
Water Quality and Corrosion: Considerations for Nuclear Reactor Systems

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The quality of water directly affects the corrosion susceptibility of metals. In reactor systems, both the fuel cladding and structural materials are subject to corrosion in poor quality water. A brief overview of important water quality parameters, and the types of corrosion of metals that can occur in poor quality water, are summarized. The discussion is focussed on aluminium-clad fuel used in research reactors since it is the material system most susceptible to a variety of types of corrosion in water. A laboratory approach to identify the impact of chemical impurity species on corrosion susceptibility of aluminium is described.

Introduction

In the vast majority of commercial power and research reactors worldwide, water is a primary source for cooling components to remove heat from fission products and for neutron moderation. Research reactors furthermore rely on water for shielding personnel from radiation so as to provide a safe working environment. Long-term operation of the nuclear reactor facilities, including the water storage systems for spent nuclear fuel, requires an understanding of the parameters of water quality¹ and their effect on the corrosion of the materials for both the fuel and the reactor systems.

Various metallic materials are commonly used in nuclear reactor systems. Particularly in commercial power reactors, stainless steels are used for structural components in the primary coolant system, and zirconium alloys are also used for fuel cladding and other reactor internal materials. Nickel-based alloys are used for heat exchangers and other minor applications. Carbon steel and copper-based alloys are typically used in the secondary coolant system. Aluminum alloys are used for various types of fuel cladding and structural components in research reactors.

The types of corrosion attack and the mechanisms are various. Table 1 below provides a list of the basic types of corrosion that can degrade metals in reactor water systems. Most of these are directly affected by water quality.

Corrosion of Fuel Cladding Materials

Nuclear fuel claddings are made from a range of materials including aluminum, stainless steel and zirconium alloys. There are important considerations for the use of each alloy as cladding for reactor fuel during reactor operation and in post-reactor fuel storage in water pools. Aluminium alloy claddings show very different oxidation behaviour from fuels produced with stainless steel and zirconium alloy claddings. During

¹ Water quality is defined by a set of parameters that are used to characterize the water physical and chemical conditions. It includes pH; conductivity; dissolved impurity species; undissolved solids; colloids; organic substances; biological organisms; and temperature

Table 1 - Corrosion types for metals in water storage

General Corrosion
Pitting Corrosion
Crevice Corrosion
Galvanic Corrosion
Intergranular Corrosion
Stress Corrosion Cracking
End-Grain Attack
Erosion-Corrosion
Blister Formation (Filiform Corrosion)
Microbial Corrosion
Sediment-Induced Corrosion

reactor operation even in highly pure water, aluminium claddings can develop relatively thick oxide layers; oxide layer thicknesses up to 61 μm have been reported under high temperature, high heat flux conditions [1]. Depending on the reactor operating condition, there is the risk of high corrosion, oxide spallation, and blistering and intergranular attack of the aluminium clad materials when the thicknesses of the oxide layers reach greater than about 10 μm [2]. After discharge from the reactor and in prolonged water pool storage, aluminium fuel is highly susceptible to corrosion in poor quality water [3].

Stainless steel and zirconium alloys are more resistant to corrosion in water than aluminium. Zirconium cladding alloys are subject to general corrosion with an adherent passive oxide film of ZrO_2 that grows with time in water at power reactor operating temperatures. After discharge from the reactor and in pool storage, zirconium alloy and stainless steel claddings are highly resistant to corrosion due to their passive oxide layers. There are typically no technical specifications or requirements for water chemistry to mitigate corrosion of zirconium alloys in pool storage due to the relatively innocuous environment of low temperature water exposure vis-à-vis reactor operation; water control is required in pool storage, however, to limit water radioactivity levels [4]. Nevertheless, keeping the conductivity and water temperature low in pool storage will minimize the intensity of electrochemical reactions [5].

Corrosion can be profound, particularly for aluminium, if the

water quality deteriorates from a fully demineralized condition. Water deterioration can occur for various reasons: utilization of poor quality water source; incorporation of environmental dirt; biological activity; ionic species and corrosion products from other materials in the system. Since water quality deteriorates, maintenance of good water quality is a key feature of reactor maintenance programs, and is essential to achieve optimum fuel performance either in the reactor core during reactor operation, or in the spent fuel storage pool, after the fuel is discharged from the reactor.

