SECTION 6. INNOVATIVE TECHNOLOGIES

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6.1 The effect of pollution of component surfaces as a result of possible contact of fresh nuclear fuel with sea atmosphere on corrosion

Analysis of the information was performed on possible effect of components of sea atmosphere in case of their precipitation on the assembly surfaces on the corrosion of structural materials of items of fuel assemblies (FAs) of water-water energetic reactor (VVER-1000) in their subsequent operation. The data are presented on static and dynamic tests of alloy E-110 at temperatures of 300-350 °C in water and standard coolant of the reactor polluted with chlorides and iodine, as well as of alloy E-110 under special pollution of its surface with chlorides. It is demonstrated that in keeping the conditions of storage of fresh fuel, as well as the recommendations of the present work, its high corrosion resistance and operability in further operation is ensured.

Key words: reactor, coolant pollution, corrosion, sea atmosphere, standard coolant.

Introduction

Salinity of water in different parts of the ocean is approximately similar and equal to 35 g/L. Among the ocean salts, the major ones are sodium and magnesium chlorides and sulphates. Among the chlorides, the basic dissolved compounds are: NaCl (27 g/L), $MgCl_2$ (6 g/L), KCl and $CaCl_2$ (1 g/L each) [283-287]. Namely such compounds and in such ratio are recommended to be taken for preparation of solution in climatic tests of the equipment under the conditions of sea (salt) fog [288-290].

Besides for the above-mentioned, the ocean water contains almost all of the remaining chemical elements, but to a considerably lesser extent. Average content of organic compounds is 2 mg/L. Approximately the same ratio of these substances is contained in aerosols formed in the surf region and transferred with air [287].

In case of loss of integrity of packing of fresh fuel, during its storage in coastal region, the indicated aerosols will get to the assembly components and with the increase in humidity, for example, in the rain period, could lead to formation on the

metal surface of thin films of electrolytic solutions with the governing elements being the chlorides mentioned above.

Thus, the conditions appear for electrochemical processes on metal surfaces. As indicated in the paper of [287], from the neutral solutions of chlorides, the chlorine-ions are concentrated in the slots, their concentration becomes 15 time higher than outside the slot that could affect the corrosion of zirconium alloy E-110. Such slots in FA are, for examples, the places of spacing grids contact with fuel rod clads.

In operation of FAs, the indicated salts will be washed by the coolant from the metal surface and then removed from the coolant with the help of ion exchangers of water purification system. However, temporary increase in concentration of chlorine-ions in the coolant is possible and could affect the corrosion resistance of zirconium components of assemblies. This problem shall be considered separately.

Besides, the chlorides will be washed out from the slots slower and under the effect of reactor radiation may transfer into other substances capable to interact with zirconium or oxide surface film on zirconium. When the zirconium surface is polluted with chlorine, the corrosion resistance of the former may change significantly. This problem also needs to be considered separately [287].

Corrosion of alloy E-110 in water containing 0.5-500 mg/L of chlorine-ions at 300 °C and equilibrium steam pressure

The paper of [285] focuses on the effect of concentration of Cl^- ions in water on corrosion of zirconium alloy E-110 at 300 °C. In this study by the data of the analysis, the initial distilled water contained not more than 0.5 mg/L of chlorine ions in total.

Results of autoclave tests in water with different content of chlorine-ions (0.5 mg/L, 5 mg/L and 500 mg/L) are shown in Figure 1. The curve of alloy corrosion in water without addition of chlorides is also presented there [287].

