_2 , O_2) as a function of dose rate at 50, 90, and 130°C.

The code was checked using published inputs and outputs from a similar program. [51] Agreement within 30% was found for argon- and hydrogen-deaerated simulations at 25°C and 3.13×10^{22} eV/l/s. Recent work [38] cited 30 ppb O_2 and H_2O_2 for gamma dose rate of 0.8 w/cm³ (5×10^{21} eV/l/s). The output of the present computer code, WR87, agrees with this value for argon-deaerated simulation between 90 and 100°C at 5×10^{21} eV/l/s.

Figure 4.11. Steady state hydrogen peroxide concentration as a function of dose rate in a radiolysis computer simulation. Argon-purged pure water.

Figure 4.12. Steady state hydrogen peroxide concentration as a function of dose rate in a radiolysis computer simulation. Hydrogen-purged pure water.

Figure 4.13. Steady state hydrogen peroxide concentration as a function of dose rate in a radiolysis computer simulation. Argon-20% O₂ purged pure water.

Figure 4.14. Steady state dissolved hydrogen concentration as a function of dose rate in a radiolysis computer simulation. Argon-purged pure water.

Figure 4.15. Steady state dissolved hydrogen concentration as a function of dose rate in a radiolysis computer simulation. Argon-20%O₂ purged pure water.

Figure 4.16. Steady state dissolved oxygen concentration as a function of dose rate in a radiolysis computer simulation. Argon-purged pure water.

Figure 4.17. Steady state dissolved oxygen concentration as a function of dose rate in a radiolysis computer simulation. Hydrogen-purged pure water.

Figure 4.18. Steady state dissolved oxygen concentration as a function of dose rate in a radiolysis computer simulation. Argon-20% O₂-purged pure water.

4.3 Passive Current Density

4.3.1 Anodic Polarization in Irradiated Solution

The use of electrochemical techniques to predict corrosion rates allows for rapid screening and comparison of metal alloy/environment combinations. [40] Potentiodynamic polarization in irradiated solution revealed the active potential shift, seen in Figure 4.2, as well as nearly an order of magnitude increase in the passive current density as opposed to non-irradiated conditions. This passive current density increase could be considered a ten fold corrosion rate increase, raising safety concerns with respect to activated corrosion product releases. On the other hand the current density increase could be due to increased surface oxidation reactions involving radiolytic species. Therefore, additional testing was required in order to draw conclusions about the measured corrosion rates

Figure 4.3 shows the polarization curves on a platinum electrode for both irradiated and non-irradiated cases. Note the high anodic current density in the hydrogen deaerated solution. This is consistent with the fact that platinum is a good catalyst for the hydrogen oxidation reaction. [4]

Similar polarization curves were obtained with argon deaeration, shown in Figure 4.4. With argon, high current densities associated with hydrogen were eliminated. Small increases in current densities between irradiated and non-irradiated solution cases can be distinguished. There is approximately a factor of 6 increase in current density in the -0.200 to 0.400 V vs. Hg/HgSO₄ potential range. The current density on a platinum electrode reflects the oxidation and reduction reactions of species at the surface. An increase in current density shows that surface reaction rates are increased with irradiation.

4.3.2 Current Density As A Function Of Time

Additional irradiated and non-irradiated tests for passive current density were performed, using the passive current density versus time technique. The ECP was fixed in the passive potential range and the current density decrease was observed with time. Figure 4.19 shows the resulting response, with the irradiated solution test exhibiting a higher steady state current density. However, the initial current density in the irradiated solution test is actually lower than the non-irradiated case. The apparent coulombic charge passed, measured as the integrated area under the curve, was only 10% greater for the irradiated case.

Figure 4.19. Passive current density of annealed Type 316 SS as a function of time, in irradiated and non-irradiated solutions. Specimen held at a potential of -0.270 V vs. Hg/HgSO_4 , 0.0005M K_2SO_4 , 50°C .