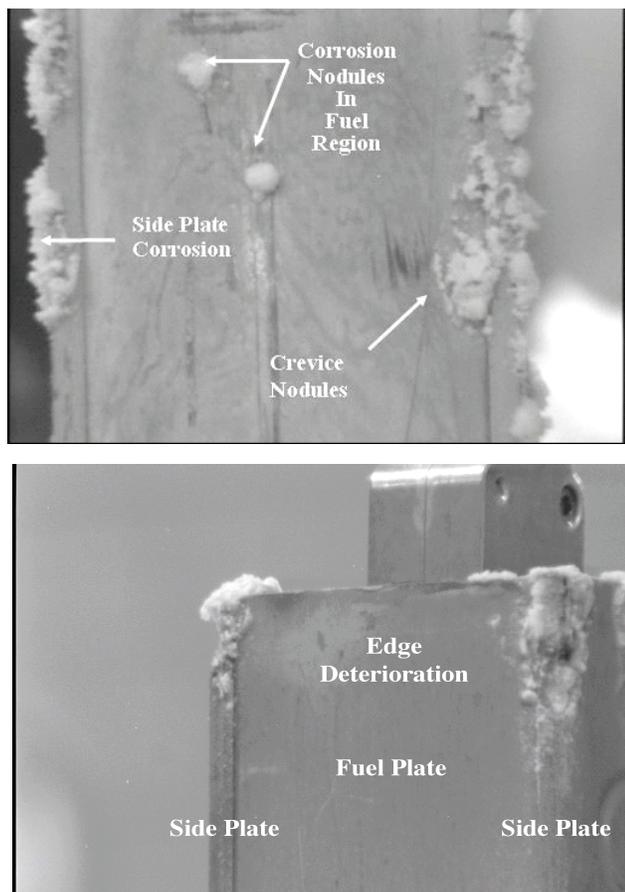


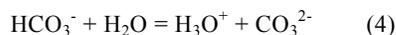
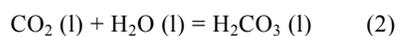
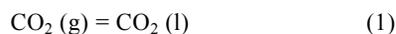
Fig. 1 Aluminum-based, aluminum-clad spent nuclear fuel in moderately degraded condition post-irradiation and storage in a basin with poor water quality (~80-170 $\mu\text{S}/\text{cm}$ during storage) storage conditions. The photographs show (a) corrosion product evidence of pitting corrosion attack and crevice corrosion attack; and (b) evidence of galvanic attack with the two different aluminum alloys coupled at the location of the fuel plate and side structural plate [SRNL photographs]

There are some documented cases² of aluminium clad spent fuel, used in research reactors, which have been in water storage for more than 40 years and remain in pristine condition. In other cases, pitting corrosion occurs after a few years of storage in low quality water, which lead to the release of radioactivity to a storage pool [6, 7]. Figure 1 show an example of moderately corroded fuel due to storage in poor

quality water. The pitting attack in the cladding over the fuel core region had led to leakage of radioactivity from the fuel into the water.

Water Quality

The pH and conductivity are the two foremost parameters used in characterizing the quality of the water. Pure water has low conductivity, but weakly conducts electric current indicating the presence of ions, i.e. H^+ and OH^- , the dissociated water molecule. At 25°C , 10^{-5} % of the water molecules are ionized and pure water has a pH value of 7. However, this is only the case for an entirely isolated volume of water. In most cases water is exposed to an atmosphere with a certain composition like air. Components from the atmosphere will be taken up (dissolved) in the water and subsequently react with it. A prominent air component is CO_2 , which dissolves and reacts with water according to the reactions starting with (1), the equilibrium between CO_2 in air and dissolved in water:



The ultimate effect of CO_2 uptake by the water from the atmosphere is formation of more H^+ , with consequent lowering of the pH to 5.7 for the present atmospheric concentration of approximately 300 ppm CO_2 . The case of CO_2 uptake is a good illustration of an interaction between water and its environment which has a significant impact on its composition. The ultimate pH is then the product of a series of reactions, the number of the reactions being a function of the number of species present. The capacity of a system to restore equilibrium is commonly referred to as the buffering capacity.

As stated, pure water has low conductivity, the ability to carry an electric current. The concentration of dissolved ionic species, other than the H^+ and OH^- already present, determines the water conductivity. The more anions and cations contained in water, the more electricity is carried, and the higher is the conductivity. Each ion makes a contribution to the total conductivity of the aqueous solution. The molar conductivity, Λ , defined as the conductivity (in S/cm) divided by the molar concentration of the ion in the solution, is one parameter used to estimate the overall conductivity. Table 2 gives the molar conductivity for some ions important for water quality control in research reactors.

Conductivity of water is reduced by adding, to the original bulk, water with lower concentrations of non- H_2O ionic species, or circulating the water through a water purification system, in which these ionic species are removed from the water. Addition of any chemical solution to the reactor cooling water may lead to activation with consequent increase in radiation dose. Continuous or frequent measurement of the conductivity is a good method to detect sudden or gradual increase in the bulk concentration of ionic species and is used to assess whether the water quality favours corrosion.

² The Receiving Basin for Offsite Fuel at the Savannah River Site maintained excellent water quality throughout its 40 years of operation. No incidence of significant corrosion degradation of aluminum fuel occurred in this storage system.

Table 2. Molar conductivity*for various common ions [8]

* Considering infinite dilution and temperature equal to 25°C

Ion	Λ [(S/cm)/(mol/cm ³)]
Cl ⁻	76.3
NO ₂ ⁻	71.8
NO ₃ ⁻	71.4
HSO ₃ ⁻	58
SO ₄ ²⁻	80
HCO ₃ ⁻	44.5
OH ⁻	198
H ⁺	349.6
K ⁺	73.5
Na ⁺	50.1

Considering that pH and conductivity are based on ion concentrations, as expected, there is a correspondence between the two values. Figure 2 shows the relation between conductivity and pH, considering the presence of hydrochloric acid in pure water. Although the pH value of water is an indication of the quality of water, a low conductivity is a more reliable indication for low corrosivity. A solution of 0.01 molar KCl will have a pH value comparable to ultrapure water, but will have a conductivity of about 15 mS cm⁻¹.