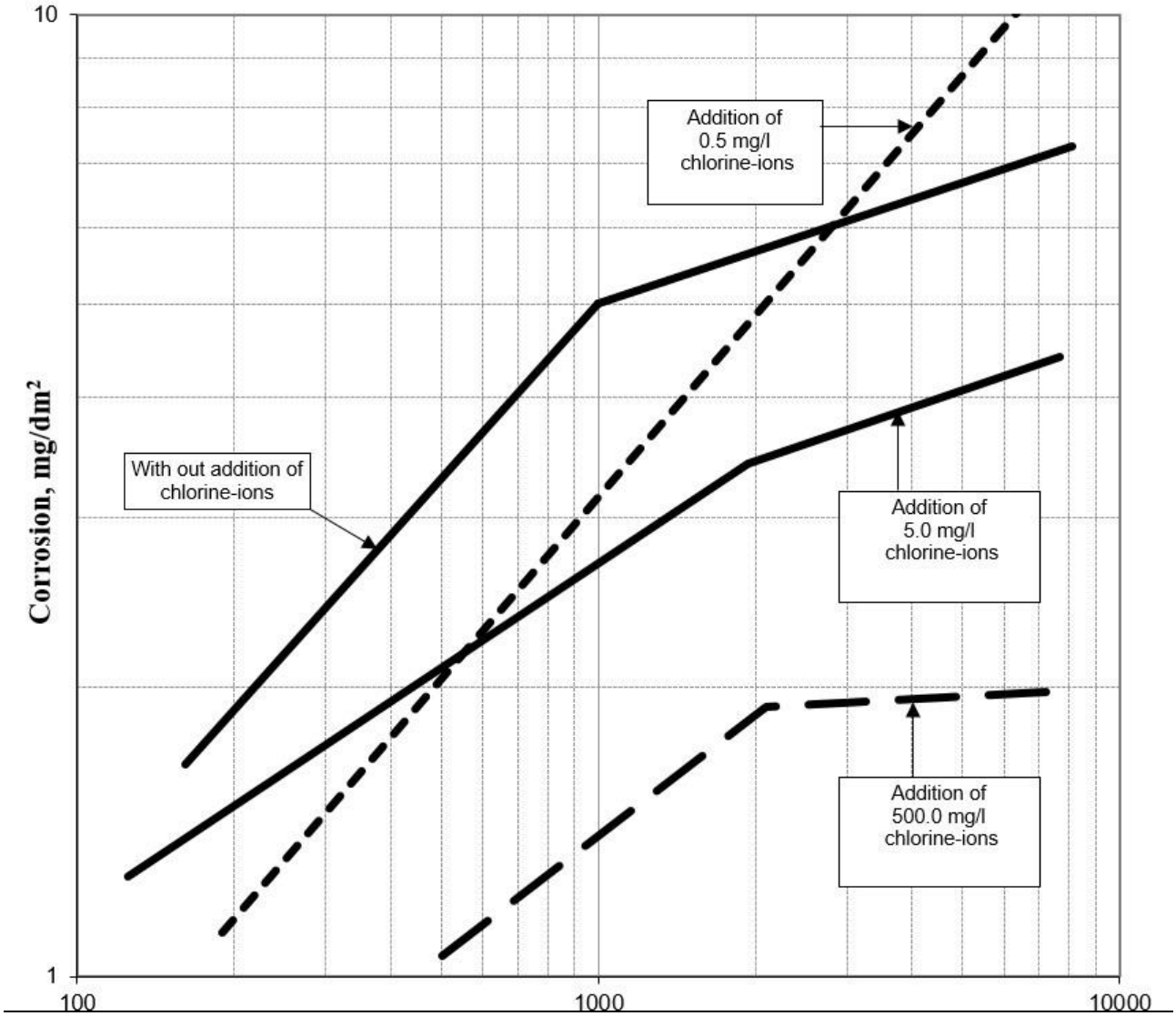

Fig. 1. Corrosion of alloy E-110 at 300 °C in water with different content of chlorides.

It is seen from Figure 1 that the alloy corrosion in distilled water takes place in two stages. At the first stage – the more considerable rise of oxide film takes place, at the second stage – this process is slowed down, that is, the film becomes more protective in nature. With addition to water of 0.5 mg/L of chlorine ions, the kinetics of alloy corrosion is changed: the second stage of the corrosion process does not occur. However, this does not influence the external appearance of specimens, which does not differ from the appearance of the specimens (black glossy surface) after the tests in water without addition of chlorine-ions [287].

Increase in concentration of chlorine-ions in water to 5-500 mg/L, according to the considered paper, leads to decrease in growth of mass of specimens in comparison with water without the addition of chlorides. This decrease in mass growth is expressed more evidently for the solution with higher chlorine-ions concentration.

With this, in both cases approximately after 2000 h for alloy E-110 the second stage of corrosion is started, which is characterized by slower growth in mass.

So, increase in concentration of chlorine-ions in water does not cause any negative effects but leads to decrease in corrosion rate of alloy E-110. Moreover, this decrease is not caused by dissolving the surface oxide film with the presence of chlorides, as the analysis of the solutions showed after corrosion tests.