The current density measured on stainless steel is the sum of the metal oxidation (corrosion) contribution and surface reactions involving H_2 and O_2 . [30] In electrochemical measurements in BWR environments, it was concluded that the reaction kinetics of H_2 oxidation and O_2 reduction obscured the contribution of metal oxidation to the measured current density. As most of this increase can be attributed to surface reactions, the corrosion rate increase is not considered significant.

4.4 IGSCC Testing of Type 316 Austenitic Stainless Steel

4.4.1 SSRT Data in Air

Several slow strain rate test (SSRT) experiments have been completed in air at 25, 50, 90, and 130°C and in the reference solution at 50°C. The significant variables in the SSRT experiments were elongation to failure (% elongation) and the tensile strength. Lower % elongation compared to air test values indicates SCC susceptibility.

SSRT data in air has been documented and were used for comparison to aqueous tests. All SSRT test results are presented in Table II. The elongation to failure data for annealed (SA) and sensitized (Sen.) 316 SS as a function of temperature in air are shown in Figure 4.20. The corresponding tensile strengths are plotted in Figure 4.21. Figure 4.21 also includes stainless steel handbook data [52] for annealed 316 SS. The trend of decreasing tensile strength in air with increasing temperature corresponds to the handbook data.

Table II Results of slow strain rate tests (SSRT) for annealed and sensitized 316 SS.

No.	Condi- tion	T, °C	Environ- ment	De- aeration	Surface Prep.	ECP at failure, V vs. Hg/HgSO ₄	%Elon- gation	UTS, MPa
6	SA	25	air		air film		57	655
7	SA	25	air		air film		60	648
9	SA	50	glycerin		polished		48	639
10	SA	25	air		air film		54	642
11	SA	50	glycerin		polished		44	604
12	SA	50	glycerin		polished		44	612
15	SA	50	air		air film		50	608
16	SA	50	air		polished		46	619
17	SA	50	air		polished		46	604
18	SA	90	air		air film		39	595
19	SA	90	air		air film		37	582
20	SA	90	air		polished		38	586
21	SA	130	air		air film		35	573
22	SA	130	air		air film		32	565
23	SA	130	air		air film		34	566
24	SA	25	air		air film		60	658
26	SA	50	solution	hydrogen	air film		43	597
27.3	SA	50	solution	hydrogen	air film		43	591
28	SA	50	solution	argon	air film		44	595
29	SA	50	solution	argon	air film	-0.59	42	608
30	SA	50	solution	hydrogen	air film	-0.69	45	612
31	Sen.	50	solution	hydrogen	polished	-1.055	39	604
32	Sen.	50	air		polished		40	600
33	Sen.	90	air		polished		30	566
34	Sen.	130	air		polished		28	558
35	Sen.	50	solution	argon	polished	-0.59	40	603
36	Sen.	50	solution	argon	polished	-0.615	43	604

Figure 4.20. Ductility as a function of temperature for solution annealed (SA) and sensitized (Sen.) Type 316 SS in air.

Figure 4.21. Ultimate Tensile Strength as a function of temperature for solution annealed (SA) and sensitized (Sen.) Type 316 SS in air, including handbook data. [52]

4.4.2 SSRT Results At Open Circuit Potential In Deaerated Solution

Figures 4.22 and 4.23 show the elongation to failure and tensile strengths versus temperature, respectively, for all tests on annealed wire. Figures 4.24 and 4.25 show the elongation to failure and tensile strengths versus temperature, respectively, for all sensitized wire tests. These figures are intended to compare the aqueous tests with air tests.

The mechanical property data for annealed 316 SS showed no significant difference between polished or air filmed wires. Annealed wires were used in the air filmed condition for the aqueous tests. Aqueous tests at 50°C on annealed 316 SS show a slight decrease in % elongation, compared to the average air value. However, this change in % elongation is not interpreted to reflect SCC susceptibility as the aqueous test results fall within the error band for air data at 50°C.

The sensitized 316 SS did not exhibit lower ductility in 50°C solution deaerated with either hydrogen or argon. One argon deaerated test showed a higher ductility than the single air test value.

Figure 4.22. Ductility as a function of temperature for solution annealed (SA) Type 316 SS: 1) in air and 2) in 0.0005M K_2SO_4 , deaerated with either hydrogen or argon gas.