Aluminum is amphoteric; its oxyhydroxides are not stable and will dissolve more readily at pH levels below about 4 and above about 10 at 25°C, when compared to pH levels within that range. At a pH between approximately 4.5 and 7, and with water conductivity below 1 μS.cm⁻¹, corrosion of aluminum is minimal.

Corrosion of Aluminum – Water Quality Limits

Pitting of the aluminium clad fuel and target materials in wet basin storage is the main mechanism of corrosion in basins around the world [6]. Pitting is an extremely localized form of corrosion in which metal is removed preferentially over very small areas on the surface to develop small cavities, or “pits”. The attack is generally limited to extremely small areas, while the remaining surface is relatively unaffected. The pits usually start at small points on the surface and enlarge with time. This enlargement of the surface area of a pit is usually small in comparison with its increase in depth and volume [9]. The hydrated aluminium oxide (Al₂O₃•H₂O) produced during pitting has a much larger volume than the corroded metal and therefore the aggregate corrosion product from a pit is seen as a small white nodule (see Figure 1).

Through previous work and operating experience at the Savannah River Site storage basins, it has been shown that the presence of certain ionic species (e.g. chloride), as well as high water conductivity, causes extensive fuel corrosion attack. This experience led to the establishment of water chemistry limits that are in force for the fuel storage basin at the site.

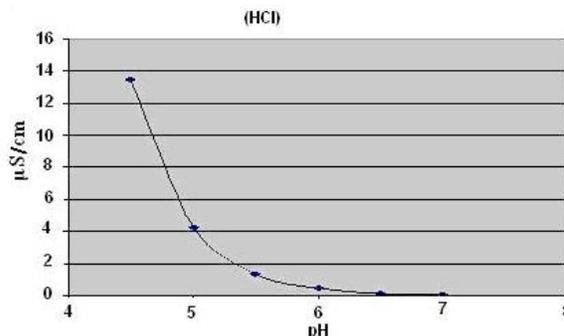


Fig. 2. Relation between conductivity and pH for an aqueous solution with HCl.

This experience base was also used, in major part, in the development of a new guide for water quality management practices for reactor operators worldwide. This guide [3] was prepared through a technical consultancy with the International Atomic Energy Agency.

Electrochemical tests were conducted to investigate the effects of exposure of aluminum cladding alloys to a range of ion levels as an approach to establish optimal water chemistry limits [10, 11]. Cyclic polarization testing was used to perform accelerated corrosion testing on coupons of 6061 and 1100 aluminum. E_{corr} was measured and used to evaluate the potential impact of the water chemistry on the pitting of the material. Cyclic polarization studies were performed on Al1100 and Al6061 coupons under a range of solution conditions. Figure 3 shows the cyclic polarization results for Al6061 obtained at several water chemistries. The results indicate that the chloride ion, even at low concentrations,

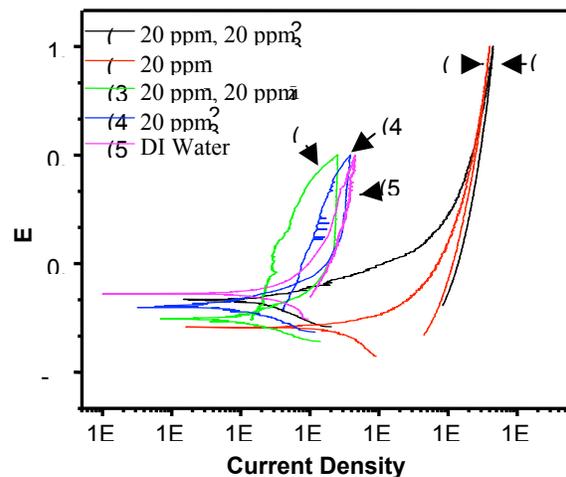


Fig. 3. Cyclic polarization results from Al6061 coupons in water chemistries [11]

strongly promotes corrosion of the aluminum fuel alloys. Service experience has also shown that the chloride ion is the most deleterious specie in water that promotes pitting corrosion. The results in Figure 3 also suggest that sulphate, at these concentrations, may mitigate the effects of the chloride specie. Results from Al1100 tests show that nitrate may inhibit the effects of the chloride specie. The inhibiting effect of these species is not however credited nor are chemistry controls

using these species being considered since this would add to the conductivity of the water.

Conclusions

The imperative for continued safe operation of nuclear reactor systems and spent fuel storage is to limit degradation of the fuel and structural materials. Water quality management is essential for materials subject to rapid corrosion attack in poor water quality water, such as aluminum. An overview of the basics in water quality and a laboratory approach to identify water conditions aggressive to cause corrosion attack was provided.

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