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Review

Corrosion mitigation in coolant systems in nuclear power plants

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ABSTRACT

Nuclear power plants have suffered various failures through corrosion causing economic losses, increasing the radiation exposure to personnel and increasing the possibility of environmental risk. Many examples of different corrosion mechanisms and their consequences for nuclear power plant (NPP) working conditions are recognized and described. Nevertheless, several issues related to the corrosion of materials used for NPP constructions are still unexplained. This paper gives short, basic information about selected methods of the corrosion reduction and corrosion inhibitors used in coolant systems in nuclear power plants, mainly in pressurized water reactors PWRs and boiling water reactors BWRs. Present data are based in the open scientific and technical literature since 1990.

1. Introduction

Nuclear power is one of the most comprehensively regulated industries. At the forefront of the energy challenge is the necessity of operating plants for as long as possible in a safe and cost-effective manner. In order to fulfil such a task, the ageing of materials, components and structures must be kept under control. Despite careful selection and treatment of construction materials used in light-water reactor (LWR), corrosion occurs in the structures exposed to the high-temperature water (HTW). In LWRs corrosion processes are strongly affected by operational measured variables such as environment medium, construction, material and/or mechanical load.

Currently there are 439 operational nuclear reactors world-wide (http://www.iaea.org/pris). The most common nuclear power reactors are water-based: pressurized water reactors (PWR)- 60% of total and boiling water reactors (BWR) –21% of total. In a PWR, pressurized, heated water from the reactor coolant system transfers heat to an electricity generator, which includes a secondary coolant stream boiling a coolant to power a turbine. In BWRs, the reactor core boils the reactor coolant directly to produce steam for the electricity generator. The reactor coolant system RCS section downstream of the electricity generators but upstream of the reactor typically is called the cold leg, and downstream of the reactor and upstream of the electricity generators is typically called the hot leg.

The main metallic materials used in PWRs and BWRs are (Hoffelner, 2013; Ashby and Smidman, 2010):

- zirconium alloys used for fuel cladding and other reactor internal components,
- stainless steels used for structural components in the primary coolant system,
- carbon steel and copper-based alloys mostly used in the secondary coolant system,
- Ni-based alloys used for heat exchangers and other minor applications,
- Ti used in the condenser tubes of seashore plants.

In the case of the pressurized water reactor, following construction materials may be used for different purposes (Ashby and Smidman, 2010):

- fuel cladding- Zircaloy 4,
- control rods-clad in 304SS, Inconel 627 tubes,
- pressure vessel: alloy steels SA 504, SA 533, clad with 308L SS or Inconel 617.

In NPP, some corrosion aspects are connected (directly or/and indirectly) with the radiation from the reactor core (corrosion of fuel and its accessories, corrosion of construction materials, water radiolysis). The other corrosion problems are similar like in conventional power plants. Zr alloys, Ni-based alloys and stainless steels are considered as a highly corrosion resistant, however, under certain operating conditions various corrosion mechanisms

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may be found to induce damage of these materials.

All mentioned above materials (except titanium) are subject to one or more of corrosion processes: general corrosion (GC), environmentally assisted cracking (EAC), stress corrosion cracking (SCC), irradiation-assisted stress corrosion cracking (IASCC), intergranular-assisted stress corrosion cracking (IGSCC), flow-assisted corrosion (FAC), ammonia corrosion (AC) and microbiologically influenced corrosion (MIC) (Cattant et al., 2008; Berg, 2009; Feron, 2012; IAEA Report TECDOC-1505, 2006). According to Berg (2009), the distribution of corrosion types in PWRs and BWRs in Germany are presented in Fig. 1.

In the most of power and research reactors, water is cooling medium to remove heat from fission products and from neutron moderation. For the minimization of corrosion processes and undesired lining formation on the hot water-affected metallic surfaces, the physicochemical characteristics of the operating medium should be well described.

A corrosion inhibitor should protect for the various construction materials during all phases of plant operation (EPRI Report NP-5569, 1987). This requires the inhibitor to be chemically stable throughout the operating temperature and radiation exposure ranges. An effective corrosion inhibitor should fulfil the following criteria:

- the maximum corrosion protection of structural materials with different properties. In nuclear power plant, cooling systems contains of specific types of metallic materials, the corrosion inhibitor should adequately protect them.
- the thermal stability. Chemical substances used in cooling system should be very resistant to temperature fluctuations not only because of the loss of corrosion protective properties. In the case of small thermal resistance, inhibitor can be partially or totally decomposed, and the decomposition products contaminate the coolant.
- effects of exposure to radiation. As in the case of temperature resistance, the corrosion inhibitors have to be resistant to high-energy gamma radiation.