Figure 4.23. Ultimate Tensile Strength as a function of temperature for solution annealed (SA) Type 316 SS: 1) in air and 2) in 0.0005M K_2SO_4 , deaerated with either hydrogen or argon gas.

Figure 4.24. Ductility as a function of temperature for sensitized (Sen.) Type 316 SS: 1) in air and 2) in 0.0005M K_2SO_4 , deaerated with either hydrogen or argon gas.

Figure 4.25. Ultimate Tensile Strength as a function of temperature for sensitized (Sen.) Type 316 SS: 1) in air and 2) in 0.0005M K_2SO_4 , deaerated with either hydrogen or argon gas.

The open circuit potential was measured for 5 of the tests in hydrogen or argon deaerated solution at 50°C. The potential is initially active, ranging from -0.870 to -0.885 V vs. Hg/HgSO₄, followed by a gradual drift in the noble direction. In nearly all aqueous tests the potential just prior to failure was between -0.590 and -0.690 V vs. Hg/HgSO₄. The exception was for sensitized wire in hydrogen-deaerated solution, which exhibited -1.055 V vs. Hg/HgSO₄ from the start through failure. The polished wire surface reflected the reversible hydrogen potential for this solution. The annealed wire test under hydrogen deaeration was expected to reflect the hydrogen potential as well. However, the initial and final potentials were -0.880 V and -0.690 V vs. Hg/HgSO₄, respectively, due to the polarizing effect of the air filmed surface. The dissolved oxygen content in all tests was measured as 100 ppb $\pm$ 30 ppb using colorimetric test indicators.

The duration of the aqueous SSRT tests was on the order of 70 hours. The noble potential drift seen in most tests is attributed to polarization through the gradual passive film growth over time. For the sensitized sample under hydrogen deaeration, the polarizing effect is not seen, rather the hydrogen reduction potential dominates as the measured potential of the wire.

4.4.3 Polarization Data and Application of the Slip Dissolution Model

The slip-dissolution model may be used in the analysis of the present data. It has been used successfully in IGSCC of sensitized Type 304 SS by others. [22,33] The model predicts that SCC will be favored in a susceptible environment at electrochemical potential ranges where the passive film is

unstable. The significant results from these tests are that SCC is not accelerated in 50°C solution in the open circuit potential range of -0.590 to -1.060 V vs. Hg/HgSO₄. These results and their implications in the slip dissolution model are best discussed in the context of anodic polarization curves for 316 SS.

The anodic polarization curve for annealed (SA) 316 SS in argon deaerated solution at 50°C is shown in Figure 4.26. This curve exhibits an active-passive transition at -0.700 to -0.550 V vs. Hg/HgSO₄. The open circuit potential at failure for SA 316 SS in this solution was -0.59 V, which places it in the active passive transition.

Figure 4.26. Anodic potentiodynamic polarization curves for Type 316 SS comparing solution annealed (SA) and sensitized (Sen.) wire samples. Argon-deaerated 0.0005M K₂SO₄ at 50°C.

Similarly, Figure 4.2 shows the anodic polarization curve of SA 316 SS in hydrogen-deaerated solution with an active-passive transition at approximately -0.6 to -0.75 V vs. Hg/HgSO₄. The open circuit potential at failure for SA 316 SS with hydrogen deaeration was -0.69 V, within the active-passive range. The slip dissolution theory predicts that SCC will occur where the film repassivation is unstable with respect to slip step emergence during plastic straining. For a susceptible alloy and environment combination this would be found in active-passive transition potential range. The SSRT tests show that the ductility at failure for the annealed 316 SS was not significantly reduced at the open circuit potential in argon- and hydrogen-deaerated, 50°C solution. Therefore the film repassivation is stable at the open circuit potential and the alloy is not susceptible to SCC.