On the basis of studies of electrochemical characteristics of corrosion of alloy E-110 at 300 °C in water with different content of chlorine-ions (0.5-500 mg/L) it was revealed that the cause of corrosion decrease with increase in concentration of chlorine-ions is their strong influence on the course of cathodic polarization curves, as seen from Figure 2, and the noticeable braking in discharging process of depolarizer ions.

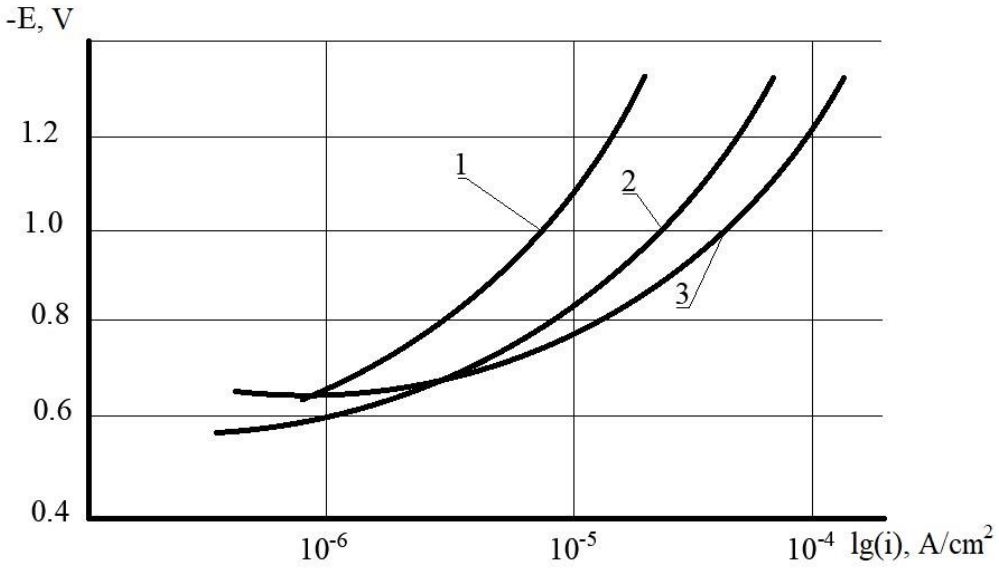

Fig. 2. Cathodic polarization curves of alloy Zr – 1% Nb at 300 °C in distilled water containing different amount of chlorine-ions: 1) – 500 mg/L Cl^-; 2) – 5 mg/L Cl^-; 3) – 0.5 mg/L Cl^-.

The higher the braking of cathodic discharge process of depolarizer ions is, that is,

the higher the slope of a curve in Figure 2, the greater is the rate of corrosion decrease of zirconium alloy E-110 [287].

Summarizing the above-mentioned, on the basis of the paper of [285], a conclusion can be made that some increase in concentration of chlorine ions in high-temperature water (to 500 mg/L) does not cause increase in corrosion of alloy E-110 and is not hazardous.

Corrosion of alloy E-110 in high-temperature water with surface polluted with chlorine

For pollution of surface of alloy E-110 with chlorine they used its short-term anodic polarization in concentrated hydrochloric acid. Both autoclave tests were performed of such polluted specimens of zirconium alloy E-110 in non-deaerated water at 350 ^{0}C and pressure 17 MPa, and dynamic bench tests in standard coolant of reactors VVER-1000 at temperature 310 ^{0}C, pressure 12 MPa and flow velocity 5 m/s [287].

For the alloy with surface pollution after ~ 1500 h the rate of growth in mass of specimens begins to increase, and for non-polluted specimens – to decrease, that is, in the latter case the rise in protective properties of the film is observed. On the whole, with maximum achieved holding time of 3000 h the growth in mass of polluted specimens is approximately 1,5 time higher in comparison with the non-polluted.

So, in static tests, even with very severe conditions of alloy E-110 surface pollution with chloride-ions, the effect is not so strong. However under dynamic conditions of the tests it may increase abruptly.

The interesting feature is some loss in mass of specimens at some stages in the initial period of the tests. This is indicative of loss of protective properties of the film and transfer of the formed corrosion products into coolant.