To be sure the inhibitor satisfies all necessary criteria, a qualification programme for its use should be established. Fig. 2 shows a schematic procedure for a chemical substance – candidate for corrosion inhibitor in NPP (EPRI Report NP-5569, 1987).

According to Polish government policy, the first Polish NPP should be built during next 10–15 years (Chmielewski, 2013; Ministry of Economy of the Republic of Poland, 2014). This paper was written as part of the research project “Study of processes occurring under regular operation of water circulation systems in nuclear power plants with suggested actions aimed at upgrade of nuclear safety”, partly financed by the National Research and Development Centre in the framework of the strategic research project “Technologies Supporting Development of Safe Nuclear Power Engineering” (http://www.ncbir.pl/en/strategic-programmes/technologies-supporting-development-of-safe-nuclear-power-engineering/). The whole program is dedicated for young Polish nuclear researchers in order to better introduce them to the issues related to the construction and operation of NPP. The cited literature and technical notes are available as an open scientific sources. It should be mentioned, that several solutions used during normal operation time is patented and/or confidential. There are many ways to reduce and prevent corrosion: material changes, isolations techniques, stress improvements, environmental improvements, mechanical repair etc. (IAEA Report NP-T-3.13, 2011). In this paper, the particular emphasis has been placed on environmental improvements, the other mitigation method have been only mentioned. The quoted examples show the ideas and solutions used in working LWRs and they include among others: Zn addition, passivating anodic inhibitors, and corrosion inhibitors used in microbiologically induced corrosion.

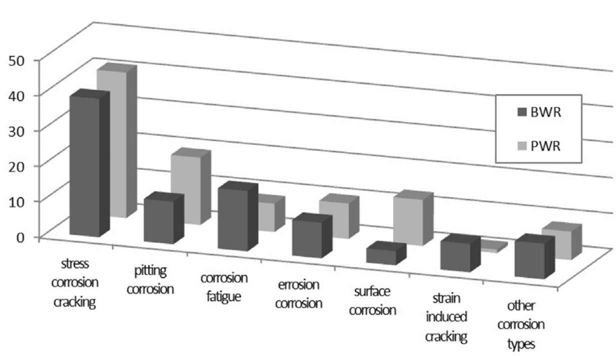

Fig. 1. The distribution of corrosion types in PWRs and BWRs in Germany.

2. General corrosion (GC)

According to Feron (2012), general corrosion results in general loss and reduction in thickness of the corroding structure or component. It can be described as an electrochemical reactions consisting of anodic dissolution coupled to cathodic reduction. During this process, the materials becomes thinner, as it corrodes until its thickness is reduced to the point of which failure occurs. General corrosion is widespread in NPPs, affecting almost all kinds of materials; however it is not normally of the great importance in nuclear power as corrosion resistant alloys are used in strategic working locations. As an example of GC could be zirconium alloys degradation (fuel cladding, fuel channels etc.). Zirconium alloys in general are highly resistant to corrosion; however, they are not immune to oxidation in the aggressive conditions that exist inside the nuclear reactors. The corrosion issues for zirconium alloys in BWRs and PWRs are unique due to the differences in operating conditions and alloys employed. Corrosion of zirconium alloys in an aqueous environment is principally related to the oxidation of the zirconium by the oxygen in the coolant, dissolved or produced by radiolysis of water. A small amount of oxygen can be dissolved in the metal, but once the thermodynamic solubility limit is exceeded, ZrO_2 is formed on the metal (Allen et al., 2012):

$$Zr + 2H_2O = ZrO_2 + 2(1-x)H_2 + 4xH$$

Other two frequently found GC types are: GC of nickel alloys (steam generator tubes) and GC of carbon steel piping (Cattant et al., 2008). The mitigation of GC in Light Water Reactors includes using new materials with improve resistant properties (eg. in the case of Ni alloys, addition of chromium to the content of 30% in Alloy 690 greatly decreases its corrosion rate compared to Alloy 600); selection of the appropriate physicochemical properties of reactor water etc.

3. Environmentally assisted cracking (EAC)

The crack initiation can occurs in different conditions; also in ultra-high purity water with hydroxyl anion content below 10 ppb, in relatively high temperatures (>150 °C)- such is the case for LWRs (Ford and Andresen, 2002). In water environments, EAC of steels is considered to occur when the crack growth rates are more than three times those observed in air (Cattant et al., 2008). In dependence of environment, EAC can be considered as stress corrosion cracking (SCC), hydrogen induced corrosion (HIC), etc. There are a