The anodic polarization behavior at 50°C for sensitized Type 316 SS in argon-deaerated solution compared to the non-sensitized, annealed alloy is shown in Figure 4.26. The sensitized alloy shows an increase in the active current density and widening of the active potential range, as well as an approximately order of magnitude increase in passive current density. The open circuit potential at failure for sensitized 316 SS in argon-deaerated solution is -0.59 to -0.615 V vs. Hg/HgSO₄. This falls within the active region rather than the active-passive range seen at -0.3 to -0.4 V. In this environment, the potential is not in a range where the film reformation would be unstable under plastic strain; rather it places the alloy in a range where active dissolution is predominant. At an open circuit potential in the active range for argon deaerated, 50°C solution, the

sensitized alloy does not fail by SCC but it is likely to suffer higher general corrosion rates.

Polarization data is shown in Figure 4.27 for sensitized 316 SS in 90°C, argon-deaerated solution compared to the annealed alloy. The active region is nearly three orders of magnitude greater in current density and covers a wide potential range. There is an apparent active-passive transition at 0.0 to -0.1 V vs. Hg/HgSO₄ and a two order of magnitude increase in the passive current density.

Figure 4.27. Anodic potentiodynamic polarization curves for Type 316 SS comparing solution annealed (SA) and sensitized (Sen.) wire samples. Argon-deaerated 0.0005M K₂SO₄ at 90°C.

After polarization, the sensitized specimen was covered with a dark brown surface layer, as opposed to the transparent passive film seen on the

annealed wire. The active-passive region is similar to the curve for a 12Cr-10Ni stainless steel alloy at 95°C. [32] The 12Cr-10Ni alloy simulated the grain boundary composition of sensitized 304 SS. It is important to note that the Ford and Povich found a maximum in intergranular crack propagation rate for sensitized type 304 SS at potentials in the active-to-passive transition range for the 12Cr, 10Ni alloy. [32]

By extrapolation of the results from 304 SS [32] to 316 SS and by virtue of the slip dissolution model, it is suspected that sensitized 316 SS will exhibit IGSCC susceptibility in the active-passive potential range. In Figures 4.26 and 4.27, this range corresponds to -0.100 to -0.300 V at 50°C and 0.0 to -0.100 V vs. Hg/HgSO₄ at 90°C.

4.4.4 Related Work in Lower Temperature ($\leq 100^\circ\text{C}$) Pure Water

Ford and Povich [32] performed SSRT tests on sensitized Type 304 SS in pure water at oxygen-temperature combinations typical of a boiling water reactor system startup. IGSCC was observed with 2 ppm O₂ and 1 ppm O₂ at 50 and 100°C, respectively.

Ford and Silverman [33] showed that in the potential range of +0.093 to +0.243 V vs. SHE for stainless steel at 100°C (corresponding to 0.2 to 8 ppm oxygen), constant extension rate tests (CERT) in 0.01N Na₂SO₄ yielded the same results as did tests in pure water. The maximum rate of crack growth was observed at $\sim +0.190$ V vs. SHE. The ECP was controlled potentiostatically in deaerated Na₂SO₄, whereas in pure water the open circuit potential was chemically controlled with dissolved oxygen. These results showed that the oxidizing effect of oxygen could be simulated with applied potential.

Constant load tests (CLT) by Herbsleb [34] showed that, at 100°C, sensitized 19Cr-10Ni stainless steel cracked intergranularly at and above a critical potential of approximately 0.200 V vs. SHE. The tests were performed under applied potential conditions in deaerated 0.0001M Na₂SO₄.

In SSRT tests on sensitized Type 304 SS in 100°C, deaerated 0.01N Na₂SO₄, Cragnolino et al.[35] noted no intergranular cracking from -0.26 to 0.4 V vs. SHE. In deaerated 0.01N NaCl, IGSCC was observed only above the pitting potential ($\approx$ 0.3 V vs. SHE).

CLT tests by Tanno et al. [36] in deaerated 0.01M Na₂SO₄, sensitized 304 SS showed IGSCC at 75°C and 100°C, with failures predominantly in the active-passive potential range.

The work cited above indicate that the SCC susceptibility of sensitized Type 304 austenitic stainless steel at temperatures below 100°C is greatest at oxidizing potentials, at or above the active-passive transition. The effect of oxygen can be simulated with potentiostatic control, and SCC susceptibility was found to be a function of the potential rather than the presence of molecular oxygen. The reported behavior of 304 SS in pure water environments may be used as a point of reference for studying SCC susceptibility in 316 SS.