In [287] it is indicated that in chloride media the pits may be formed on the surfaces of zirconium alloys, filled with black powder of metal zirconium and dark corrosion products. In particular, $ZrCl_2$ - of black colour.

With loss of passive film on zirconium, in metal scratching the edge of metal and pits being formed, the release of gas bubbles is observed. In paper of [287] this is explained by the following reaction:

$$2Zr+O^{2-} + 2Cl^{-} = ZrCl_2 + Zr + O_2 + 4e.$$

Normal potential of this reaction is 0,5 V. It is noted that local corrosion centres are located most of all at the grain boundaries, and at crossings of grain boundaries, especially of three grains, as well as at the places of accumulation of some intermetallic compounds, by scratches and scribes. It should be noted that in all such sections there is a local metal deformation. By the data of [287] the normal potential of deformed sections may displace to negative side by – 0,11 V, and the value of normal potential of breakdown may be 0,39 V, that is, protective properties of the film are weakened considerably. The value of breakdown potential is practically similar in solutions of NaCl and KCl , but depends greatly on the metal surface condition.

Activation energy of reaction, that causes violation of passive state of zirconium alloys and formation of pits, is ~45 kJ/ mole [287]. Duration of period prior to formation of a pit is the lesser, the higher is the concentration of chloride-ions and temperature.

Corrosion of alloy E-110 at 350 °C in the presence of bromine or iodine

The available data show that addition of small amount of I_2 into non-deaerated water does not cause noticeable increase of general corrosion of zirconium alloy E-110 at 350 °C, in comparison with water without iodine addition (Figure 3). With this, the effect of iodine on corrosion depends on the condition of metal surface and is expressed more essentially for anodized alloy E-110. Surface of specimens after the mentioned tests is black and glossy, the same as after the tests in distilled water, that is, on the basis of the performed tests (1500 h) no sharp negative effect of small content of iodine on corrosion of alloy E-110 was revealed [287].

According to reference data of [288], the water solutions of iodine compounds (NaI, KI), even with their high concentration (10-60%), do not cause considerable corrosion of zirconium and its alloys at temperatures to 100-105 °C. Authors of paper

of [285] consider that ions of iodine and bromine (content of bromine in ocean water according to the data of [289] is approximately 1000 time higher in comparison with iodine) can cause local corrosion of zirconium alloys. Iodine, as well as bromine, forms oxy acids and the corresponding halogenide-ions when dissolving in water, for example:

$$I_2 + H_2O \rightarrow I^- + H^+ + HIO.$$

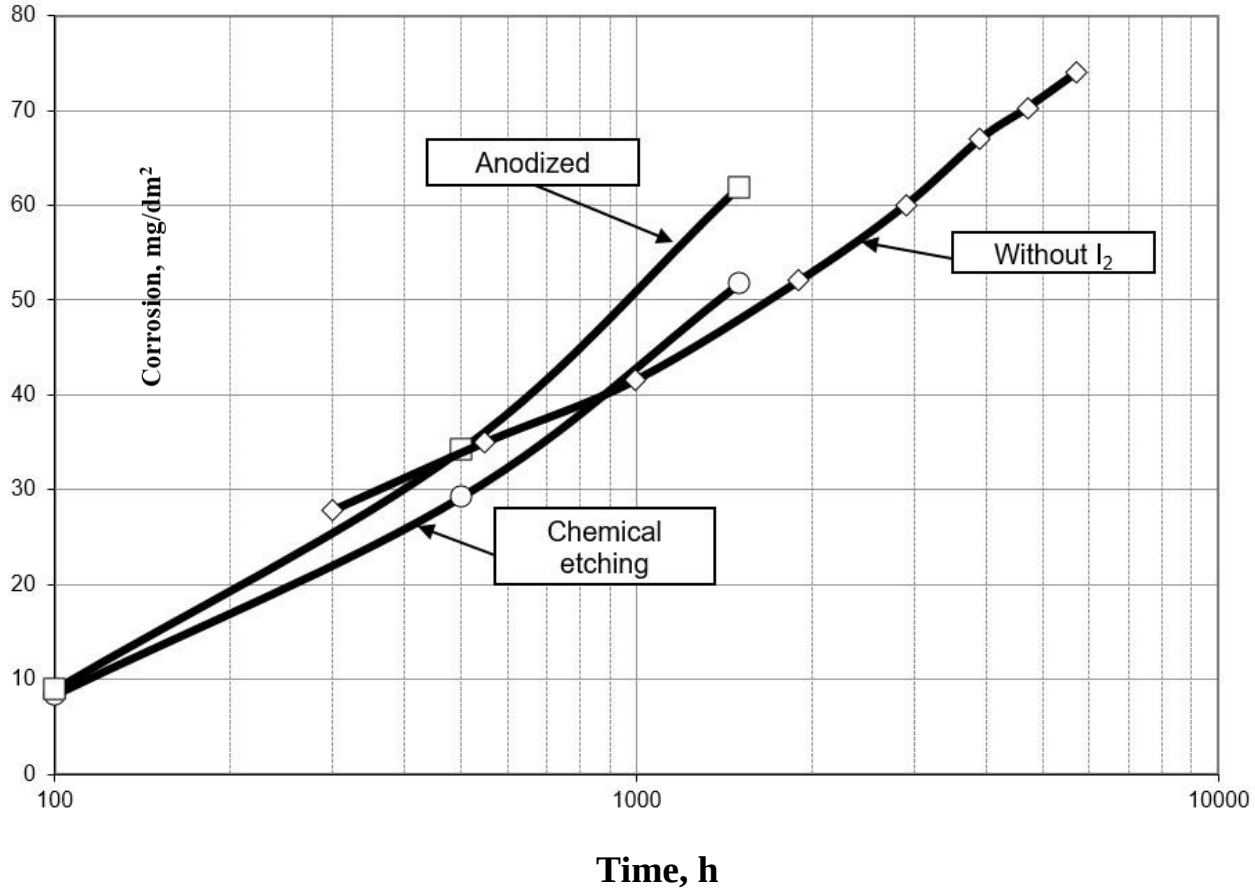

Fig. 3. Corrosion of alloy E-110 at 350 °C and 12 MPa in non-deaerated water with addition of 2.5 mg/kg I_2.

Oxy acids are strong oxidizers and displace the shift in the stationary potential to the region of positive potentials. The paper of [285, 287] describes the experiments when the specimens of zirconium alloys, loaded with bending or axial tension, were polarized with current of 1.6 mA/cm^2. After 30-50 min of tests the deep pits developed. When water solution contained 28 mg/L of iodine, the pits and cracks were formed on specimens of alloy Zr-1%Nb (E-110), being under axial stress of 280 MPa

[287]. The pits and cracks were filled with corrosion products of black colour. The authors of paper of [285, 287] consider that at potentials, being positive more than 0.6 V, zirconium dissolves in active state. In their opinion, the following reaction on the zirconium surface is the cause of violation of the passive state:

$$2Zr^{+}O^{2-} + 2I^{-} = ZrI_2 + Zr + O_2 + 4e.$$

According to the whole set of the above-mentioned data, under definite conditions (tensile stresses, etc.) the pollution of zirconium components of fresh FAs with halogenide-ions (Cl^{-}, Br^{-} or I^{-}) could lead to increase of general corrosion of zirconium alloy E-110 and development of local types of corrosion on its (pittings, corrosion cracks). This needs the special precautionary measures to be taken during storage of fresh fuel at nuclear power plant (NPP) located in the coastal ocean region to minimize both the amount, and the possibility of getting the sea salts on fuel surface [287-290].

Recommendations on the conditions of fresh fuel storage

1. Fresh fuel shall be stored, if possible, with presence of silica gel in the sealed containers preventing or making difficult the FAs contact with atmospheric air.

2. In case of loss of integrity of packing and possible pollution of assembly components with corrosive elements of sea atmosphere the FAs shall be stored further in water till their placing into the reactor.

3. Fuel handling procedures shall not be used, unless there is an urgent need, to reduce a possibility of loss of the packing integrity.

4. When loading the fresh FAs into the reactor core, the daily monitoring of content of chlorine-ion in the coolant shall be performed.

5. Bringing the reactor to nominal power shall be performed only at reaching the standard indices of water chemistry as to chlorides.

Conclusion

Design method of fresh fuel storage at NPP in the coastal ocean region in the south shall provide for its further reliable operation.

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