4.5 Simulated Radiolysis Water Chemistry

4.5.1 Water Chemistry Modeling

As mentioned previously, H₂O₂, H₂, and O₂ were added to laboratory solutions in order to model irradiated conditions. Initially, the intent was

to model the conditions of water radiolysis as it occurred in the actual irradiated solution tests, that is in hydrogen-deaerated solution at 50°C with a dose rate of approximately 3×10^{18} eV/l/s. However, the calculated molecular species concentrations under these conditions were ≈ 1460 ppb H_2 , < 1 ppb H_2O_2 and $< 10^{-6}$ ppb O_2 . A laboratory model of this water chemistry would differ little from the non-irradiated, hydrogen-deaerated solution. Moreover, the reducing radicals e_{aq}^- , H_2 which acted to shift the potential, could not be added. In addition, the dose rate of 3×10^{18} eV/l/s was considered to be low compared to a fusion reactor design value of approximately 3.3×10^{22} eV/l/s. [53] An irradiation dose rate of 10^{24} eV/l/s was chosen as an upper bound or maximum if the design value is 3.3×10^{22} eV/l/s. Due to safety concerns involving hydrogen, it was anticipated, in this program, that argon would be favored over hydrogen as a purge gas in experimental reactors.

As a result, higher dose rates and argon-deaerated pure water radiolysis simulations were considered for laboratory solution modeling. Following the radiolysis code simulation for argon-deaerated water at 50°C with a dose rate of 10^{24} eV/l/s, radiolytic species concentrations of 1 ppm O_2 , 1-1.2 ppm H_2O_2 , and 0.2 ppm H_2 were targeted.

4.5.2 Electrochemical Potential Effects

The solution was initially argon-deaerated, and the combined effects of the H_2 , O_2 and H_2O_2 were recorded by measuring the electrochemical potential as a function of time for both sensitized and annealed 316 SS wire. The results are shown in Figures 4.28 and 4.29.

Figure 4.28. Open circuit potential as a function of time for sensitized 316 SS in 0.0005M K₂SO₄ at 50°C, with additions of H₂, O₂ and H₂O₂.

Figure 4.29. Open circuit potential as a function of time for annealed 316 SS in 0.0005M K₂SO₄ at 50°C, with additions of H₂, O₂ and H₂O₂.

Introducing hydrogen initially shifted the potential by approximately 35 mV in the active direction, toward the reversible hydrogen electrode potential [4] of -1.056 V vs. Hg/HgSO₄ at 0.17 atm H₂ and pH 7.5. The introduction of oxygen at 0.038 atm caused a noble shift of 400 - 500 mV towards the reversible oxygen electrode potential [4] of +0.126 V vs. Hg/HgSO₄ at pH 7.5. The addition of hydrogen peroxide at 1.2 ppm resulted in a noble shift of 400 - 450 mV, resulting in a steady-state potential of -0.180 V for the sensitized 316 SS wire and -0.096 V vs. Hg/HgSO₄ for the annealed 316 SS wire. Bockris and Oldfield [54] observed reversible behavior for hydrogen peroxide on platinum at pH of 0 to 14 and at H₂O₂ concentrations of 10⁻⁶ to 5 mole/liter:

$$E_{H_2O_2} = 0.835 - 0.059 pH \text{ vs. SHE at } 25^\circ\text{C}$$

This predicts that the reversible potential on platinum in the present solution would be -0.25 V vs. Hg/HgSO₄, compared to the measured value of -0.13 V.

It is important to note that this behavior is not dependent on hydrogen peroxide concentration or dissolved oxygen content. Less than 0.1 ppm H₂O₂ is required to observe the potential effect. [55] In a separate experiment, H₂O₂ was added before the oxygen gas was introduced. The final potential was the same regardless of whether oxygen was admitted to solution before or after the H₂O₂.

Hydrogen peroxide has been shown by others to be a potent oxidizing species. One to 2 ppm H₂O₂ caused a +100 to 200 mV shift in argon deaerated, 40°C solution. [20] The addition of 5 to 20 ppb H₂O₂ forced a +200

mV potential shift in BWR water at 274°C under hydrogen water chemistry (HWC). [56]

4.5.3 SCC under Simulated Radiolysis Water Chemistry Conditions

The steady-state electrochemical potential for sensitized 316 SS of -0.180 V which was reached falls within the active-passive transition region of the anodic polarization curve at 50°C, seen in Figure 4.26. The slip dissolution model predicts that SCC will occur in this potential range if the film repassivation is unstable with respect to slip step formation at the surface. In the case of annealed 316 SS, the steady-state potential of -0.096 V falls within the passive region of the anodic polarization curve in Figure 4.26. It is within this potential range that passivity is very stable and SCC is not expected in this case. Recently, work was performed [38] to examine SCC susceptibility of Type 316 and 316NG stainless steels under conditions relevant to the ITER design. Tests were made at 50 - 150°C with 8 ppm O₂ and 6-9 ppm H₂O₂. The potential measured for Type 304 SS at 52°C was +0.56 V vs. SHE (-0.04 V vs. Hg/HgSO₄). At 95 and 150°C, annealed, non-creviced 316 SS and 316NG (nuclear grade) failed predominantly by ductile failure, whereas creviced 316NG showed slight susceptibility to transgranular cracking. The present work is somewhat similar, using 316 SS and the same radiolysis code. However, the water chemistry modeling in this work follows more closely the values predicted by the radiolysis code. Fox et al [38] cited 0.8 watt/cm³ (5×10^{21} eV/l/s) as the expected dose rate, giving 30-50 ppb of O₂ and H₂O₂ in deaerated pure water. However, the tests were run at 8 ppm O₂ and 6-9 ppm H₂O₂ for

conservatism. In addition, sensitized 316 SS was not tested [38] and this metallurgical condition may be more likely to fail by IGSCC.

4.6 Effect of Gamma Irradiation on IGSCC

IGSCC testing of lightly sensitized Type 316 stainless steel under gamma irradiation in the ITER program [39] reduced the sub-critical crack growth rate as compared to the non-irradiated condition. Tests were at 100°C in pure water with 10 ppm Cl⁻. Although ECP was not measured, it was believed to have shifted under irradiation in the active direction, away from the critical potential for SCC. The initial conclusion was that gamma irradiation was not detrimental. However, these tests were performed on lightly sensitized 316 SS; heavier sensitization may have fostered intergranular attack. In addition, the gamma dose rate of 6.5×10^5 rad/hr (1.13×10^{19} eV/l/s) was low compared to expected design value, 10^{22} eV/l/s [53]. It is expected that the concentrations of oxidizing molecular species, H₂O₂, and O₂, will be greater with higher dose rates and in the presence of higher LET neutron radiation. This more aggressive environment may be sufficiently oxidizing to promote SCC in sensitized 316 SS and possibly in annealed 316 SS.

5. CONCLUSIONS

1. Solution annealed Type 316 stainless steel was studied in hydrogen-deaerated, 0.0005M K_2SO_4 at 50°C. Gamma irradiation with an average energy of 20 MeV and a dose rate of approximately 340 krad/hour (3×10^{18} eV/l/s) resulted in the following observations:
 - A shift in the electrochemical potential of approximately 100 mV in the active direction. This shift was attributed to the polarizing effect of reducing radiolysis products (e^-_{aq} , H, H_2) on the surface of the stainless steel.
 - Potentiodynamic polarization tests showed nearly an order of magnitude increase in the passive current density compared to non-irradiated conditions. Similar tests on platinum indicated that the current density increase was reflecting enhanced surface reactions involving radiolysis products, as well as increases in corrosion rate. Passive current density measurements as a function of time showed that the apparent coulombic charge passed under irradiation was only 10% greater than the non-irradiated condition. Therefore, the increase in corrosion rate was not considered to be significant.
2. Computer simulations of pure water radiolysis at 50, 90, and 130°C and at dose rates of 10^{18} - 10^{24} eV/l/s were performed, with the following observations:

- Increasing dose rate increased the yield of molecular radiolysis products, H_2 , H_2O_2 , and O_2 by promoting the inter-radical reactions that lead to their formation.
 - Increasing temperature of the simulation was accompanied by decreasing molecular radiolysis product concentrations. This result was due to increased diffusion of radicals (H , OH) out of the radiation track such that inter-radical reactions were less probable.
 - In simulations of pure water deaerated with argon + 20% oxygen, the yield of hydrogen peroxide was highest above a dose rate of 10^{21} eV/l/s. Oxygen promoted H_2O_2 formation by reacting with reducing radicals that would otherwise scavenge hydrogen peroxide. The H_2O_2 yield was lower in argon-deaerated simulations. Hydrogen-deaerated simulations showed the lowest yield of hydrogen peroxide, due to the scavenging action of H_2 on H_2O_2 .
 - Oxygen yields were higher in argon-deaerated simulations than in hydrogen-deaerated simulations. These results coincide with theory, which predicts that hydrogen scavenges oxidizing radicals (OH , HO_2) which normally react to produce oxygen.
3. Slow strain rate tests suggest that Type 316 stainless steel was not susceptible to SCC in hydrogen- or argon-deaerated 0.0005M K_2SO_4 at 50°C. This has been shown for both annealed and the sensitized

stainless steel at the open circuit potential. The slip dissolution model was applied to the analysis of these results.

- For the annealed alloy, the results were interpreted as stability of film repassivation with respect to slip step formation at -0.690 to -0.590 V vs. Hg/HgSO₄ in approximately the active-passive potential range.
- For the sensitized case, this was regarded as active dissolution rather than unstable passivity at -0.690 to -0.590 V and protection at -1.055 V vs. Hg/HgSO₄, similar to that under HWC in boiling water reactors.

4. Modeling irradiated solutions in the laboratory based on radiolysis computer code simulations showed the following:

- The actual solution irradiation conditions were hydrogen-deaerated, 50°C solution with a dose rate of approximately 3×10^{18} eV/l/s. The predicted concentrations of molecular species were ≈ 1460 ppb H₂, < 1 ppb H₂O₂ and $< 10^{-6}$ ppb O₂. Solution modeling using these concentrations was not considered to be significantly different from non-irradiated, hydrogen deaerated tests.
- In modeling irradiated water chemistry based on simulations for argon-deaerated, 50°C water at a dose rate of 10^{24} eV/l/s, the effects of incremental additions of approximately 0.2 ppm H₂, 1 ppm O₂, and 1 - 1.2 ppm H₂O₂ to argon-deaerated, 0.0005M K₂SO₄ at 50°C were observed. The open circuit potential of both sensitized and annealed 316 SS showed a net shift of

approximately 800 mV in the noble (positive) direction. The effect of hydrogen was to induce an active shift, where oxygen and hydrogen peroxide shifted the potential in the noble direction. Steady-state potentials of -0.180 V for the sensitized 316 SS wire and -0.096 V vs. Hg/HgSO₄ for the annealed 316 SS wire were achieved within 12 hours of adding H₂O₂. The final potential associated with H₂O₂ was independent of the presence of oxygen. The resulting potential shift for sensitized 316 SS to -0.180 V vs. Hg/HgSO₄ is likely to promote SCC, based upon the predictions of the slip dissolution model.

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7. APPENDIX A

Radiolysis Computer Code

A radiolysis code was employed in this work in order to model irradiated water chemistry for laboratory corrosion and stress corrosion tests. Other computer codes have been used for similar purposes. Burns and Moore [51] used a computer program CHEK [57] which calculated the concentration of all species with time, based upon inputs of G values for the primary products, secondary reactions and respective rate constants, and initial concentrations of the species. Other radiolysis codes have been developed and used in research since Burns and Marsh's [51] work: FACSIMILE, [21,58,59] FORSIM and MAKSIM, [60] AQUARY, [47,61,62] RADIOLYSIS MODEL, [49,63] Recent work in the ITER program [38] employed a radiolysis code WR87 [64] based upon Schmidt's homogeneous reaction kinetics program. [65] The majority of these radiolysis programs employ a very useful differential equation system solver, GEAR [66,67,68]

A copy of the Fortran program WR87 was recently updated to run on the VMS/VAX computer system at Rensselaer Polytechnic Institute. This latest version of WR87 was used to model radiolytic environments in the present work. This program requires G values, species, secondary reactions with rate constants, initial concentration of all species, irradiation dose rate, and temperature. All species information for argon-deaerated simulations are listed in Table A1. The G values [69] for gamma radiation were used in the present work and are included in Table A1.

The initial concentrations varied based upon the cover gas. Dose rates of 1×10^{18} to 1×10^{24} eV/l/s were selected to include the range of experimental values in this work and others [20,21], 10^{18} - 10^{20} eV/l/s, and the predicted value for an Aqueous Lithium Salt Blanket design [53], 3.3×10^{22} eV/l/s. The temperatures used were 50, 90 and 130°C.

Table A1 Radiolytic species information for radiolysis code WR87, including G values for gamma radiation and initial concentrations for argon-deaerated pure water.

#	NAME	MOL. WT	CHARGE	YIELD (G)	INIT. CONC. MOL/LITER	FIXED (?)
1	*	0	0	0	0.100D+01	YES
2	EAQ-	0	-1	2.7	0.000D+00	NO
3	H	1.01	0	0.61	0.000D+00	NO
4	H+	1.01	1	2.7	0.250D-06	YES
5	H2	2.02	0	0.43	0.718D-09	NO
6	H2O	18.02	0	-4.14	0.556D+02	YES
7	H2O2	34.02	0	0.61	0.000D+00	NO
8	HO2	33.01	0	0.03	0.000D+00	NO
9	HO2-	33.01	-1	0	0.000D+00	NO
10	O2	32	0	0	0.933D-09	NO
11	O2-	32	-1	0	0.000D+00	NO
12	OH	17.01	0	2.86	0.000D+00	NO
13	OH-	17.01	-1	0	0.400D-07	YES
14	SO4-2	0	-2	0	0.105D-04	YES
15	NA+	0	1	0	0.208D-04	YES

The secondary reaction data [21,70] are listed below. K= second order rate constant in units of liter/mole/sec or first order rate constant in units of 1/sec. EA = Activation energy in kcal/mole.

$\text{HO}_2 + * \rightarrow \text{H} + \text{O}_2$,K=8.500D+05, EA=3.000D+00: 22

$\text{H} + \text{O}_2 \rightarrow \text{HO}_2$,K=5.000D+10, EA=3.000D+00: 23

$\text{HO}_2 + \text{O}_2 \rightarrow \text{O}_2 + \text{HO}_2$,K=1.500D+07, EA=4.500D+00: 24

$\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$,K=2.700D+06, EA=3.000D+00: 25

$\text{H} + \text{OH} \rightarrow \text{H}_2\text{O}$,K=1.438D+11, EA=3.000D+00: 26

$\text{H}_2\text{O} + * \rightarrow \text{H} + \text{OH}$,K=2.600D-05, EA=3.000D+00: 27

$\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2 + \text{H}_2\text{O}$,K=1.000D+08, EA=4.500D+00: 28

$\text{HO}_2 + \text{H}_2\text{O} \rightarrow \text{OH} + \text{H}_2\text{O}_2$,K=1.022D+04, EA=4.500D+00: 29

$\text{H} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{OH}$,K=1.040D-04, EA=2.040D+01: 30

$\text{H} + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2$,K=2.000D+10, EA=3.000D+00: 31

$\text{EAQ} + \text{EAQ} \rightarrow \text{H}_2 - \text{H} + - \text{H} +$,K=5.000D+09, EA=3.000D+00: 32

$\text{O}_2 + \text{O}_2 \rightarrow \text{O}_2 + \text{H}_2\text{O}_2 - \text{H} + - \text{H} +$,K=5.600D+03, EA=4.500D+00: 33